CATALYSIS BY SULPHATED TIN OXIDE MODIFIED WITH SOME TRANSITION METAL OXIDES

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By

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AUGUST - 2002

To My

Beloved Amma and Achan ……

CERTIFICATE

This is to certify that the thesis is an authentic record of research carried out by Ms. Deepa C.S. under my supervision, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, Cochin University of Science and Technology, and that no part thereof has been submitted before for award of any other degree.

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DECLARATION

I hereby declare that the work presented in this thesis entitled **"Catalysis by sulphated tin oxide modified with some transition metal oxides"** is an authentic work carried out by me independently under the supervision of Dr.S.Sugunan, Professor in Physical Chemistry, Department of Applied Chemistry, Cochin University of Science and Technology, and has not been included in any other thesis submitted previously for award of any other degree.

Deepa C.S.

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30-08-2002

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PREFACE

Solid acid catalysts offer environmentally friendly alternatives to conventional materials used in chemical and petroleum industries. Among these alternatives of solid acids, metal oxide modified by sulphate ions is one of the emerging class. These sulphate modified metal oxides are found to be highly acidic and exhibit excellent activity for acid demanding reactions such as alkylation, isomerisation, cracking etc. Sulphation also enhances the oxidation activity of metal oxides The acid strength variation among the different sulphated oxides is found to be on the basis of difference in the electronegativity of the metal present in the corresponding metal oxide.

Catalysis by sulphated ZrO_2, TiO_2 and Fe_2O_3 were extensively studied in the last few decades. Catalysts based on sulphated tin oxide are less studied when compared to these metal oxide systems. Pure tin oxide is the main component in many oxidation catalysts and sulphation also enhances the oxidation capacity of the metal oxides. But sulphated systems suffer from the inherent drawbacks of rapid deactivation and low thermal stability of the sulphate species. It is found that addition of a second component enhances the structural and textural properties of metal oxides to a considerable extent. Modification with various transition metal ions has been reported to influence the surface properties of the catalysts depending on the nature of the ion incorporated. But there are much less reports regarding the sulphated mixed oxides of tin and transition metals.

In the present work, we have tried to evaluate systematically the surface properties of sulphated tin oxide systems modified with three different transition metal oxides *viz.* iron oxide, tungsten oxide and molybdenum oxide. The catalytic activities of these systems are checked and compared by carrying out some industrially important reactions such as oxidative dehydrogenation of ethylbenzene and Friedel-Crafts reactions.

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1

INTRODUCTION

1.1 CATALYSIS

Catalysis based chemical synthesis accounts for 60% of today's chemical products and 90% of current chemical processes and hence it is of crucial importance for chemical industry, which manufactures value - added fine chemicals. Catalysis development and its understanding thus become very essential. Catalysis can be defined as an acceleration of the rate of a process or reaction, brought about by a catalyst, usually present in small-managed quantities. Catalysts can be defined as materials, which change the rate of attainment of equilibrium without themselves being consumed in the process. Thus catalyst is a substance that changes the kinetics, but not the thermodynamics of a chemical reaction. A catalyst permits reactions or processes to take place more effectively or under milder conditions than would otherwise be possible. The basic requirements of a catalyst are activity, selectivity, stability, and it should be regenerable, reproducible, mechanically and thermally stable, economical and should have suitable morphological characteristics.

The number of catalysts applied in industry is very large and they come in many different forms, from heterogeneous catalysts in the form of porous solids and homogenous catalysts dissolved in the liquid reaction mixture to biological catalysts in the form of enzymes. The use of homogenous catalysts poses several problems such as difficulty in separating the catalysts and products, low thermal stability of the catalysts, formation of large amount of hazardous waste products, etc. Increased consciousness towards the health hazards caused by many toxic materials emitted into the air and water during the chemical manufacturing and other processing techniques have led to rapid increase in the effort to replace the hazardous homogenous catalysts with more eco-friendly heterogeneous catalysts.

The vast majority of industrial catalytic reactions involves heterogeneous catalysis. Heterogeneous catalysis has not only become the basis of industrial chemistry during this century, but its scientific foundation has been developing rapidly. It is an interdisciplinary subject which involves aspects from solid state chemistry, physics, surface science, analytical chemistry, reaction kinetics and mechanisms, theoretical chemistry, etc. Nowadays, heterogeneously catalysed reactions play an important role in the efficient and cost effective production of fine chemicals. In heterogeneous catalysis, the catalytic substance is found as an active site or centre at the surface of a solid. The important types of heterogeneous catalysts are metals, metal oxides, clays, zeolites and solid supported heteropoly acids.

1.2 SOLID ACIDS

Acid catalysis plays a key role in many important reactions of the chemical and petroleum industries. Conventional industrial acid catalysts such as sulphuric acid, $AlCl_3$ and BF_3 possess unavoidable drawbacks because of their severe corrosive nature and high susceptibility to moisture. The search for environmentally benign heterogeneous catalysts has driven worldwide research towards the development of new materials, which can act as substitutes for current liquid acids and halogen based solid acids (1). More recently, increasing applications for solid acids are being found in heterogeneous catalysis, for a wide variety of applications such as hydrocarbon isomerisation, cracking, hydrocracking, dehydration and alkylation. Generally used solid acids catalysts for these reactions include zeolites (2), modified clays (acid treated and pillared clays) and metal oxide based systems. Acid treated clays were the first successful acidic heterogeneous cracking catalyst, but they were completely superseded by synthetic amorphous silica-alumina and later by zeolites (1). Hence solid acids offer more nature friendly alternatives to conventional materials used in various industries.

1.3 SOLID SUPERACIDS

An acid media, which is more acidic than 100% sulphuric acid, is defined as a superacid (3,4). Recently various kinds of solid superacids have been developed, *viz.* (i) metal oxides, mixed oxides, graphite, metal salts, etc. treated or combined with antimony fluoride or aluminium chloride, (ii) metal oxides and mixed oxides containing small amounts of sulphate ion, (iii) perfluorinated polymer sulphuric acid (Nafion-H), (iv) zeolites (H-ZSM-5), (v) heteropolyacids and (vi) mixed oxides (WO_3/ZrO_2, MoO_3/ZrO_2, WO_3/SnO_2, etc.). Among these different solid superacids, systems in the first group have a possibility of leaching or evaporating of halogen compounds, due to which these systems are proven to be environmentally undesirable as catalysts (1,5-7). Recent studies revealed that sulphate modified metal oxides are promising catalysts for many industrially important reactions.

1.4 SULPHATED METAL OXIDES

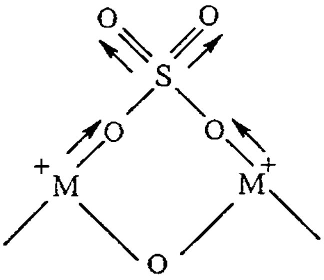
Different metal oxides like TiO_2 (8,9), ZrO_2 (10,11) and Fe_2O_3 (12-14) on strong co-ordination with sulphate anion showed high acidity and can be utilised as solid acids (15). SnO_2 also showed enhanced acid strength on modification with sulphate ion (16). These superacids are found to be satisfactorily active in a heterogeneous system for reactions like skeletal isomerisation of butanes and pentanes and acylation of aromatics with carboxylic and other acylating agents (17-19). which are generally catalysed by strong acids, especially superacids such as Sb_5-HF and Sb_5-FSO_3H.

Important reactions that are catalysed by sulphated metal oxides include polymerisation of ethers (20), benzoylation of toluene with benzoyl chloride (21), esterification of alcohol with acetic acid (22) and benzylation of toluene with benzyl chloride (23,24). Sulphated ZrO_2, Fe_2O_3 and TiO_2 are found to be powerful catalysts for various acid catalysed reactions such as the skeletal isomerisation of butane to isobutene, acylation of benzene derivatives with acyl chlorides and the ring opening isomerisation of cyclopropane (25). Sulphated TiO_2 is found to be active for selective catalytic reduction of NO with NH_3 (26).

In sulphate treated metal oxides the superacidic sites are created only when the sulphate ions are doped on amorphous oxides followed by calcination to crystallisation. The sulphate ions can be introduced on the metal surface by using, different sulphating agents like H_2SO_4, $(NH_4)_2SO_4$, SO_2, SO_3 and H_2S. Among these H_2SO_4 and $(NH_4)_2SO_4$ are most commonly used for sulphation. Sulphated metal oxides are prepared by impregnating hydrous metal oxide with sulphating solution for a fixed time, followed either by evaporation of solution to dryness, or filtering off the excess solution. It was pointed out that existence of covalent S=O in sulphur complexes formed on the metal oxide surface is necessary for the generation of high acidity (27-29).

1.5 ACIDITY OF SULPHATED METAL OXIDES

Yamaguchi *et al.* suggested that strong surface acidity generation on sulphate modification can be attributed to the electron withdrawing effect of sulpahte group, which lead to co-ordinatively unsaturated and electron deficient metal centres (Model 1) that behave as strong Lewis acid sites (28,29). It was shown that in the sulphate modified metal oxides the sulphate groups are described as covalently bonded. Besides the inductive effect of the sulphate group, three other factors *viz.* valency, electronegativity and co-ordination number of the metal cation of metal oxide are found to affect the acidic strength of sulphate promoted metal oxides (29).



Model 1

Infrared spectrum of sulphated zirconia obtained after evacuation gave peaks at 1390, 1190, 1020 and 930 cm^{-1} in S-O stretching frequency region. The former two bands and the latter two bands are assigned to asymmetric and symmetric stretching frequencies of the O=S=O and O-S-O groups respectively (29). The 1390 cm^{-1} band representing the asymmetric stretching frequency of S=O is often regarded as the characteristic band of sulphate promoted superacids.

1.6 METAL PROMOTED SULPHATED OXIDES

Sulphated metal oxides have several drawbacks like sulphur leaching during the reaction, coke deposition at high temperatures, changes in sulphur oxidation state, etc. So these factors limit the industrial use of these catalysts. In recent years, metal promoted sulphated oxides have been receiving increasing interest especially owing to their high thermal stability and enhanced catalytic activity (30-32). The iron-manganese modified sulphated zirconia (SFMZ) catalyst developed by Hsu *et al.* has generated strong interest due to its exceptionally high activity towards butane isomeristion at low temperatures (33). More recently, it has been found that Cr and Mn promoted sulphated zirconia have activity comparable to SFMZ (34). Mioa *et al.* has reported that the catalytic activity of sulphated oxides of Cr-Zr, Fe-Cr-Zr and Fe-V-Zr is 2-3 times greater than that of SFMZ (35). Incorporation of a transition metal can enhance the acid strength, *via* electronic interactions. Introduction of the metal cation into the crystal lattice may result in the formation of some complex structures (Scheme 1) in some local areas on the surface.

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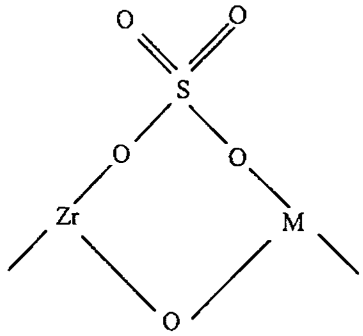
which?



Scheme 1

According to the principle of electronegativity equalisation proposed by Sanderson (36) the electronegativity S_{int} of the complex structure and the partial charge δ_{Zr} on Zr^{4+} can be written as

$$S_{int} = [S^X_M\, S_{Zr}\, S_S\, S^Z_O]^{1/2+X+Z}$$

$$\delta_{Zr} = (S_{int} - S_{Zr}) / 2.08\, S_{Zr}^{1/2}$$

where S_M, S_{Zr}, S_S and S_O are the electronegativities of M, Zr, S and O and x, z are the numbers of M and O in the neighbourhood of Zr^{4+}. The electronegativity of Fe^{3+} being larger than that of Zr^{4+}, the electronegativity of the surface complex, S_{int} is increased and δ_{Zr} becomes more positive when Fe is introduced, thereby resulting in enhanced Lewis acidity.

1.7 METHODS FOR ACIDITY DETERMINATION

The selectivity for reactions were found to be dependent on the nature of catalysts which in turn is a function of preparation method, reaction temperature and mode of pretreatment. The acid type present on the sulphate modified metal oxide is also controversial (37). There are claims that the catalytic activity derives mainly or completely from Brönsted acid sites. Reports are equally available suggesting the active sites as Lewis acid sites. Various methods for the determination of acidity of sulphated metal oxides are described below.

1.7.1 Amine titration method

(Reference Should have been included

The amount of acid sites on the catalyst surface can be measured by the amine titration method. This method generally involves titration of solid acid suspended in benzene with *n*-butylamine, using an indicator. This method is also called Hammett indicator method. This is based on the visual colour change of indicators adsorbed on catalyst surface. The amine titration method gives the sum of the amounts of both Lewis and Brönsted acid sites. However, this method is not applicable to the coloured samples.

1.7.2 Temperature programmed desorption of bases

Another method used for the acidity determination is temperature programmed desorption of basic molecules such as ammonia, pyridine, *n*-butylamine, etc. (38). Temperature programmed desorption is a useful method to estimate the acid strength of the solid surface for both coloured and colorless materials (39). Gaseous base molecules which are adsorbed on an acidic surface, desorb at different elevated temperatures depending upon the strength of acid sites to which they are adsorbed. Molecules that are adsorbed to weak sites will be evacuated preferentially compared to those adsorbed to the strong acid sites. Thus the proportion of adsorbed base evacuated at various temperatures can give a measure of the acid strength of the catalyst.

1.7.3 Test reactions

(Reference [illegible]

Catalytic activity towards certain reactions has been used as a measure of acidity and acid strength. The activity for dehydration of alcohols is used as a test reaction to determine the acidity of the catalyst surface. Acid catalysed reactions like cracking of cumene, alkylation of benzene with propene, hydration of olefins, isomerisation of cyclopropane, esterification of acetic acid with ethanol, etc. can also be used for the estimation of acidic property of solid acids.

Infrared

1.7.4 Infra-Red analysis of adsorbed probe molecules

Majority of the methods used for determining the acidity of a catalyst usually determine the total acidity of the system. However, for solid acids, to account for catalytic activity towards different reactions, it becomes necessary to distinguish between the Lewis and Brönsted acid sites. Infrared spectroscopic studies of ammonia and pyridine adsorbed on solid surface help to differentiate between Lewis and Brönsted acid sites. NH_3 adsorbed on the surface as co-ordinatively bonded NH_3 and NH_4^+ can be detected by means of their absorption bands (40). Infrared spectroscopic method using pyridine as an adsorbate is extensively used and considered to be the most reliable method to distinguish between the two types of acid sites. When pyridine is co-ordinatively bonded to Lewis acid sites, characteristic bands are observed at 1450, 1490 and 1610 cm^{-1}. The adsorption of pyridine on Brönsted acid site leads to the formation of pyridinium ion, which gives a band at 1540 cm^{-1} (41).

1.8 CATALYSIS BY TIN OXIDE BASED SYSTEMS

Tin oxides are active catalysts for oxidation and are also an important counter part in many catalytic systems used in oxidation reactions (42). When 2-butanol is reacted over SnO_2 at 573K, only dehydrogenation product is formed indicating that pure tin oxide is acting more as a basic oxide (43). There are reports regarding the oxidation of olefins (44) and isomerisation (45) over SnO_2. Takahashi *et al.* showed that hydrous tin(1V) oxide is active for reduction of 2-propanol (46). Chemball *et al.* studied the isomerisation of 1-butene over SnO_2 and found that the major product was butadiene, which is formed by oxidative dehydrogenation along with small amounts of *cis-* and *trans-* 2-butene (45). SnO_2 is tested for several reactions such as SO_2 oxidation (47-49), CO oxidation (50-54), NO_x reduction by CO (55-57) and CH_3Cl oxidation or decomposition (58). More recently, SnO_2 is employed as a support for Pt and Pd to prepare catalysts for CO and CH_4 oxidation (59-64). Even then pure SnO_2 is found to be impractical as an oxidation catalyst because of its low activity.

For any good catalyst to give high activity and maintain long time stable performance, high thermal stability is a criteria. However single component SnO_2 has been proven to sinter easily at high temperatures and hence have poor thermal stability (65,66). Modification of pure SnO_2 by suitable methods to get more stable catalysts that can maintain larger surface areas even at high temperatures and show high activity than individual SnO_2 is rather desirable.

Tin oxide has a relatively high surface area and amphoteric property; hence it can also be used as a support metal oxide like ZrO_2 and TiO_2. The mixed oxide systems with transition metal oxides are known to be more effective (42,67-70) as these modifications improve the stability and activity of pure SnO_2. Wang *et al.* prepared a series of SnO_2 based catalysts modified with Fe, Cr and Mn and found that these systems showed high activity for CH_4 oxidation (71).

Takte *et al.* noted that isomerisation of 1-butene over pure SnO_2 took place at 473K, but the reaction proceeded smoothly at room temperature over SnO_2 containing small amounts of sulphide ions (72). Teraoka *et al.* (73) reported that SnO_2 shows good activity for NO reduction by hydrocarbons such as CH_4, C_2H_4 and C_3H_4 in presence of oxygen. Tabata *et al.* found that the activity of Al_2O_3 for NO reduction by methanol is enhanced at temperatures below 150°C by the addition of SnO_2 (74). The systems formed by deposition of SnO_2 on SiO_2 or Al_2O_3 are of great interest because of the use of SnO_2 as a gas sensor and conductive coating (75). Moreover, there is great interest on the SnO_2 based catalysts, because of their wide range of applications in promoting various reactions like oxidative dehydrogenation (76-78) and selective reduction of NO by hydrocarbons (73,79-82) or by methanol in oxidising atmosphere (74).

SnO_2-MoO_3, SnO_2–V_2O_5 systems were analysed for methanol oxidation and found that these systems showed high selectivity for formaldehyde (83). Allakhverdoa *et al.* (84,85) demonstrated the technical feasibility for production of acetic acid from ethanol in a single step using catalysts based on Sn-Mo oxides in the presence of water steam. In fact, catalysts based on Sn-Mo oxides are pointed out as efficient systems for oxidation of alcohols into aldehydes (86,87), unsaturated hydrocarbons (88), esters (89) and acids (84,85,90).

Sn-Mo oxides can be obtained by the impregnation of molybdenum salt on SnO_2 (86,87) or on hydrated SnO_2 (88). These catalysts can also be synthesised by co-precipitation of molybdenum and tin salts (84,85). Ai *et al.* observed that the behaviour of SnO_2-MoO_3 systems strongly depends on their acid-base characteristics (89). Goncalves *et al.* (91) studied ethanol oxidation over SnO_2 supported molybdenum oxides prepared by impregnation and co-precipitation methods and found that samples prepared by co-precipitation method showed better activity and high selectivity for the formation of acetic acid.

Among SnO_2-MoO_3 and SnO_2-WO_3 systems, SnO_2-MoO_3 systems are more acidic (92). Ai *et al.* observed that SnO_2-WO_3 catalysts are much less active for the oxidative dehydrogenation of methanol than SnO_2-MoO_3 systems, because the oxidising capacity of WO_3 based oxides is less than that of MoO_3 based oxides (93). But for pure acid/base catalysed reactions like Tischenko reaction, in which the activity is independent of oxidising function, WO_3 based oxides showed high activity, compared to MoO_3 based oxides. SnO_2-MoO_3 based systems are found to be active for the selective formation of methyl formate from methanol and formaldehyde by Tischenko reaction (89).

1.9 CATALYSIS BY SULPHATED TIN OXIDE

It is found that on sulphation with H_2SO_4, SnO_2 showed superacidity like other sulphated systems such as SO_4^{2-}/ ZrO_2, SO_4^{2-}/Fe_2O_3, and SO_4^{2-}/TiO_2. IR studies revealed that sulphated SnO_2 catalysts possess a bidentate sulphate ion co-ordinated to the metal as observed in the case of other sulphated oxides (17,94). Fe_2O_3 and SnO_2 are known to be oxidation catalysts; hence their superacids would be oxidation catalysts with super acidity. Hydration of ethane and decomposition of cyclohexanol are examples of acid catalysed reactions involving oxidation (95,96). Matsuhashi *et al.* have reported that the addition of sulphate anion to SnO_2 improves oxidation activity of the system for dehydrogenation of cyclohexanol (97). As a result of sulphate treatment the electron density around the metal ions (Sn^{4+} sites) decreases due to the electron withdrawing inductive effect of chemisorbed sulphate anion. Hence the strength of Lewis acid sites increases as a result of sulphation. The Lewis acid sites thus created on the metal oxide surface will have greater tendency to accept the electrons from the species undergoing oxidation, thereby enhancing the oxidation capacity of metal oxide (98).

Sulphated SnO_2 showed remarkable activity for decomposition of 2-butanol. In the decomposition of 2-butanol, dehydration predominated over dehydrogenation suggesting the enhancement of acid strength due to sulphation. (16). Matsuhashi *et al.* showed that sulpahted SnO_2 is an active catalyst for the isomerisation of butane and pentane even at room temperatures (97). Sulphated tin oxide prepared from tin (II) octylate was found to be highly effective for the catalysis of dehydrogenation of cyclohexanol to cyclohexanone (99). Wang *et al.* sulphated SnO_2 and observed that sulphate ion treatment was effective for increasing the catalytic activity for cyclopropane isomerisation (16).

Since metal oxide systems containing tin oxide are widely used in oxidation, alkylation (100), acylation (101) and isomerisation reactions, it is also expected that sulphate modification will further enhance their catalytic activity. Sugunan *et al.* observed that rare earth modified sulphated tin oxide showed enhanced activity and high selectivity for benzoylation of toluene with benzoyl chloride (102). Jyothi *et al.* studied the influence of rare earth oxides and sulphation on the activity and selectivity of SnO_2 for methylation of phenol and found that rare earth oxide incorporation leads to the formation of weak acid sites and comparatively strong basic sites which are suitable for the selective methylation of phenol to *o*-cresol and 2,6-xylenol (103). Lanthanum promoted SnO_2 catalyst showed high activity for the selective formation of 2,6-xylenol in the methylation of anisole (104). But the sulphate modification caused dealkylation of anisole due to the creation of strong acid sites.

SnO_2 modified with rare earth oxides like La_2O_3, Sm_2O_3 and CeO_2 are active catalysts for the oxidative dehydrogenation of cyclohexanol to cyclohexanone. The high oxidation ability of these systems can be attributed to the labile oxygen species present in the rare earth oxides. CeO_2 containing the most labile oxygen species showed better selectivity towards cyclohexanone formation (98). The sulphated analogues of these systems also showed excellent selectivity for dehydrogenation, which may be due to the fact that sulphation enhances the oxidation capacity of the catalysts. Jyothi *et al.* also observed that rare earth promoted sulphated tin oxide exhibits better oxidation activity for the oxidative dehydrogenation of ethylbenzene to styrene compared to the non-sulphated analogues and sulphated tin oxide (105). The enhanced oxidation activity is ascribed to the combined effect of sulphate anion and rare earth oxide promoter. The strong acid sites formed by sulphation activates ethylbenzene molecule, and rare earth oxide enhances the reaction between adsorbed oxygen atoms and adsorbed ethylbenzene (105).

1.10 CATALYSIS BY MOLYBDENUM OXIDE BASED SYSTEMS

Transition metal oxides supported on oxide carriers are used mainly in the field of selective oxidation reactions (106). Supported molybdenum oxide catalysts have been extensively studied because of their numerous catalytic applications in petroleum, chemical and pollution control industries (107,108). These catalysts are usually prepared by deposition of catalytically active molybdenum oxide component on the surface of an oxide support (TiO_2, Al_2O_3, ZrO_2, SiO_2 and MgO). Catalysts based on molybdenum oxides are widely used in the selective alkene oxidation reactions. Mo-Mg-O catalysts exhibited very high alkene selectivity for the oxidative dehydrogenation of alkanes (109,110).

Many investigations showed that molybdenum oxide could be readily supported over oxides like SnO_2 (68), Fe_2O_3 (111), ZrO_2, TiO_2 and Al_2O_3 (112). All these systems showed high activity for oxidation of methanol and the highest activity were shown by SnO_2 based systems. Molybdena supported silica catalysts are widely used in a number of reactions such as propene metathesis (113,114), propene oxidation (115), methanol oxidation (116), oxidative dehydrogenation of ethanol (113), selective oxidation of ammonia to nitrogen (117) and the selective oxidation of methane (118) There are only few reports regarding the acid-base properties of simple molybdenum oxide (119). The acidity increases when MoO_3 is supported on TiO_2, Al_2O_3 or SiO_2 and their mixed oxides. Pyridine adsorbed IR studies of these systems revealed the existence of both Lewis and Brönsted acid sites (119-121).

Ono *et al.* observed that molybdena dispersed on ZrO_2 is an active catalyst for oxidation of ethanol and propene and the maximum activity is shown at 10 atom % of Mo (122). TiO_2-MoO_3 systems are very active in NO reduction by NH_3 (123) and are useful precursors of hydrodesulphurisation catalysts (124). Ramis *et al.* studied the acidity of TiO_2-MoO_3 systems by FTIR spectroscopy of different probe molecule such as pyridine, acetonitrile, acrolein and propylene and detected the presence of very strong Brönsted and Lewis sites as well as strong oxidising sites (125). Banares *et al.* carried out selective oxidation of methane to formaldehyde at atmospheric pressure in N_2O and O_2 flow over a series of silica supported molybdena systems and observed that all the systems showed high methane conversion and formaldehyde selectivity when O_2 is used as the oxidant (126).

1.11 CATALYSIS BY IRON OXIDE BASED SYSTEMS

Sulphated iron oxide systems are found to be active for direct coal liquefaction (DCL) (127,128). Fe_2O_3/SO_4^{2-} catalysts have a hematite structure with sulphate anions at the surface. (128). Pradhan *et al.* showed that the dispersion and DCL conversion can be further improved by incorporating molybdenum and tungsten into the sulphated iron oxide system (129). Fe_2O_3 is regarded as weakly basic and acidic. It catalyses the dehydrogenation of ethanol (130), but for 2-butanol (131) and isopropanol (132) only dehydration takes place.

Iron oxides are generally used as oxidation or dehydrogenation catalysts in the form of single or mixed oxides or promoted by alkali. Important reactions catalysed by these systems include oxidative dehydrogenation of ethylbenzene (Fe_2O_3-K), water –gas shift reaction (Fe_2O_3-Cr_2O_3), ammoxidation of propylene (Fe_2O_3-Sb_2O_5) and dehydrogenation of methanol (Fe_2O_3-MoO_3). Acidic properties of iron dispersed on TiO_2, Al_2O_3, SiO_2 and MgO have been studied by pyridine adsorption and Mössbauer spectroscopy and the results showed that Fe dispersion on TiO_2 improved the Lewis acidity (133,134). Suja *et al.* prepared iron promoted sulphated zirconia with varying amounts of iron (2 to 10%), by impregnation of hydrous zirconium oxide with ferric nitrate solution and dilute sulphuric acid followed by calcination at 700°C and observed that the catalytically active tetragonal phase of zirconia is further stabilised by iron incorporation. The catalytic activity of the systems was studied by carrying out liquid phase benzoylation of arenes (135).

1.12 CATALYSIS BY TUNGSTEN OXIDE MODIFIED SYSTEMS

WO_3 supported on different metal oxides are found to be superacidic. Many studies are devoted to the use of WO_x- ZrO_2 systems in acid catalysed isomerisation reactions (136-138). The acidity of WO_x- ZrO_2 systems is found to be strongly dependent on tungsten loading. The acidity of these systems is determined by *n*-pentane isomerisation activity and maximum activity is obtained at 16 wt% tungsten loading (138). Yori *et al.* investigated the isomerisation of *n*-butane over WO_x-ZrO_2 and found that this system is active for the reaction (139). Zirconia-tungstate promoted with platinum shows superior selectivity in isomerisation of larger alkanes such as *n*-heptane (140,141). Tungsten based catalysts supported on oxides like TiO_2, Al_2O_3, ZrO_2 and SiO_2 have been used in various important processes like hydrodesulphurisation (142,143), selective catalytic reduction of NO_x (144) and olefin metathesis (145,146). Acid properties of tungsten-based catalysts have also been employed to improve alkane isomeristion activity, which is a very important step in the synthesis of high octane rating petrol (147-150).

1.13 REACTIONS IN THE PRESENT STUDY

Sulphated tin oxide systems were found to be acidic. In the present study the utility of various prepared systems towards acid catalysed Friedel-Crafts benzylation and benzoylation and vapour phase methylation of aniline were tested. Tin oxide systems were found to have high oxidising nature. Hence oxidative dehydrogenation of ethylbenzene was carried out over these systems to check their ability to act as oxidation catalysts.

1.13.1 Friedel-Crafts benzylation and benzoylation

Friedel -Crafts type of alkylation and acylation is one of the important reactions used for the synthesis of fine chemicals such as pesticides, food additives, pharmaceuticals, etc. Generally alkylation and acylation reactions are carried out in the presence of homogeneous Lewis acids such as $AlCl_3$, BF_3, and $FeCl_3$ and protonic acids like HF and H_2SO_4. (151,152). The acylation requires molar quantities of Lewis acid, which forms complexes with both the acylating agent and the carbonyl product; hence large amount of work up is needed to decompose these complexes and the catalysts are not reusable. The disposal of these catalysts poses several environmental problems due to their corrosive nature. In the present day, due to the high awareness towards pollution, there is thrust to replace these corrosive systems with eco-friendly catalysts. Highly acidic solids such as zeolites (153-158), clays (159) and sulphated ZrO_2 and Fe_2O_3 (160,161) were found to be excellent catalysts for alkylation and acylation reactions.

1.13.2 Methylation of aniline

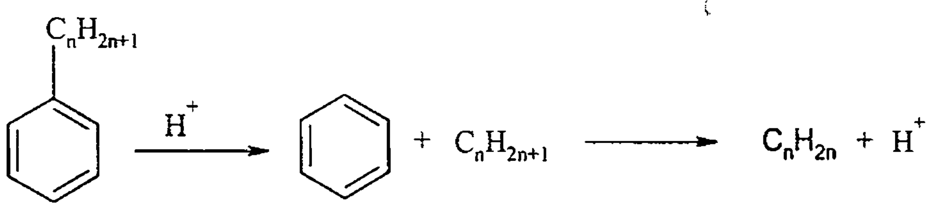
Methylation of aniline is an important reaction since the different products obtained from the reaction are used as intermediates in the manufacture of dye stuffs, explosives, plastics and pharmaceuticals. The main products for the methylation of aniline are N-methylaniline and N,N-dimethylaniline which are formed by N-alkylation and toluidines which are produced by C-alkylation. A wide variety of catalysts such as zeolites, clays metal oxides and molecular sieves are presently used for this reaction (162-171) ?

1.13.3 Oxidative dehydrogenation of ethylbenzene

Styrene is manufactured by simple dehydrogenation of ethylbenzene using iron oxide containing catalysts. But this conventional method has several drawbacks due to its high endothermic nature. So efforts have been made to replace this simple dehydrogenation by oxidative dehydrogenation in which the hydrogen abstracted from the molecule is made to react with an oxidant to form water. Air is generally used as the oxidant. This makes the reaction exothermic and hence oxidative dehydrogenation reactions are excellent alternative to classical dehydrogenations. This reaction seems to be influenced by both the basic and acidic sites on the catalyst. Ai *et al.* showed that catalytic activity variation with acid-base properties can be explained on the basis of the interaction between the reactant molecules and the active sites on the catalyst surface (172,173).

1.13.4 Cracking of alkyl aromatics

Cracking of alkylaromatics is a very specific reaction, since the aromatic nucleus will be inert towards fragmentation. Hence the splitting of C-C bond is limited to the non- aromatic part of the hydrocarbon. The C_{arom} - C_{aliph} bond is the most sensitive one for the fragmentation (174). The activity of a catalyst for the cracking of an alkylaromatic hydrocarbon indicates the existence of acidic hydroxyl groups on its surface (Brönsted acid sites), whereas the Lewis acid sites bring about dehydrogenation of alkylaromatics. Hence this reaction can be utilised as a model reaction for determining both the amount of Lewis and Brönsted acid sites on the catalyst surface. The generally used alkylaromatic for this study is cumene (175,176). On cumene cracking the Lewis acid sites generate α-methylstyrene and Brönsted acid sites gives benzene. The general scheme for cracking of an alkylaromatic hydrocarbon is given in Scheme 2.



Scheme 2 Cracking of alkyl chains

1.13.5 Decomposition of cyclohexanol

Selectivity in an alcohol decomposition reaction is regarded as a typical test reaction for investigating the acid-base properties of the catalytic sites on the metal oxides (177-181). Metal oxide surface can catalyse both dehydration and dehydrogenation of alcohols. Studies utilising different alcohols showed that acid sites on the catalyst surface cause dehydration (182) of the alcohol molecule and the basic sites cause dehydrogenation. The common alcohols used for this test reaction include isopropanol (183), cyclohexanol (184), 2-butanol (185,186), etc. Cyclohexanol is the alcohol selected for the present study; on dehydrogenation it gives cyclohexanone and dehydration gives cyclohexene.

1.14 PRESENT WORK

Sulphated metal oxides have attracted considerable attention in the last decade and among the sulphated oxides the most studied systems are based on zirconia and titania. Much less studies are devoted on sulphated tin oxide systems. Tin oxide due to its inherent oxidising ability forms an important ingredient in many oxidation catalysts. The sulphate modification also seems to enhance the oxidation ability. So in this investigation an attempt was made to modify tin oxide with different transition metal oxides and sulphate, and how this modification influences the acid-base and oxidation properties and catalytic activity of pure tin oxide.

1.15 OBJECTIVES OF THE WORK

Main objectives of the work includes

- Preparation of sulphated tin oxide containing varying amounts of MoO_3, Fe_2O_3 and WO_3.The metal oxide loading was varied from 4 to 24 (wt)%.
- To investigate the physico-chemical characteristics of the prepared samples by various techniques like EDX, XRD, FTIR, TGA, BET surface area and pore volume measurements.

- To evaluate the surface acidic properties of the systems using various independent techniques. The total acidity of the catalysts was obtained by ammonia TPD and thermodesorption of pyridine. The adsorption studies using perylene determines Lewis acidity of the systems.

- To compare the acid-base properties by cyclohexanol decomposition reaction

- To determine the surface Lewis to Brönsted acid site ratio by cumene cracking

- To analyse the applicability of the samples towards industrially important Friedel-Crafts benzylation and benzoylation of aromatics. To examine the influence of various reaction parameters such as substrate to benzylating or benzoylating agent molar ratio, reaction temperature, reaction time, moisture, etc. on catalytic activity and selectivity.

- To evaluate the catalytic activity of the systems towards methylation of aniline, which is another industrially important reaction.

- To test the efficiency of the prepared systems for the oxidative dehydrogenation of ethylbenzene.

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2

EXPERIMENTAL

1.1 INTRODUCTION

Catalysis involves the interaction of the reactant molecules with the active sites of the catalysts. The texture of the catalyst particles and their surface properties largely influence the catalytic activity of these systems. Many experimental parameters such as metal oxide preparation procedure, sulphate and metal oxide loading method, temperature of calcination before reaction, etc, have been observed to affect the strength and nature of the active sites of sulphate modified metal oxides. The physico-chemical analysis gives a picture about the texture, phase and chemical composition of the catalyst. Thus, a methodological preparation and catalyst characterisation becomes highly essential. This chapter covers the preparation methods and characterisation techniques employed in the present work.

2.2 CATALYST PREPARATION

2.2.1 MATERIALS

Stannous chloride	Qualigens
Conc. HNO_3	Merck
Conc. HCl	Merck
Conc. H_2SO_4	Merck
Ammonia	Merck
Ferric nitrate	Qualigens
Ammonium heptamolybdate	Merck
Tungstic acid	Merck

2.2.2 METHODS

i) Tin hydroxide

Hydrous tin oxide was prepared by the hydrolysis of stannic chloride using ammonium hydroxide (1). Stannic chloride solution was prepared from stannous chloride by oxidation with conc. HNO_3. Conc. HNO_3 was added to stannous chloride taken in a beaker until a pasty material was formed. It was then dissolved in minimum amount of aqua-regia on a sand bath to get stannic chloride solution. It was diluted with distilled water and heated to 80°C and 1:1 ammonia solution was added dropwise to this solution with constant stirring to complete the precipitation. The final pH of the solution was maintained as 4. The solution was boiled for 10 minutes and kept overnight. The precipitate was then washed several times with deionised water, until it was free from chloride and nitrate ions, filtered and dried in an air oven at 110°C for 12 hours. The dried sample was then sieved to get particles of 75-100 microns mesh size.

ii) Metal oxide loaded sulphated tin oxide

Metal oxide loaded sulphated tin oxide systems were prepared from tin oxide by single step wet impregnation using metal salt solution and 1N H_2SO_4. Iron, molybdenum and tungsten oxide loaded samples were prepared using ferric nitrate, ammonium heptamolybdate and tungstic acid solution respectively. The systems prepared are represented in Table 2.1.

To pure tin hydroxide, sulphuric acid and metal salt solution were added and stirred for four hours and then the solution was dried off. The samples thus obtained were subjected to overnight drying at 110°C. Then these were sieved to get particles of size < 100 microns. After sieving the samples were calcined. The calcination temperature employed for pure, sulphated and iron oxide modified systems was 550°C and that for molybdenum and tungsten series was 700°C. Pure and sulphated tin oxides were designated as S and SS respectively.

Table 2.1 Catalyst systems used for the present study

% of metal oxide loaded over tin oxide	Notation for iron systems	Notation for molybdenum systems	Notation for tungsten systems
4	F_4	M_4	W_4
8	F_8	M_8	W_8
12	F_{12}	M_{12}	W_{12}
16	F_{16}	M_{16}	W_{16}
20	F_{20}	M_{20}	W_{20}
24	F_{24}	M_{24}	W_{24}

2.3 CATALYST CHARACTERISATION

The catalyst systems prepared were characterised using various physico-chemical techniques such as X-ray diffraction (XRD), BET surface area and pore volume measurements, infrared spectroscopy, energy dispersive X-ray analysis, thermal analysis (TG), scanning electron microscopy and Laser Raman Spectroscopy. The acidic properties of the samples were determined by ammonia TPD and thermodesorption study using pyridine. The electron accepting properties of the catalyst systems were studied by adsorption studies using perylene, which provide a measure of the Lewis acidity of the catalysts.

2.3.1 MATERIALS

Liquid nitrogen	Manorama Oxygen Pvt. Ltd.
Potassium bromide	Merck
Perylene	Merck
Pyridine	Merck
Benzene	Merck

2.3.2 METHODS

i) Surface area and pore volume measurements

Gas adsorption isotherm measurements are widely used for determining the surface area of various solids (2-4). N_2 is the usually recommended adsorbate for determination of surface areas higher than $5m^2 g^{-1}$. N_2 adsorption is usually carried out at liquid nitrogen temperature (77 K). BET method is generally used for analysing the surface area of the catalysts. The BET equation can be represented as

$$P/[V(P_0-P)] = [1/V_mC] + [(C-1)/V_mC](P/P_0)$$

where, C is a constant for a given system and is dependent on adsorbent - adsorbate interaction

P – adsorption equilibrium pressure

P_0 – saturation vapour pressure of the adsorbate

V – volume of nitrogen adsorbed at equilibrium pressure, P

V_m – volume of adsorbate required for monolayer coverage

A plot of $P/[V(P_0-P)]$ against P/P_0 gives a straight line with slope $(C-1)/V_mC$ and intercept $1/V_mC$. From these two, surface area can be obtained by applying the value of V_m in the equation

$$\text{Surface area} = V_m N_A A_m / 22414$$

where, N_A is the Avagardo number and A_m the molecular cross sectional area of the adsorbate ($0.162\ nm^2$ for N_2)

In the present study Micromeritics Gemini surface area analyser was used for determining the surface area and total pore volume of the samples simultaneously. Prior to the measurement, the samples were activated for two hours at the appropriate temperature and then degassed at 200°C under nitrogen flow. The degassed samples were then subjected to N_2 adsorption at 77 K maintained using liquid nitrogen.

ii) X-Ray diffraction studies

X-ray diffraction analysis is the most frequently employed method for the structural analysis of the solids. It helps to identify the crystalline phases present in the analysed material, by comparing the experimental results with the XRD data banks. Analysis of diffraction patterns allows the determination of the XRD detectable phases, unit cell parameters, degree of structural order, size and shape of crystallites, purity of the substance, randomness and imperfections in the lattice and composition of solid solutions.

XRD analysis is based on the interaction of X-rays with the crystalline phases of the solid samples, which leads to the scattering of the X-rays in different directions. A monochromatic X-ray beam is allowed to fall on the powdered sample and the diffraction pattern is obtained by plotting the intensity of the scattered radiation as a function of scattering angle 2θ. Bragg's equation $n\lambda= 2d \sin\theta$, gives the value of interplanar spacing (d), where n is the order of diffraction, λ is the wave length of the monochromatic X-ray used, θ is the angle between the crystal plane and X-ray. The crystallite size of the sample can be determined from the broadening of the diffraction peak, using the Scherrers equation, $t = \lambda/B\cos\theta$, where B is the Full-Width –Half Maximum of the strongest peak, t-crystal diameter, θ-Bragg angle. In the present study XRD patterns of the samples were recorded using Rigaku D-max C X-ray diffractometer using Ni filtered Cu- K_α radiation (λ = 1.5406 Å). The data obtained were compared with the standard data file (Joint Committee on Powder Diffraction Standards).

iii) Energy dispersive X-Ray analysis

Energy dispersive X-ray analysis is used for the qualitative and quantitative elemental analysis of solid samples. This method is based on the fact that when electrons of appropriate energy strike a sample surface it causes emission of X-rays. The principle of this emission is that electron beam striking a solid surface ejects an electron from the inner shell of the sample atom. Electron from a higher energy level will fill the resulting vacancy. When the electron falls from a higher to a lower energy level it will emit some amount of energy, which will be equal to the energy difference between the two electronic levels involved. Due to the large energy difference of the inner shells, the resulting radiation will be in the form of X-rays. Each element will have a unique electronic configuration; hence the energy and the intensity of the X-rays emitted will be dependent on the composition of the solid sample. EDX of the samples were analysed using a Stereo scan 440 apparatus.

iv) Infrared spectroscopy

Infrared spectroscopy is another important technique used for the structural analysis of samples. This spectral analysis gives information about the metal-support interactions, metal-metal interactions and the functional groups present on the catalyst surface. It also identifies the adsorbed species on the catalyst surface, which makes this method useful for the surface acidity determination of catalyst using suitable probe molecules such as ammonia and pyridine. The IR analysis of the samples adsorbed with pyridine helps to identify both the Lewis and Brönsted acid sites.

The IR spectrum is produced during the change in dipole moment of the molecule due to the vibrations in the molecule. IR analysis helps to identify the surface sulphate species of the modified tin oxide systems. FTIR spectra of the activated powdered samples were determined using Shimadzu DR 8001 spectrophotometer by KBr pellet method.

v) Thermogravimetric analysis

Thermogravimetric analysis helps to determine the phase transformations, decomposition temperature, drying ranges, etc. of the solid samples. In TGA, the weight of the sample subjected to controlled linear heating was recorded as a function of time or temperature. The weight of the sample was plotted against temperature to get a thermogram. The dips in the thermogram indicate the weight loss due to decomposition, and the horizontal portions in the graph indicate that the sample is thermally stable at that temperature range. The thermogravimetric analysis of the samples was performed using Shimadzu TGA-50 equipment. The analysis was done in nitrogen atmosphere using a heating rate of 10°C/minute.

vi) Scanning electron microscopy

The scanning electron microscopy allows the imaging of the topology of a solid surface (5). In SEM, a fine probe of electrons is used to scan the catalyst surface with the help of deflection coils. This technique gives an idea about the morphology and crystal size of the samples. The main disadvantage of this analysis is that the result represents only a spot in the sample and not of the entire sample. In order to overcome this disadvantage we should take the images of various spots on the catalyst surface. The scanning electron micrographs of the samples were recorded using Stereoscan 440 scanning electron microscope.

vii) Acidity determination

The surface acid-base properties play an important role in determining the activity and selectivity of the catalysts. Sulphation improves the surface acidity of tin oxide, so only the acidic properties of the samples were analysed. Acidity of the samples were obtained by different methods such as temperature programmed desorption of ammonia, thermodesorption of pyridine, perylene adsorption studies and test reactions like cumene cracking and decomposition of cyclohexanol.

a) Temperature programmed desorption studies

Conventional Hammett method for acidity determination is not useful for the coloured samples. Temperature programmed desorption of base molecule is found to be an efficient method for determining the acidity of the catalysts (6,7). NH_3- TPD is now widely used for evaluating the surface acidity of the solid catalysts. This method gives the total acidity and acid strength distribution of the catalyst since NH_3 molecules can bind to acid sites of any strength and type.

For the TPD analysis, 0.5 g of the pelletised and subsequently activated catalyst was loaded into a steel reactor of 30 cm length and 1 cm diameter kept in a cylindrical furnace. The pellets were degassed at 300°C for half an hour under nitrogen atmosphere. It was then brought to room temperature and a fixed amount of ammonia was injected into the reactor in the absence of nitrogen flow and the pellets were allowed to adsorb the ammonia for 20 minutes. Excess ammonia was then flushed off by passing nitrogen. The temperature was then raised in a stepwise manner and the ammonia desorbed in the temperature range 100-600°C at intervals of 100°C was trapped in dilute sulphuric acid of known normality. It was then back titrated with NaOH to get the amount of ammonia desorbed at that particular temperature.

[illegible]

b) Perylene adsorption studies

Perylene molecule readily donates an electron to form a radical since the radical formed is stabilised by resonance. Hence perylene adsorption analysis gives the amount of Lewis acid sites present in the catalyst (8,9). For the adsorption studies, perylene solutions of varying concentrations were prepared using benzene as solvent. Definite weight of preactivated samples were stirred with 5 ml of these solutions then get adsorbed on the catalyst surface as radical cation, by donating its electron to the Lewis acidic center. The amount of perylene adsorbed was obtained by measuring the absorbance of the solution before and after adsorption. The absorbance was measured using Shimadzu UV- 160 A UV-Vis spectrophotometer. By plotting equilibrium concentration of the electron donor against amount of perylene adsorbed, limiting amount of perylene adsorbed is calculated.

c) Thermodesorption of pyridine

Thermodesorption of probe molecules is another method used for determining the acidity of catalyst systems. The probe molecules used includes pyridine, *n*-butyl amine, 2,6-dimethylpyridine, etc. Pyridine has affinity to both Brönsted and Lewis acid sites so thermodesorption study using pyridine as probe helps to determine the total acidity of the system (10). The activated samples were kept in a dessicator containing pyridine for 48 hours, for the equilibrium adsorption of the probe molecule on the catalyst surface. The samples were then subjected to thermogravimetric analysis in N_2 atmosphere at a linear heating rate of 20°C/min. The amount of pyridine desorbed gives the measure of the total acidity of the system. These data can be compared with the TPD results.

2.4 CATALYTIC ACTIVITY STUDIES

The catalytic activity of the systems was tested by carrying out some industrially important reactions. The reactions can be carried out either in liquid or in vapour phase. The main drawback of liquid phase reactions is that the maximum reaction temperature attained is limited to the refluxing temperature of the reaction mixture, whereas in vapour phase we can easily carry out the reaction at higher temperatures. The liquid phase reactions carried out in the present study are Friedel-Crafts benzylation and benzoylation. Vapour phase reactions carried out include methylation of aniline and oxidative dehydrogenation of ethylbenzene. Cumene cracking and decomposition of cyclohexanol were done in vapour phase, as test reactions for acidity.

2.4.1 MATERIALS

Benzene	Merck
Toluene	Merck
o-Xylene	Merck
Benzyl chloride	Merck
Benzoyl chloride	Merck
Aniline	Merck
Methanol	Merck
Ethylbenzene	CDH
Cumene	Merck
Cyclohexanol	Qualigens

2.4.2 METHODS

i) Liquid phase reactions

a) Friedel-Crafts benzylation

Friedel-Crafts benzylation of toluene and *o*-xylene using benzyl chloride was carried out in batch wise manner. The reaction mixture containing the substrate and benzylating agent in a definite molar ratio was added to 50 mL double-necked round bottomed flask fitted with a spiral condenser containing 0.1 g catalyst. It was then placed in an oil bath maintained at a selected temperature and the reaction mixture was stirred magnetically. The product analysis was done using Chemito 8610 Gas Chromatograph equipped with flame ionisation detector and SE-30 column.

The reaction was carried out using excess substrate and the yield was calculated based on the amount of benzyl chloride. The selectivity for a particular product is expressed as the amount of that product divided by the total amount of all the products multiplied by 100. The catalytic activity was studied by varying different parameters such as reaction temperature, reaction time and molar ratio between the substrate and benzyl chloride. The effect of metal leaching and moisture was also investigated.

b) Friedel-Crafts benzoylation

Reaction mixture containing *o*-xylene and benzoyl chloride in the required molar ratio was taken in a 50 mL RB flask (mounted on a magnetic stirrer) containing 0.1 g of catalyst maintained at a definite temperature using an oil bath. Influence of reaction parameters like substrate to benzoyl chloride molar ratio, reaction temperature and time was studied in detail. The effect of moisture and metal leaching on catalytic activity was also scrutinised. The product analysis was done using Chemito 8610 Gas Chromatograph equipped with FID and SE-30 column.

ii) Vapour phase reactions

The vapour phase reactions were carried out in a vertical, fixed bed, flow type, quartz reactor of 2.5 cm diameter and 30 cm length mounted in a cylindrical furnace vertically. The preactivated catalyst powder (0.5 g) was placed in a glass wool bed in the middle of the reactor, packed with silica beads. A thermocouple placed near the catalyst bed monitored the reaction temperature. A temperature controller was used to maintain the temperature of the furnace. The reactants were introduced into the reactor by means of a syringe pump. The circulation of cold water in the condenser connected to the reactor cooled the reaction mixture eluting out of the reactor. The condensed reaction mixture was collected in the receiver. This mixture was then analysed at definite time intervals with the help of Gas Chromatograph. → [illegible] calculation of [illegible] conversion

a) Methylation of aniline

A mixture of aniline and methanol in a definite molar ratio was fed into the reactor maintained at the required temperature. The products were analysed using Chemito 8610 Gas Chromatograph containing an SE-30 column. The change of catalytic activity with feed rate, time on stream, reaction temperature and aniline to methanol molar ratio was also investigated.

b) Oxidative dehydrogenation of ethylbenzene to styrene

The ethylbenzene feed was introduced at the top of the reactor maintained at a fixed temperature at a particular flow rate. The reaction was carried out in presence of air, for certain selected samples catalytic activity was analysed in the absence of air also. The effect of reaction parameters such as feed rate and reaction temperature was studied in detail. Deactivation studies were carried out for few systems. The products were analysed using FFAP column.

b) Decomposition of cyclohexanol and cumene cracking

Decomposition of cyclohexanol and cumene cracking were done as test reactions for acidity. In the case of cumene cracking the product analysis was done in FFAP column, while for cyclohexanol, carbowax column was used.

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3

PHYSICO-CHEMICAL CHARACTERISATION

The catalysts prepared were characterised by various techniques like XRD, EDX, IR, TGA, SEM, surface area and pore volume measurements. The acidity of the systems was determined by TPD of ammonia, thermodesorption of pyridine, adsorption of perylene, and by two different vapour phase test reactions *viz.* cumene cracking and cyclohexanol decomposition. The results obtained in the different analyses are presented in this chapter.

3.1 SURFACE AREA AND PORE VOLUME MEASUREMENTS

The surface area and pore volume values of pure, sulphated and metal oxide incorporated sulphated tin oxide are given in Tables 3.1 to 3.3. Sulphated tin oxide has higher surface area than pure tin oxide. The sulphate group introduced was well dispersed on the metal oxide surface, thereby preventing the tin oxide particles from coming closer, which reduce the crystal growth In addition, the sulphate species offer high resistance to the sintering of the metal oxide (1). Addition of another metal oxide component further enhances the surface area values. For all the three systems under study, the surface area increases up to a certain percentage of metal oxide incorporation. Further addition of the metal oxide seems to have a negative effect. The percentage loading at which maximum surface area was obtained was different for each metal oxide species. The increase in the surface area values at low metal oxide loading may be due to a considerable decrease in the crystal growth caused by the newly incorporated species. The metal oxide along with the sulphate ions gets dispersed on the surface and prevents the agglomerisation of tin oxide particles. At high percentage loading the metal oxide species may not be well dispersed on the surface and itself gets agglomerated causing a decline in the surface area.

The pore volume of the samples showed the same trend as that of the surface area. The sulphation and low metal oxide loading enhanced the pore volume of tin oxide. Higher

% incorporation of metal oxide reduced the pore volume of the samples indicating that high metal oxide loading leads to the blockage of the catalyst pores.

Table 3.1. Surface area and pore volumes of tungsten oxide modified sulphated tin oxide systems

Systems	BET (m^2/g)	Total Pore volume (cc/g)
S	5	0.0820
SS	24	0.0189
W_4	41	0.0289
W_8	50	0.0398
W_{12}	55	0.0452
W_{16}	62	0.0531
W_{20}	57	0.0461
W_{24}	51	0.0289

Table 3. 2 Surface area and pore volumes of sulphated tin oxide modified with molybdenum oxide

Systems	BET (m^2/g)	Total Pore volume (cc/g)
S	5	0.0820
SS	24	0.0189
M_4	51	0.0401
M_8	67	0.0610
M_{12}	82	0.0891
M_{16}	88	0.0920
M_{20}	73	0.0752
M_{24}	66	0.0382

Table 3. 3 Surface area and pore volumes of sulphated tin oxide modified with iron oxide

Systems	BET (m^2/g)	Total Pore volume (cc/g)
S	20	0.0165
SS	83	0.0882
F_4	90	0.0893
F_8	96	0.0912
F_{12}	102	0.0977
F_{16}	77	0.0490
F_{20}	54	0.0397
F_{24}	39	0.0287

3.2 ENERGY DISPERSIVE X-RAY ANALYSIS

The surface composition of the prepared samples was determined by EDX analyais. In the case of tungsten and molybdenum samples, EDX analysis was done after calcining the samples at 700°C and iron samples were calcined at 550°C before EDX analysis. The values are presented in the Tables 3.4 - 3.6. The composition of the metal oxides obtained from EDX measurement showed some variations when compared with the theoretical values. In the theoretical calculations, the percentage of sulphate incorporated in tin oxide was not considered. The weight of metal oxide necessary for loading alone was determined and then it was sulphated using a fixed amount of sulphuric acid. But EDX determines the amount of sulphate retained in addition to the amount of metal oxide. This accounts for the variation. The amount of sulphate retained did not vary much with increase in metal oxide loading. Molybdenum and tungsten systems that were calcined at 700°C exhibited excellent sulphate retaining capacity compared to the iron systems. This implies that the surface sulphate species are stable at high temperatures [illegible] based on

[illegible]

[illegible] oxide samples

(Table [illegible]

Table 3.4 Chemical composition of molybdenum oxide incorporated samples

Systems	Percentage composition		
	Tin oxide	Molybdenum oxide	Sulphate content
SS	99.36	-	0.64
M_4	93.02	2.67	4.31
M_8	90.33	5.78	3.89
M_{12}	85.08	10.09	4.83
M_{16}	81.63	14.23	4.14
M_{20}	77.44	17.87	4.69
M_{24}	75.01	20.73	4.26

Table 3.5 Chemical composition of tungsten oxide modified sulphated tin oxides

Systems	Percentage composition		
	Tin oxide	Tungsten oxide	Sulphate content
SS	99.36	-	0.64
W_4	92.94	3.11	3.95
W_8	89.69	6.43	3.88
W_{12}	85.80	9.83	4.37
W_{16}	81.81	14.08	4.11
W_{20}	79.10	16.92	3.98
W_{24}	74.96	21.29	3.75

Table 3.6 Chemical composition of iron oxide modified sulphated tin oxides

Systems	Percentage composition		
	Tin oxide	Iron oxide	Sulphate content
SS	98.43	-	1.57
F_4	93.24	2.98	3.78
F_8	89.62	6.15	4.23
F_{12}	84.99	10.53	4.48
F_{16}	82.11	13.95	3.94
F_{20}	78.47	17.52	4.01
F_{24}	75.35	21.13	3.52

3.3 X-RAY DIFFRACTION ANALYSIS

XRD patterns of iron, tungsten and molybdenum series are represented in Figures 3.1, 3.2 and 3.3. respectively. Pure tin oxide showed the tetragonal cassetterite phase only. It is well evident from the diffraction patterns that the addition of sulphate ion and metal oxide component lowers the intensity of the XRD peaks. Matsuhashi *et al.* (1) have reported that the degree of crystallisation of sulphated oxides is much lower when compared to the pure oxides. Even after modification, the diffraction patterns predominantly contain the tetragonal phase of tin oxide. This implies that sulphation and metal oxide loading lead to a reduction in the crystallisation of tin oxide by preventing the particle growth. But the prominent phase remains the same even after the incorporation of a second component. The reduction in the intensity of the diffraction peaks is more prominent in the case of iron oxide modified samples (Figure 3.3). This may be due to the greater tendency of the iron oxide particles for agglomerisation and the low calcinations temperature used in the case of these samples.

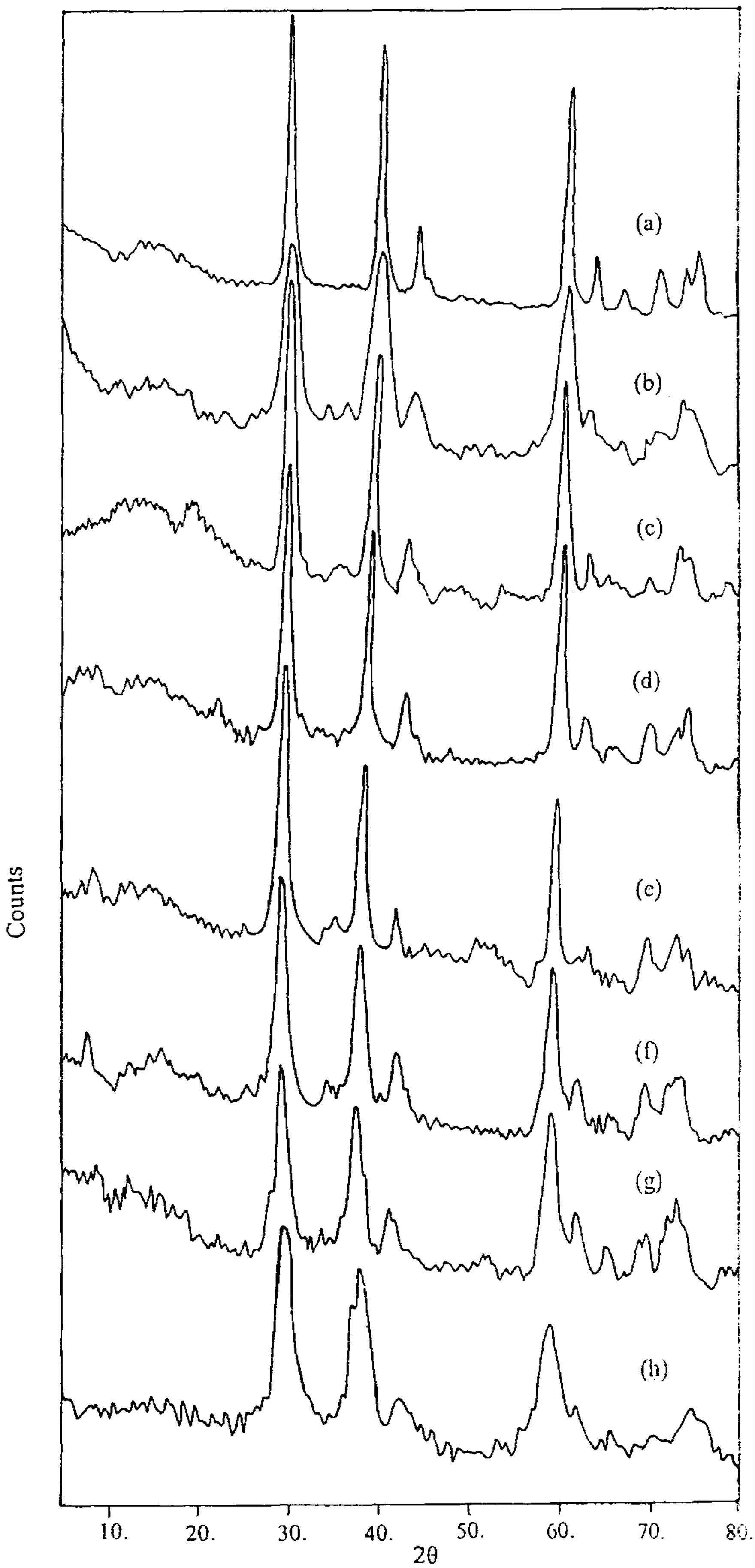


Figure 3.1 XRD patterns of molybdenum series

(a) S, (b) SS, (c) M_4, (d) M_8, (e) M_{12}, (f) M_{16}, (g) M_{20}, (h) M_{24}

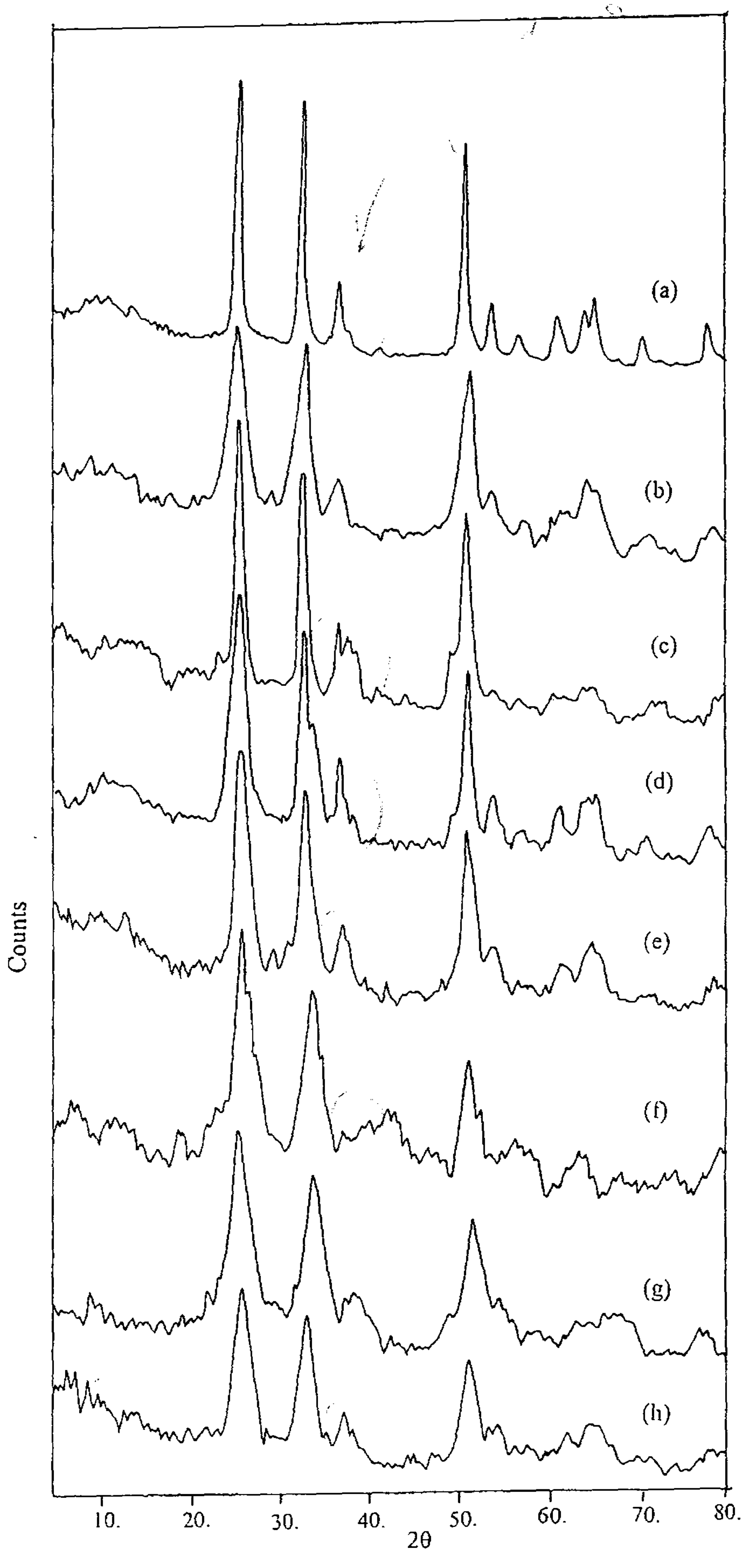


Figure 3.2 XRD patterns of tungsten series

(a) S, (b) SS, (c) W_4, (d) W_8, (e) W_{12}, (f) W_{16}, (g) W_{20}, (h) W_{24}

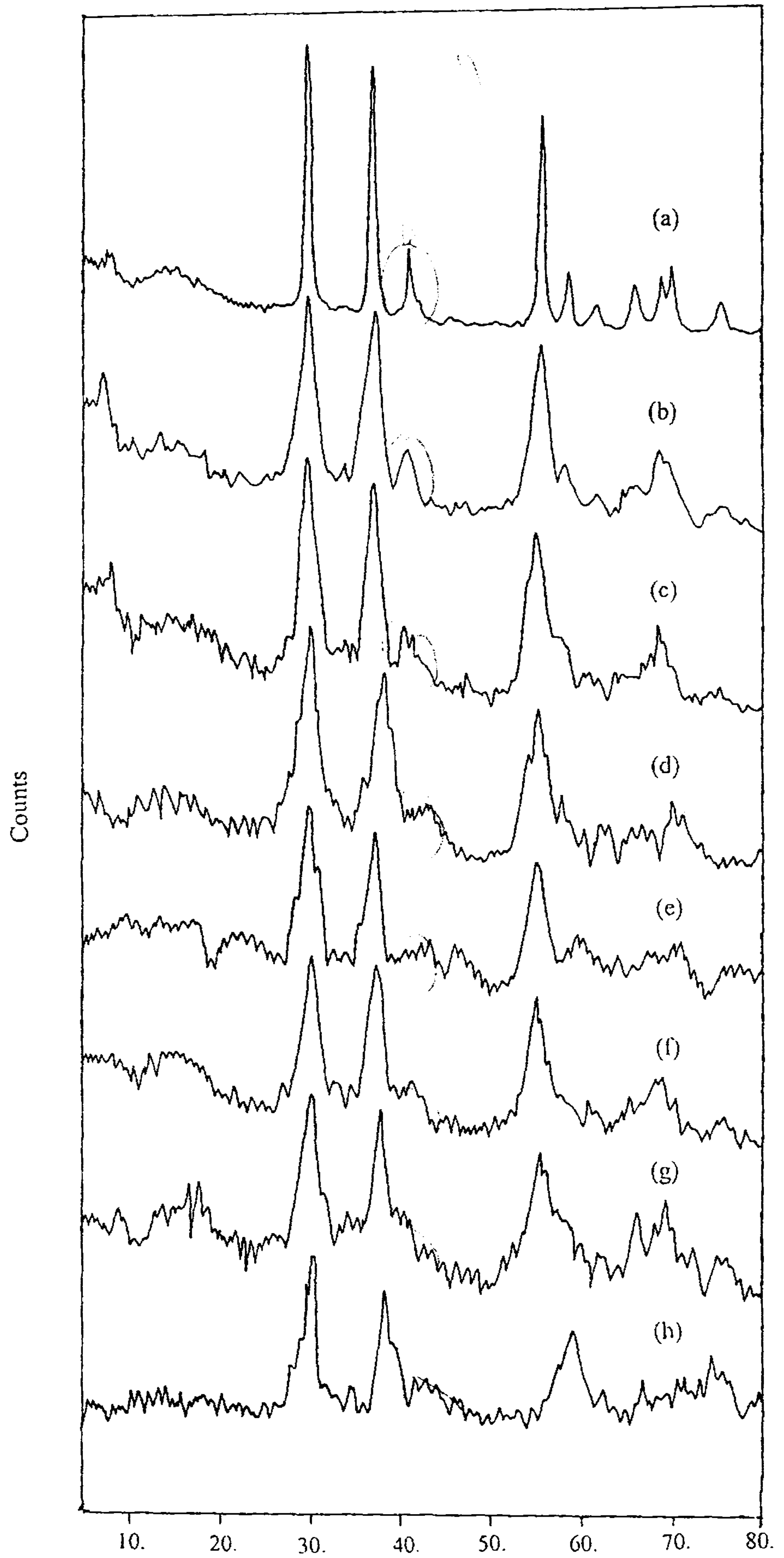


Figure 3.3 XRD patterns of iron series

(a) S, (b) SS, (c) F_4, (d) F_8, (e) F_{12}, (f) F_{16}, (g) F_{20}, (h) F_{24}

3.4 INFRARED SPECTROSCOPY

The IR spectra of F_{20}, W_{20}, M_{20}, SS and pure tin oxide are given in Figure 3.4. General peaks observed in the case of sulphated samples are at 1210, 1130-1140, 1020 and 970 cm^{-1} (2). These peaks are due to chelating bidentate sulphate ions co-ordinated to the metal. The spectra of W_{20} and M_{20} systems exhibited a small peak in the region 1370-1390 cm^{-1}; the band around this region arises due to the highly covalent nature of the S=O on a highly dehydrated metal oxide surface. But in the case of sulphated tin oxide and F_{20} systems this peak was not observed indicating that, S=O in these systems are less covalent in nature. The existence of highly covalent S=O is the essential requirement for the superacidity in sulphated metal oxides. The absence of bands in the 1400 cm^{-1} indicates the absence of polynuclear sulphate species on the catalyst surface (3). Other bands observed in these spectra are at 3460 and 1620 cm^{-1}, which correspond to the bending and stretching vibrations of surface hydroxyl groups.

3.5 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis gives an idea about the thermal stability and the phase transitions of the catalyst systems. Figure 3.5 represents the TG curves of the representative samples (F_{20}, W_{20} and M_{20}). For all thermograms, an initial weight loss in the temperature region 90-150°C was observed that might be due to the loss of physisorbed water. In the case of F_{16} system, weight loss in the 390-440°C region was observed. This is found to be the decomposition temperature of ferric nitrate to form oxide. In case of molybdenum and tungsten samples the weight loss below the region 500°C may be due the transformation of impregnated compound to the corresponding oxides. The sulphate species in suphated tin oxide is stable even at 650°C and incorporation of transition metal oxides further stabilises the sulphate moiety. In all these thermograms no apparent weight loss was observed up to 700°C after transformations of metal salts to corresponding metal oxide.

3.6 SCANNING ELECTRON MICROSCOPY

Scanning electron micrographs of pure, sulphated and some metal oxide samples are given in Figures 3.6 and 3.7. The figures indicate that the sulphated tin oxide has lower

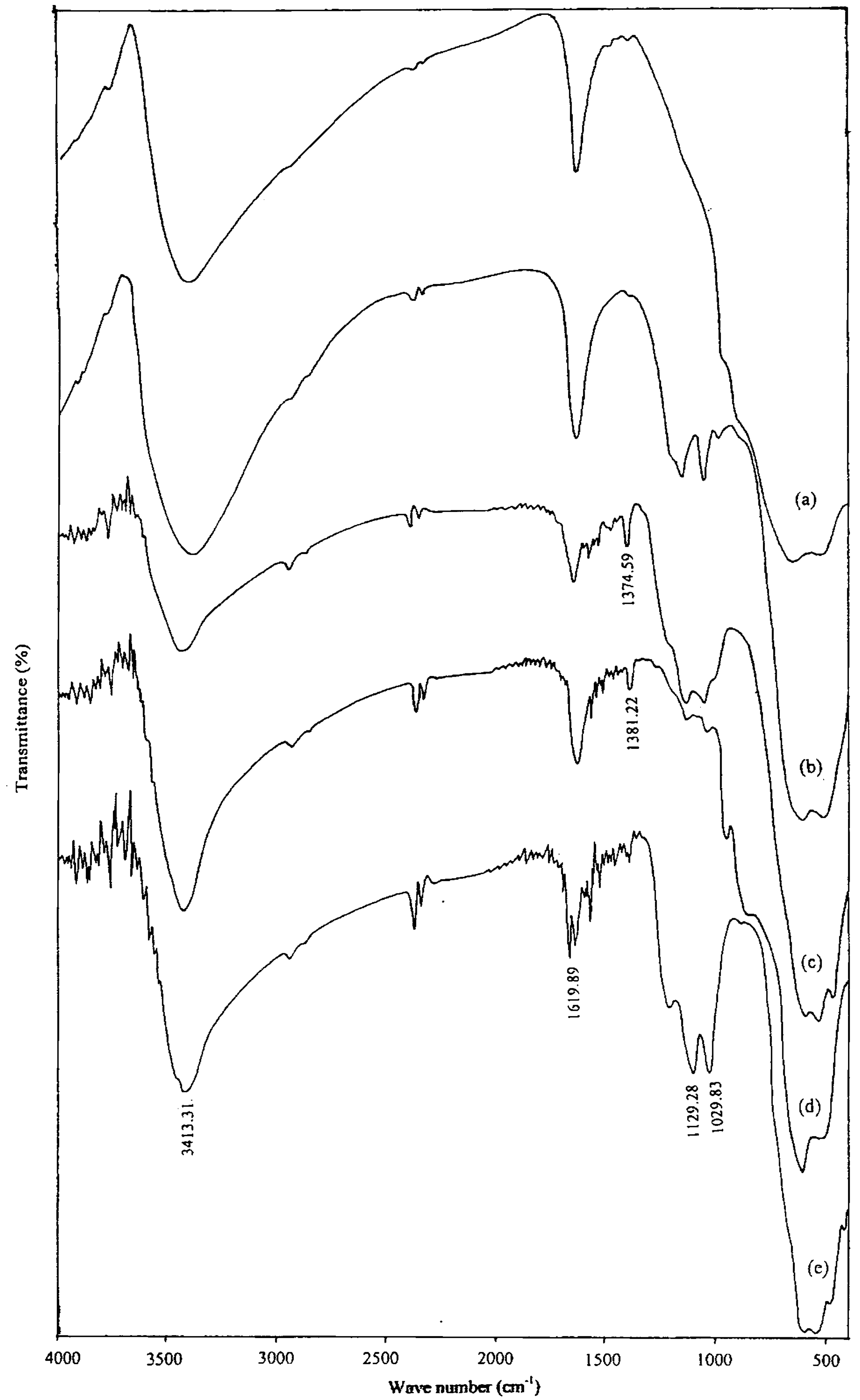


Figure 3.4 IR of some representative systems

(a) S, (b) SS, (c) M_{20}, (d) W_{20}, (e) F_{20}

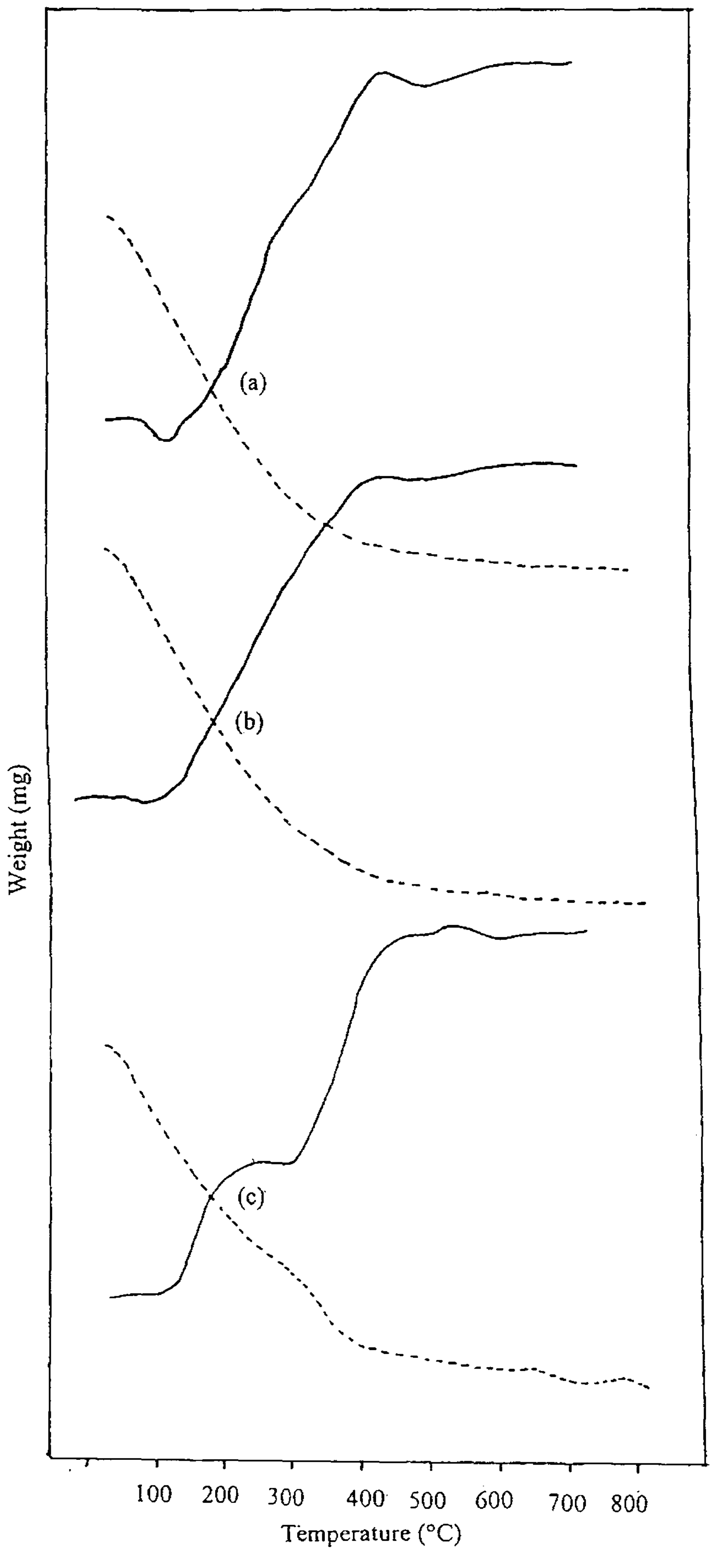
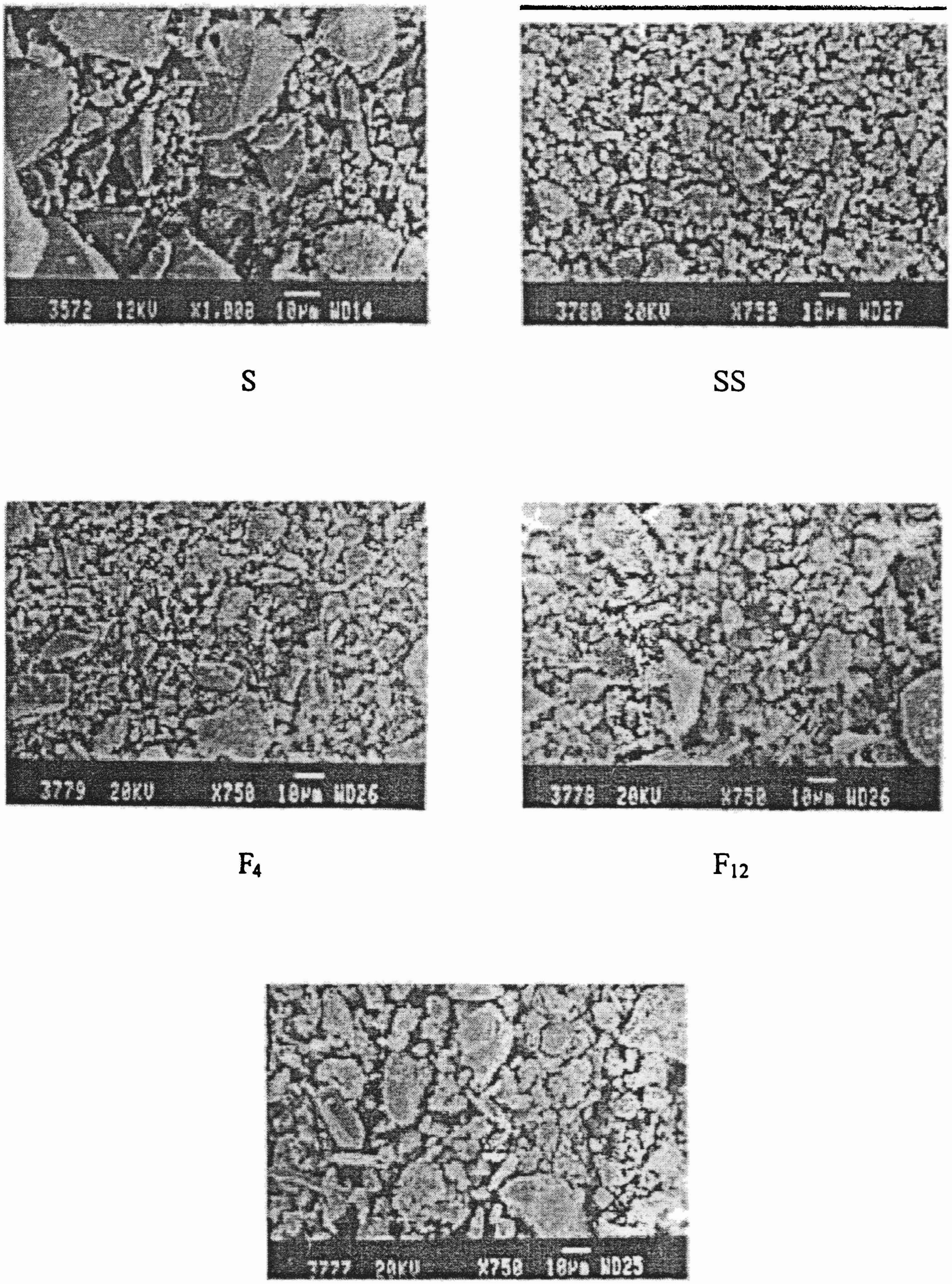


Figure 3.5 TG and DTG of some representative systems

(a) M_{20}, (b) W_{20}, (c) F_{20} (---TG , —DTG)

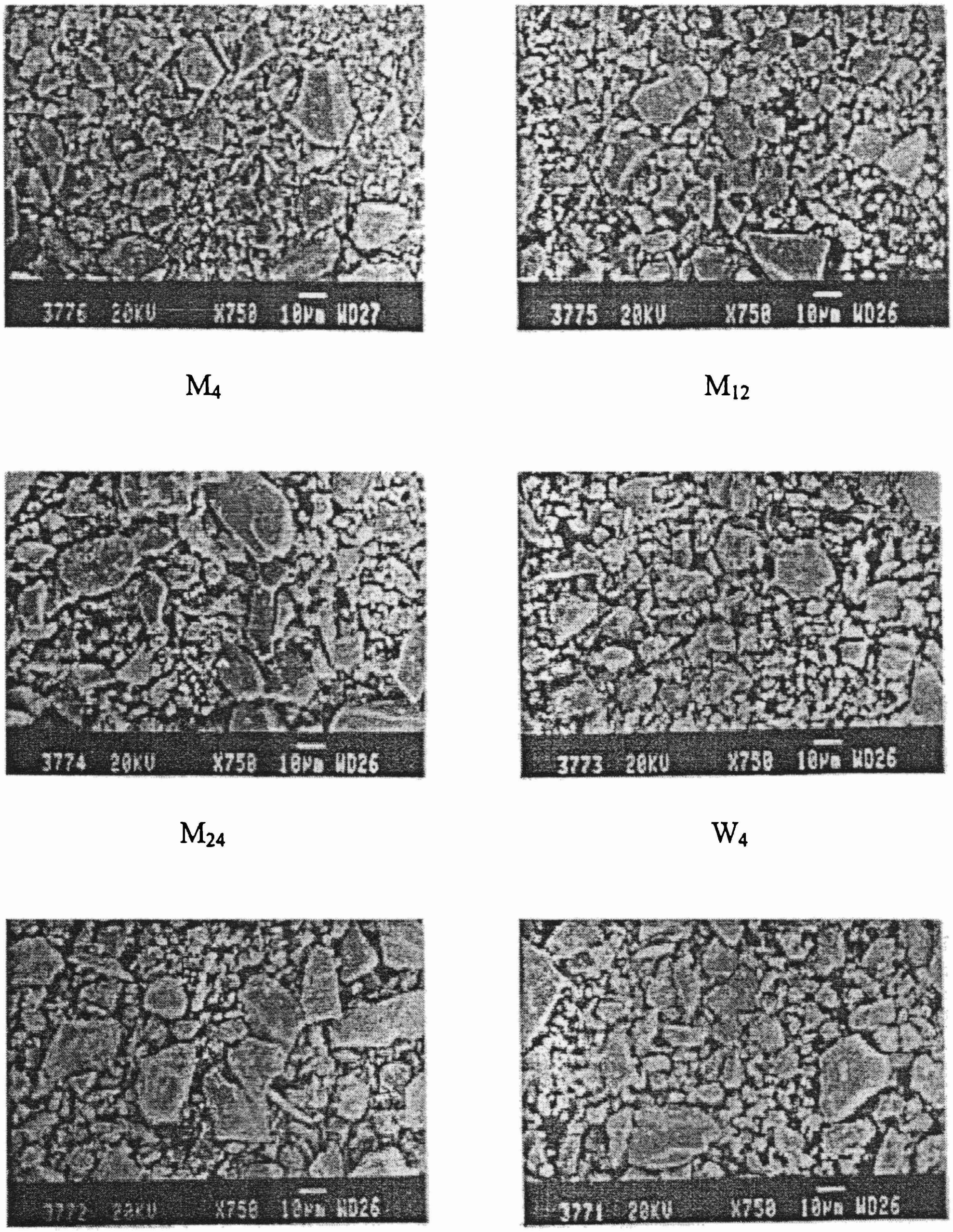


S SS

F_4 F_{12}

F_{24}

Figure 3.6 SEM pictures of S, SS, F_4, F_{12} and F_{24}



M_4 M_{12}

M_{24} W_4

W_{12} W_{24}

Figure 3.7 SEM pictures of M_4, M_{12}, M_{24}, W_4, W_{12} and W_{24}

crystallite particles when compared to that of pure tin oxide. Addition of another metal component further decreases the crystallite size. But this decrease is observed only to an optimum metal oxide loading and further addition of metal oxide causes an increase in the particle size.

3.7 ACIDITY MEASUREMENTS

It is well established that the acidity plays an important role in virtually all-organic reactions carried out over solid catalysts. Acidity is found be the most important catalytic function of sulphated oxides. Hence determination of the acid sites exposed on the surface as well as their distribution is an essential requirement to evaluate the catalytic properties of acidic solids.

3.7.1 Temperature programmed desorption of ammonia

Temperature programmed desorption of simple bases is a widely used method to assess the total number and strength of acid sites (4-7). Basic molecules such as ammonia (8-10), pyridine (4) and *n*-butylamine are the generally used probe molecules. Among these molecules ammonia is most widely used; being a small molecule it has greater accessibility to almost all acidic sites including the weak ones. Ammonia TPD has been employed to characterise the acidity of ZSM-5 (4,11,12) mordenite (4,5), Y-zeolite (13), sulphated zirconia (14), SnO_2-MoO_3 systems (15), etc. In this method the concentration of desorbing ammonia gas in the effluent gas may be monitored by adsorption/titration, thermal conductivity, flame ionisation or mass spectroscopy. In the present work adsorption/titration method is utilised. The different types of ammonia adsorption on the catalyst surface can be classified as, (i) weak chemisorption (desorption of ammonia in the range 100-200°C) (ii) moderately strong chemisorption (desorption in the range 300-400°C) (iii) and strong chemisorption (desorption above 450°C).

It was found that sulphation and transition metal oxide loading improved the total acidity of pure tin oxide. TPD data for the molybdenum, tungsten and iron systems are given in Tables 3.7, 3.8 and 3.9 respectively. In the case of all the thee systems the acidity value increased with an increase in the amount of metal oxide incorporated, reached a maximum value at a particular percentage of metal oxide loading and thereafter decreased. For iron series the maximum acidity was shown by F_{12}, for molybdenum series M_{20} showed maximum acidity and for tungsten series W_{20} exibited maximum acidity. Further addition of metal oxide caused a reduction in total acidity values. Another important observation was that for all the three systems, the weak and medium acidity showed the maximum enhancement. The increase in the strong acidity was minimal for all the three sets of catalysts. Among the three series studied molybdenum systems showed the maximum total acidity, whereas iron systems were found to be least acidic.

Table 3.7. Acidity distribution of molybdenum systems obtained from TPD measurements

Systems	Weak m mol/g	Medium	Strong	Weak + Medium	Total (mmol/g)
S	0.1587	0.1000	0.0767	0.2587	0.3354
SS	0.2351	0.1231	0.1023	0.3582	0.4605
M_4	0.3682	0.2143	0.0934	0.5875	0.6809
M_8	0.4023	0.2677	0.0804	0.6700	0.7504
M_{12}	0.5331	0.3704	0.2236	0.9035	1.1271
M_{16}	0.7117	0.3451	0.2071	1.0568	1.2644
M_{20}	.8432	0.5518	0.2062	1.2950	1.6012
M_{24}	0.6391	0.3564	0.1290	0.9955	1.1245

It is well reported that for the sulphated metal oxides the electron withdrawing inductive effect of the sulphate groups though the bridged oxygen atoms generates high surface acidity. The maximum inductive effect will be shown by those groups which have high covalent character for S=O. From the IR spectral studies it is clear that only the molybdenum and tungsten systems showed the band in 1370-1390 cm^{-1} region which corresponds to highly covalent S=O. The spectra of iron and sulphated tin oxide has all other peaks corresponding to the chelating sulphate ligand except the one representing highly covalent S=O. This provides a good explanation to the low total acidity of the iron systems.

Table 3.8 Data for TPD studies over tungsten oxide incorporated sulphated tin oxide

Systems	Weak	Medium	Strong	Weak + Medium	Total (mmol/g)
S	0.1587	0.1000	0.0767	0.2587	0.3354
SS	0.2351	0.1231	0.1023	0.3582	0.4605
W_4	0.3606	0.1665	0.0971	0.5271	0.6242
W_8	0.3850	0.2923	0.2068	0.6773	0.8841
W_{12}	0.3920	0.3318	0.2659	0.7238	0.9897
W_{16}	0.4793	0.4403	0.2022	0.9197	1.1214
W_{20}	0.5995	0.4270	0.1934	1.0265	1.2199
W_{24}	0.5332	0.1874	0.0908	0.7206	0.8204

Table 3.9 Acidity values obtained from TPD measurement for the iron modified sulphated tin oxide

Systems	Weak	Medium	Strong	Weak + Medium	Total (mmol/g)
S	0.1587	0.1000	0.0767	0.2587	0.3354
SS	0.2351	0.1231	0.1023	0.3582	0.4605
F_4	0.2595	0.2422	0.0692	0.5017	0.5709
F_8	0.4024	0.2632	0.0817	0.6656	0.7443
F_{12}	0.4278	0.3834	0.0764	0.8112	0.9876
F_{16}	0.5227	0.1768	0.1153	0.6995	0.8148
F_{20}	0.6225	0.0966	0.0644	0.7191	0.7835
F_{24}	0.3215	0.2120	0.0316	0.5335	0.5651

3.7.2 Thermodesorption of pyridine

Thermodesorption studies of various bases are used to determine the acidity of catalyst systems. Pyridine molecule was used for the present study. The results for the three series are depicted in Tables 3.10 and 3.11. Since pyridine molecules get adsorbed on both Lewis and Brönsted acid sites, this study helps to determine the total acidity of the systems. The data obtained by this analysis supported the TPD results.

Table 3.10 Data for thermodesorption of pyridine on molybdenum and tungsten systems

Systems	Relative (wt %) of pyridine desorbed			
	Weak	Medium	Strong	Total
S	1.03	0.77	0.52	2.32
SS	1.39	0.73	0.95	3.07
M_4	1.61	1.21	1.14	3.96
M_8	3.11	1.32	0.88	5.31
M_{12}	3.59	1.75	1.54	6.88
M_{16}	4.38	2.68	1.73	8.79
M_{20}	6.87	2.48	1.69	11.04
M_{24}	3.95	2.38	0.83	7.16
W_4	1.98	1.14	0.91	4.03
W_8	2.13	1.88	1.43	5.44
W_{12}	2.82	2.23	1.48	6.53
W_{16}	3.75	2.52	1.25	7.55
W_{20}	5.98	2.61	1.31	9.90
W_{24}	3.51	1.28	0.62	5.41

Table 3.11 Data for thermodesorption of pyridine over iron systems

Systems	Relative (wt %) of pyridine desorbed			
	Weak	Medium	Strong	Total
S	1.03	0.77	0.52	2.32
SS	1.39	0.73	0.95	3.07
F_4	1.37	1.28	0.98	3.63
F_8	3.02	1.42	0.74	5.18
F_{12}	4.84	2.05	0.79	7.68
F_{16}	3.13	1.02	0.99	5.14
F_{20}	4.33	0.98	0.73	6.04
F_{24}	1.58	1.24	0.93	3.75

3.7.3 Perylene adsorption studies

The base adsorption method and amine titration help to establish only the total acidity of the systems. Neither of these methods allows the quantitative determination of Lewis acidity of the surface. Lewis acidity, in presence of Brönsted acid sites, can be quantitatively obtained by utilising the ability of the catalyst surface to accept a single electron. The polyaromatic compounds which are generally used in the studies of one electron acceptor properties of solids are perylene, pyrene, chysene (16,17) and phenothiazine (18,19).

When an acidic surface is exposed to electron donor molecules, these molecules get adsorbed on the catalyst surface by the donation of an electron. Hence the amount of surface sites, which act as electron acceptors, can be obtained by measuring the amount of adsorbed molecules. Usually strong electron donors form charge transfer complexes with surface active site, which exhibits a characteristic ESR spectrum (20,21). The intensity measurement of ESR signal corresponding to the surface charge transfer complex will give the amount of one electron acceptor sites on the surface. Electron spectroscopy can also be used for analysing the surface charge transfer complex. In this case an adsorption band describes the energy involved during the formation of the charge transfer complex. The quantitative measurement of donor molecules that are adsorbed on the one electron accepting sites indirectly determines the amount of electron deficient sites i.e., the Lewis acid sites.

Experimental [illegible]

In the present study activated catalyst systems were stirred with a solution of perylene in benzene at room temperature; in the course of stirring perylene gets adsorbed on the solid surface, leading to colour change of the solution. For molybdenum systems pale green fluorescent perylene solution turns clear; in the case of tungsten systems also the colour of the solution was considerably reduced, but as the iron systems themselves were coloured, the colour change of the perylene solution was not clearly visible. Perylene readily donates an electron to the Lewis acid site and gets adsorbed on the solid surface. Thus after adsorption, the concentration of perylene in the solution was considerably reduced. The decrease in the amount of perylene in solution can be obtained by measuring the absorbance of the solution before and after adsorption studies. The amount of perylene adsorbed increases with concentration of perylene solution. This increasing trend continues up to a particular perylene concentration and thereafter the amount of perylene adsorbed decreases with increase in concentration. This constant value is called the limiting amount, which corresponds to the surface one electron accepting capacity or Lewis acidity.

The data for perylene adsorption studies of the three series are given in Table 3.12, 3.13 and 3.14. Both tin oxide and sulphated tin oxide did not respond to perylene adsorption. Incorporation of metal oxide enhanced the Lewis acidity. The Lewis acidity value increased with the increase in percentage loading and this increasing trend continued till a certain percentage loading. After this value further addition of metal oxide caused a reduction in the limiting amount of perylene adsorbed. The percentage loading at which the maximum Lewis acidity was observed varies for different metal oxides. For molybdenum systems the maximum value was obtained for M_{20}, for iron it was F_{16} and for tungsten series, the maximum value was shown by W_{16}. In this analysis, a comparison among the three series showed that molybdenum loading was most effective for the Lewis acidity enhancement followed by tungsten and iron systems. This was in good agreement with the trend shown by TPD and thermodesorption of pyridine. In all the thee series the magnitude of perylene adsorption value is much lesser than the TPD values; this may be due to the larger size of the perylene molecule, which prevents its accessibility to all the surface acidic sites.

Table 3.12 Perylene adsorption data for molybdenum systems

Catalyst	Limiting amount (10^{-6} mol/g)
S	-
SS	-
M_4	4.4
M_8	5.45
M_{12}	6.95
M_{16}	8.31
M_{20}	9.60
M_{24}	7.46

Table 3.13 Perylene adsorption data over iron systems

Catalyst	Limiting amount (10^{-6} mol/g)
S	-
SS	-
F_4	0.87
F_8	1.73
F_{12}	4.97
F_{16}	5.63
F_{20}	4.11
F_{24}	3.97

Table 3.14 Data for perylene adsorption over tungsten systems

Catalyst	Limiting amount (10^{-6} mol/g)
S	-
SS	-
W_4	1.84
W_8	2.62
W_{12}	4.94
W_{16}	7.01
W_{20}	5.21
W_{24}	5.94

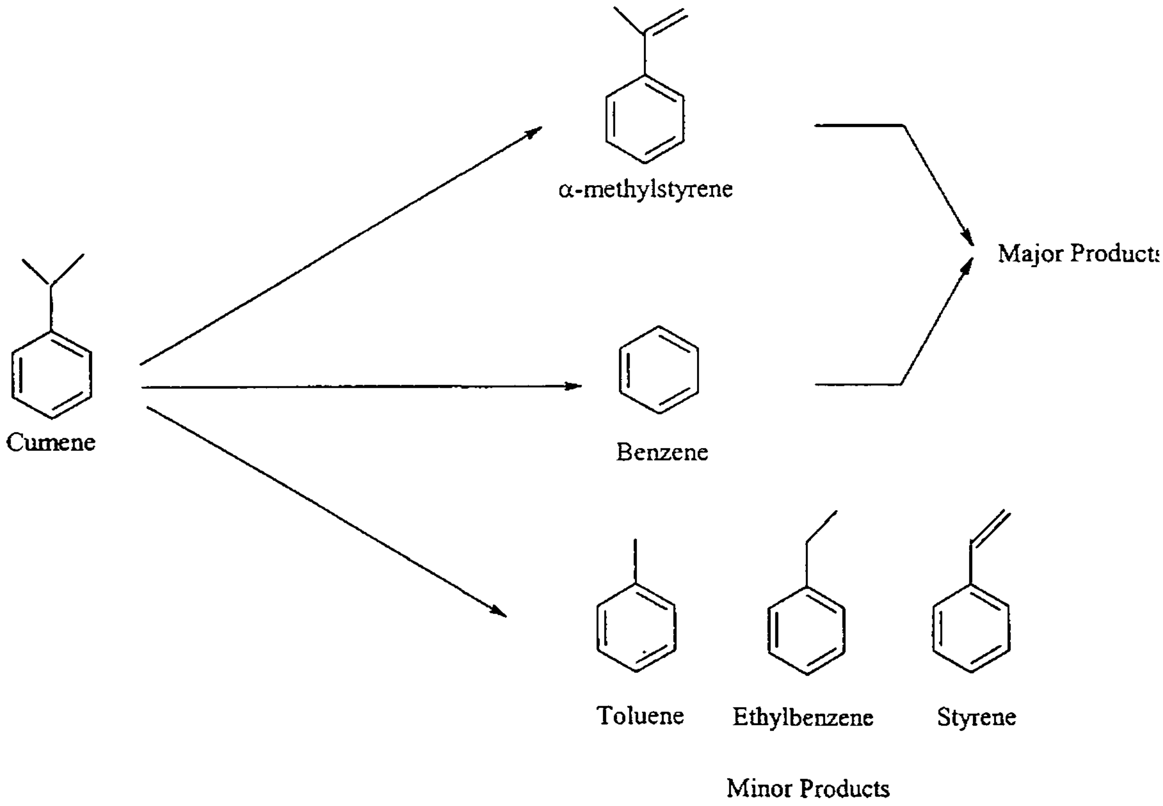
3.8 TEST REACTIONS

The acidity of catalysts can also be determined using appropriate test reactions. In certain cases, the activity in the test reaction could be related to the number and distribution of acid sites on the catalyst surface. The generally used test reactions are isomerisation of alkenes, dehydration of alcohols and cracking of alkylaromatics. The test reactions selected for the present study are cracking/ dehydrogenation of cumene and decomposition of cyclohexanol.

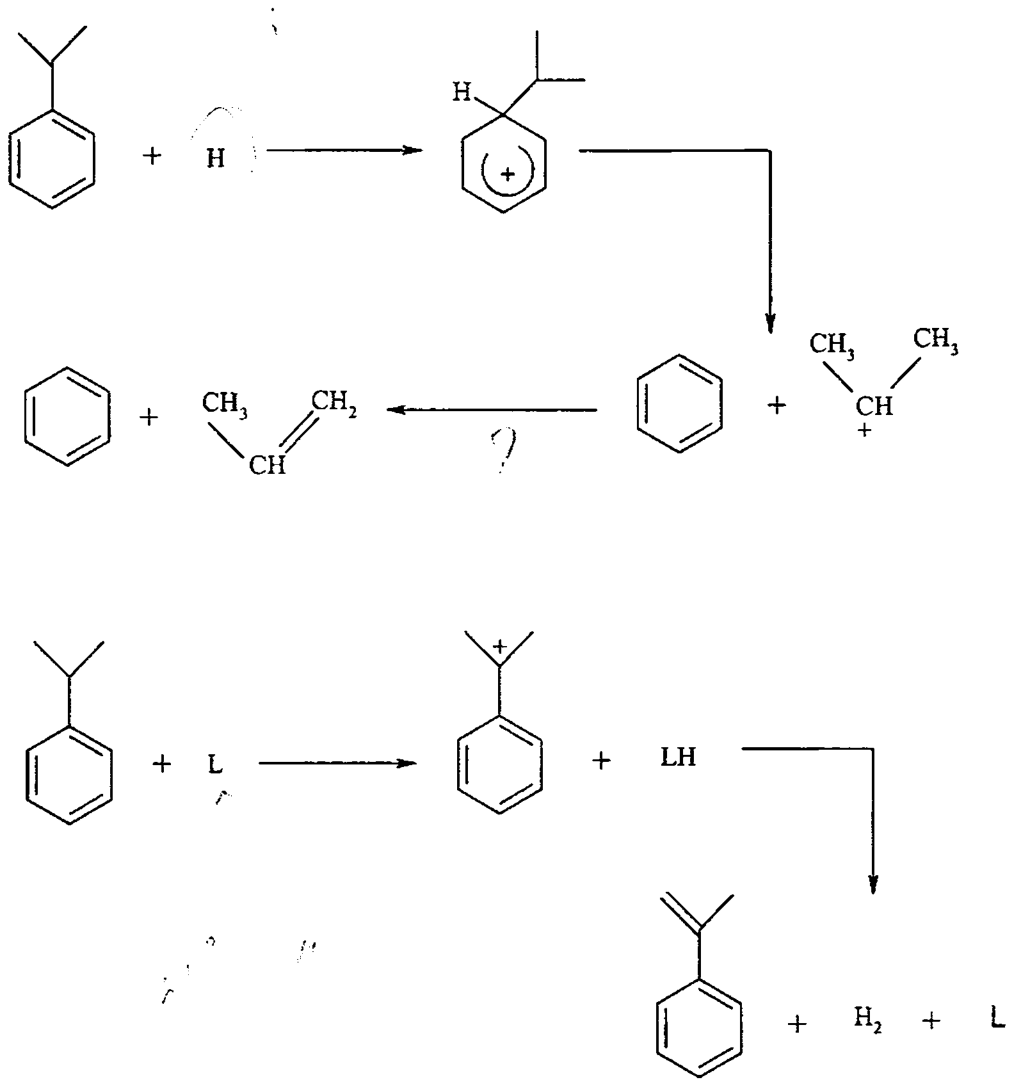
3.8.1 Cumene cracking

Cumene is a convenient model compound for acidity studies, as it undergoes different reactions over different type of active sites. The main reactions in cumene decomposition are dealkylation and dehydrogenation. Over Brönsted acid sites, cumene is cracked to benzene and propene via a carbocation mechanism (22-25) and on Lewis acid sites, cumene is converted into α-methylstyrene (26). The reaction thus helps in determining the Lewis/ Brönsted acid ratio of the catalyst. There is also some probability for cracking of the alkyl chain giving ethylbenzene, which on dehydrogenation gives styrene. Thus major products in cumene cracking are benzene and α-methylstyrene and minor ones are toluene, ethylbenzene and styrene (Scheme 3.1)

Sarbak *et al.* have studied the effect of fluoride and sodium ions on the activity of γ-alumina for cumene cracking and observed that pure γ-alumina that gave mainly α-methylstyrene on cracking, showed drastic increase in the activity and high selectivity towards benzene after the incorporation of fluoride ions. But sodium ion addition made this system completely inactive towards dealkylation and produced only α-methylstyrene (27). Cumene cracking was carried out over γ-alumina impregnated with fluoride, cobalt, molybdena and combination of these additives by Boorman *et al.* The catalytic activities of these systems were correlated with the acidity (28,29).



Scheme 3.1 Different pathways involved in cumene cracking



Scheme 3.2 Mechanism for cumene cracking

3.8.1.A. PROCESS OPTIMISATION

To find the optimum reaction parameters, cumene cracking was carried out over M_{16} system at different flow rates and temperature. In order to determine the stability of the catalyst for long runs the reaction was carried out for five hours and the product mixture was analysed at definite time intervals.

i) Influence of flow rate

To determine optimum feed rate the reaction was carried out at flow rates 4, 5, 6 and 7 mL/h at a reaction temperature of 350°C over M_{16}. The results obtained are depicted in Figure 3.8. As the feed rate is increased from 4 to 7 mL/h, the conversion decreased from 20.88 to 9.42 %. The contact time between the reactant and the catalyst surface is a decisive factor in determining the activity of the catalyst. At higher flow rates the contact time will be less leading to decrease in conversion. At all flow rates major product was α-methylstyrene with small amounts of benzene, toluene, ethylbenzene and styrene. The catalyst showed above 90% selectivity to α-methylstyrene at all flow rates and with increase in flow rate no considerable decrease in the dehydrogenation activity is observed. This indicates that surface acidity of this system is mainly due to the Lewis acid sites.

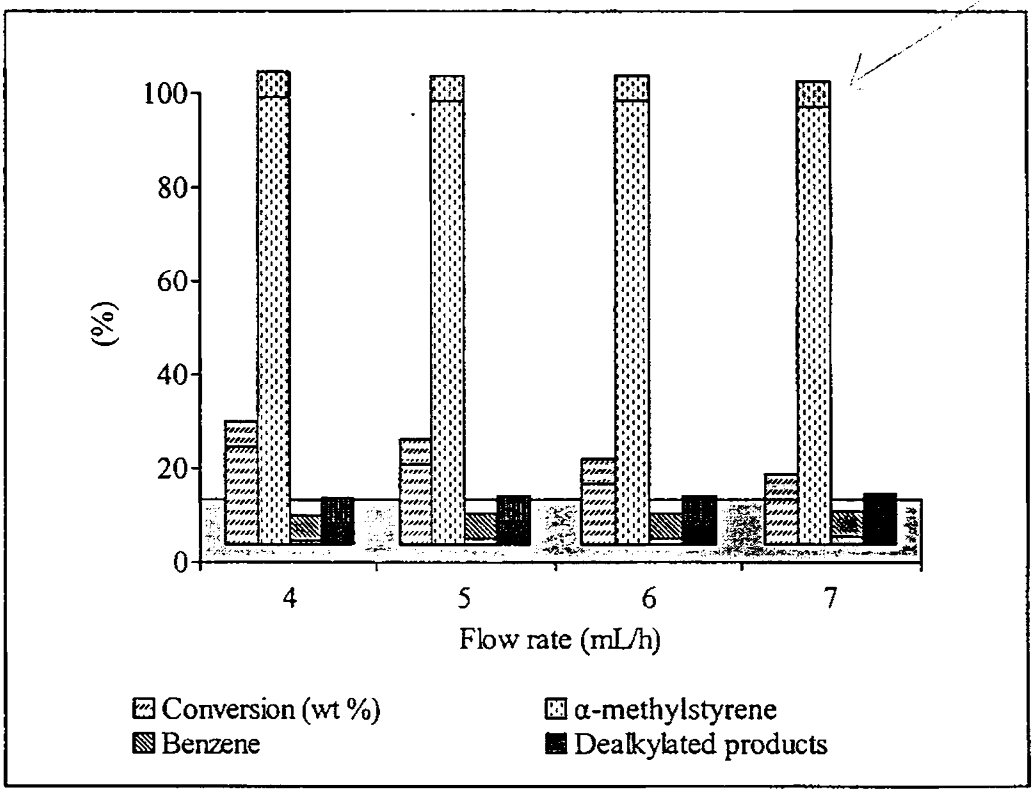


Figure 3.8 Variation in catalytic activity and selectivity for cumene cracking at different flow rates

Reaction conditions: 0.5 g of M_{16} activated at 700°C, Reaction temperature- 350°C, Duration- 2 h

ii) Influence of reaction temperature

The temperatures selected for this study was from 350°C to 500°C. The flow rate used was 4 mL/h. Figure 3.9 shows the effect of temperature on the conversion and selectivity for cumene cracking reaction over M_{16} system. The conversion for the reaction increased with the increase in temperature. At 350°C the conversion was only 16.91%, this increased to about 99% at 500°C. The selectivity towards α-methylstyrene was considerably reduced when the temperature was increased from 350 to 500 °C. At the initial temperature the system showed about 95% selectivity towards α-methylstyrene, but as the reaction temperature was increased, the selectivity for α-methylstyrene decreased steadily to 41% at 500°C. The amount of toluene, ethylbenzene and styrene showed an increase as the temperature increased. The increase in the amount of these products may be due to the rate of increase in dealkylation with the increase in temperature.

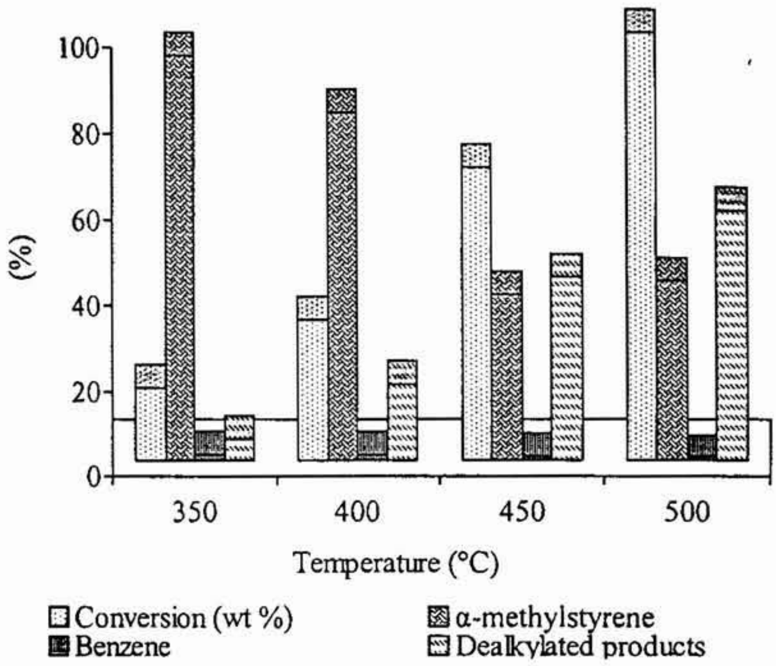


Figure 3.9 Influence of reaction temperature on activity and selectivity for cumene cracking over M_{16}

Reaction conditions: 0.5g of M_{16} activated at 700°C, Flow rate- 4 mL/h, Duration- 2 h

iii) Influence of time on stream - Deactivation studies

Time on stream studies was performed over M_{16} system under optimised reaction conditions and the product mixture was analysed after each hour. The result obtained for the deactivation studies are represented in Figure 3.10. An important observation was that conversion remained almost same thoughout the course of reaction. So this implies that the time factor does not have much effect on the catalytic activity of the catalyst system selected. The product distribution also remained almost constant after five hours, α-methylstyrene being the major product with selectivity around 90%. This implies that the system is stable for cracking of cumene, and the active (Lewis) sites over the catalyst surface were intact even after five hours. The catalyst pores are not at all blocked by deposition of coke formed during the course of reaction.

Has coke formation [illegible]

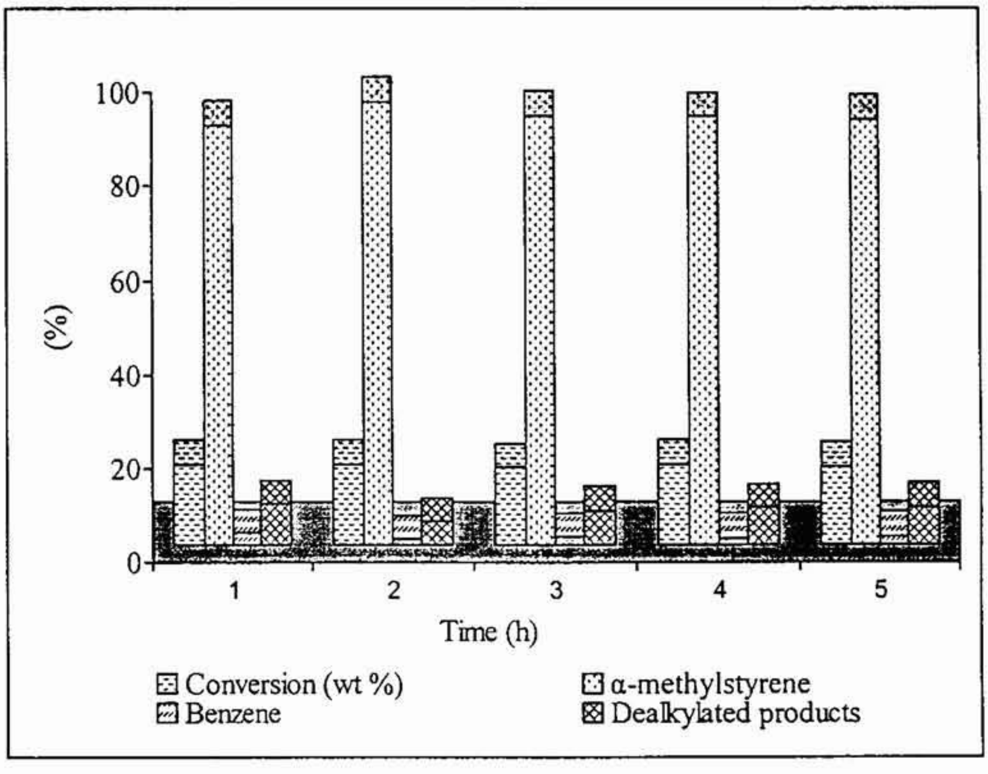


Figure 3.10 Deactivation studies for cumene cracking reaction

Reaction conditions: 0.5g of M_{16} activated at 700°C, Flow rate- 4 mL/h, Reaction temperature- 350°C

iv) Catalyst comparison

The activity and selectivity for the cumene cracking for the three series are given in Tables 3.15 - 3.17. The metal oxide incorporation has a positive influence on the activity of tin oxide towards cracking reaction. Pure tin oxide did not give any cracked products. Sulphate modification improved its catalytic activity, but these samples gave about 25% toluene, ethylbenzene and styrene. Modification of tin oxide with both sulphate ions and a second metal oxide further improved the activity. This also leads to the reduction of side chain dealkylation to give ethylbenzene. Metal oxide modified systems showed high selectivity for α-methylstyrene. This is the case with all the three series of systems. All the systems including sulphated tin oxide showed low selectivity for benzene (the maximum being 7% for sulphated tin oxide).

Table 3.15 Variation in the cumene cracking activity of sulphated tin oxide with the incorporation of molybdenum oxide

Systems	Conversion (wt %)	Selectivity (%)				
		Benzene	Toluene	Ethyl benzene	α-methylstyrene	Styrene
S	-	-	-	-	-	-
SS	6.03	3.63	9.28	19.21	66.12	1.76
M_4	11.39	3.16	2.65	3.81	89.25	1.10
M_8	13.88	2.36	-	5.27	92.36	-
M_{12}	15.11	1.49	1.81	1.35	94.01	1.34
M_{16}	16.91	1.04	0.94	1.77	96.25	-
M_{20}	29.49	-	0.18	0.74	98.77	0.31
M_{24}	15.58	1.73	2.03	2.77	91.15	-

Reaction conditions: 0.5g of M_{16} activated at 700°C, Duration- 2 h, Reaction temperature- 350°C, Flow rate-4 mL/h

Table 3.16 Data for cumene cracking over tungsten oxide loaded sulphated tin oxide

Systems	Conversion (wt %)	Selectivity (%)				
		Benzene	Toluene	Ethyl benzene	α-methylstyrene	Styrene
S	-	-	-	-	-	-
SS	6.03	3.63	9.28	19.21	66.12	1.76
W_4	12.37	4.29	5.87	8.68	80.11	1.15
W_8	14.50	1.94	5.48	7.50	83.26	1.82
W_{12}	17.08	3.78	4.76	5.58	85.03	0.85
W_{16}	18.53	0.86	-	5.79	91.24	2.11
W_{20}	18.24	2.56	5.78	3.43	88.23	-
W_{24}	13.98	5.00	2.72	5.70	86.57	-

Reaction Conditions: 0.5 g catalyst activated at 700°C, Reaction temperature-350°C, Duration –2 h, Flow rate- 4 mL/h.

It was reported earlier that for molybdenum containing systems dehydrogenation is the major reaction even in the presence of considerable amount of Brönsted acid sites and it was assumed that in such systems the Brönsted acid sites are rapidly destroyed under the reducing hydrocarbon atmosphere and therefore have no role in the cracking reaction. Among the three series of systems molybdenum series showed the maximum activity and high selectivity towards α-methylstyrene. This may not be due to the destruction of Brönsted acid sites under the reducing atmosphere as reported earlier since α-methylstyrene was the major product for the cracking reaction carried out over all the thee transition metal oxide loaded systems. Even 4% metal loaded samples showed about 80% selectivity for α-methylstyrene, and the selectivity showed a steady increase up to a particular metal oxide loading. Hence this high activity and selectivity exhibited by molybdenum systems could be well accounted as they posses maximum total acidity and Lewis acidity amongst the systems selected for the present investigation. Iron systems showed the least activity, as these systems are much less acidic than molybdenum and tungsten systems. An attempt was made to correlate the activity and selectivity to the acidity of the systems. The activity of molybdenum and tungsten systems could be correlated to the total acidity of these systems (Figures 3.11 and 3.12) and α-methylstyrene selectivity could be correlated to Lewis acidity determined by perylene adsorption studies (Figures 3.13 and 3.14). However, in the case of iron systems no such correlation could be obtained.

Table 3.17 Influence of iron oxide loading on the activity and selectivity of sulphated tin oxide for cumene cracking

Systems	Conversion (wt %)	Selectivity (%)				
		Benzene	Toluene	Ethyl benzene	α-methylstyrene	Styrene
S	-	-	-	-	-	-
SS	6.03	3.63	9.28	19.21	66.12	1.76
F_4	10.95	4.32	1.56	9.94	84.19	-
F_8	12.93	2.88	0.82	8.35	87.95	-
F_{12}	11.84	3.48	0.68	5.11	90.73	-
F_{16}	14.88	2.38	-	5.92	91.70	-
F_{20}	14.64	1.15	0.43	4.23	94.19	-
F_{24}	14.61	3.72	3.23	1.10	91.95	-

Reaction Conditions: 0.5 g catalyst activated at 550°C, Reaction temperature-350°C, Duration - 2 h, Flow rate- 4 mL/h.

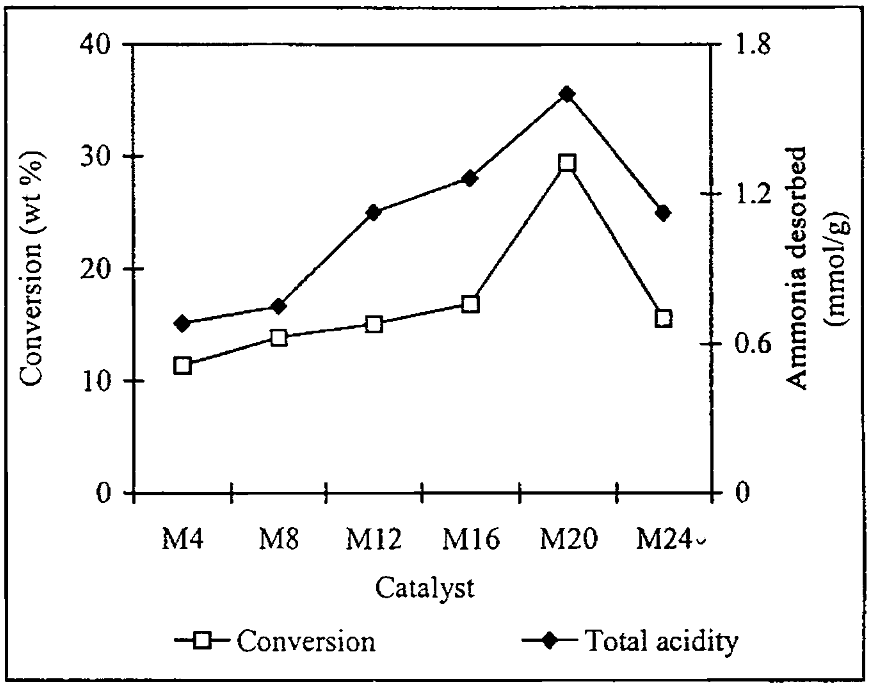


Figure 3.11 Correlation of cumene cracking activity with total acidity for molybdenum systems

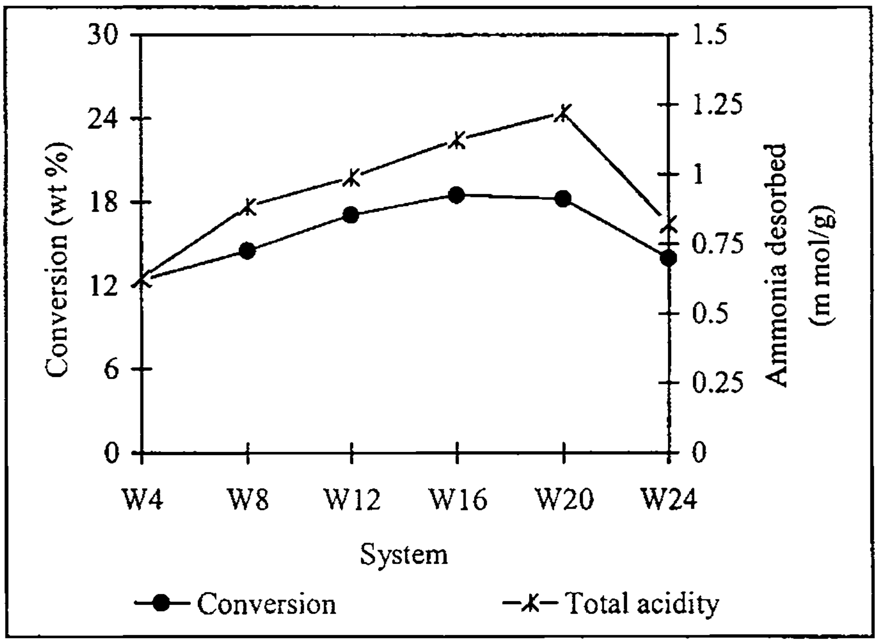


Figure 3.12 Correlation of cumene cracking activity with total acidity for tungsten series

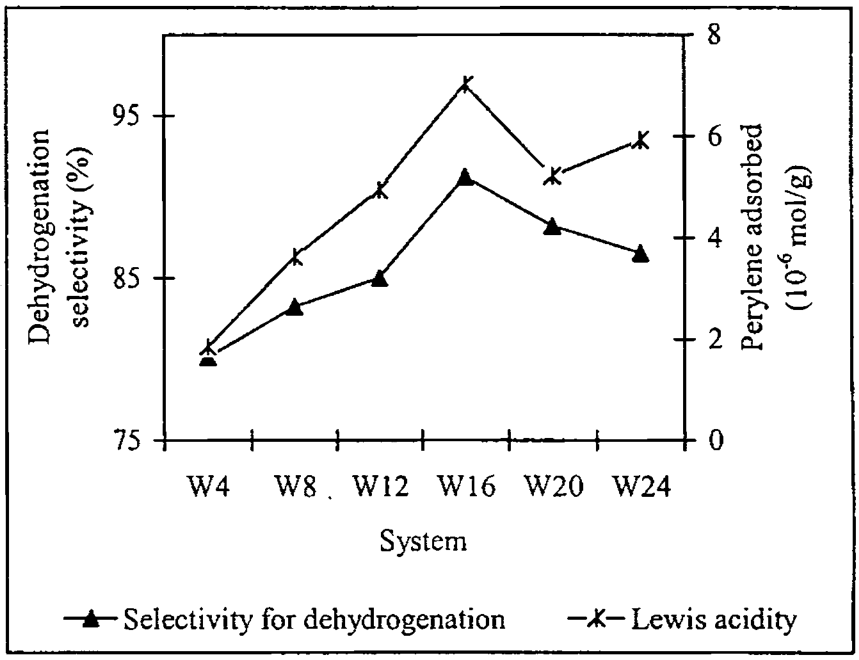


Figure 3.13 Correlation of α-methylstyrene selectivity with Lewis acidity for tungsten series

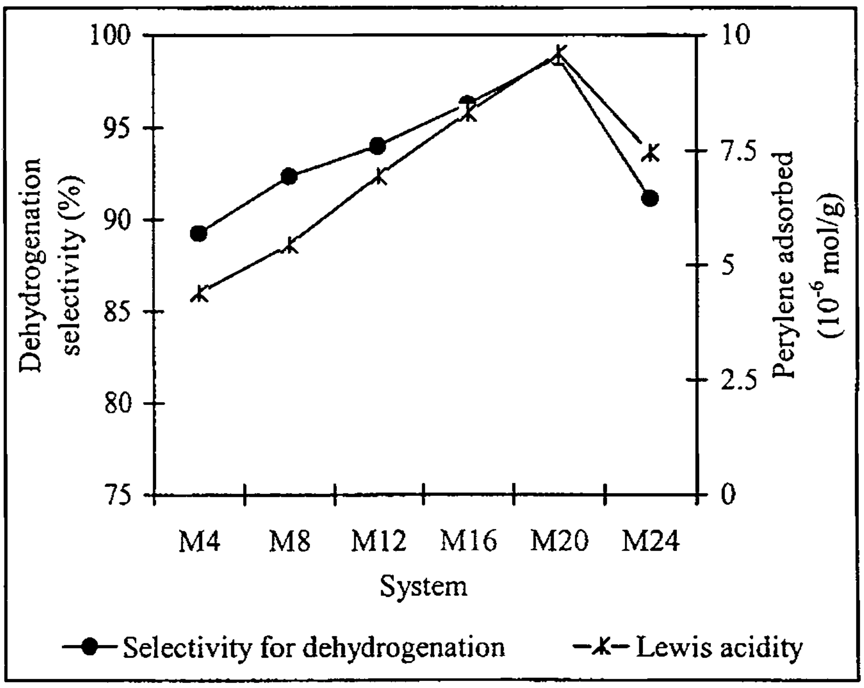
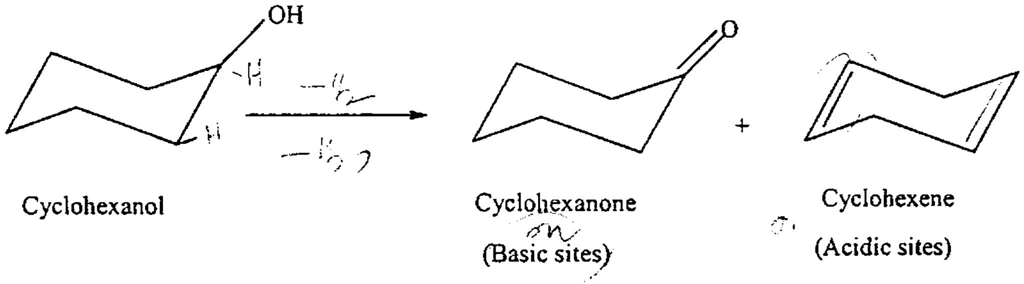


Figure 3.14 Correlation of α-methylstyrene selectivity with Lewis acidity for molybdenum series

3.8.2 CYCLOHEXANOL DECOMPOSITION

Alcohol decomposition comprises an important test reaction that gives information about both acidic and basic sites present on the catalyst surface (30-33). Alcohol, being amphoteric, can interact with both the sites. On the basic sites it undergoes dehydrogenation to give a ketone (2° alcohol) or an aldehyde (1° alcohol) depending on the alcohol selected, whereas interaction with acidic sites leads to the production of alkene by dehydration (Scheme 3.3) (34-35). Thus, by this reaction catalysts can be classified as acids or bases on the basis of their propensity towards dehydrogenation or dehydration.



Scheme 3.3 Cyclohexanol decomposition

Aramendia *et al.* have studied the decomposition of cyclohexanol over sodium carbonate doped zinc phosphate systems and observed that the presence of sodium carbonate on the solid increases the surface basicity and inhibits dehydration of cyclohexanol (36). Cyclohexanol decomposition was also used to characterise the acid-base properties of HZSM-5, HY, silicoaluminophosphates, molecular sieves and commercial chomite catalysts (37).

3.8.2. A. PROCESS OPTIMISATION

For any catalyst system under study, the activity and selectivity towards a particular reaction depend on reaction parameters in addition to the physical and chemical properties of the catalysts. The optimum parameters for cyclohexanol decomposition were determined by carrying out the reaction at different temperatures and flow rates over a selected catalyst system.

i) Influence of flow rate

In order to analyse the influence of feed rate on activity, the reaction was carried out at feed rates from 4 to 7 mL/h. The results are represented in Figure 3.15. It can be seen that conversion decreases with the increase in flow rate. This shows that conversion of cyclohexanol is proportional to the time of contact between the reactant and the catalyst surface. Decrease in contact time leads to reduction in conversion. The maximum –ene selectivity of 86% was observed at the flow rate of 4mL/h. When flow rate was increased from 4mL/h to 5mL/h –one selectivity increased from 11% to about 23%. However, further increase in flow rate did not alter the selectivity of catalyst to a considerable extent. At all flow rates about 70% selectivity for –ene was observed.

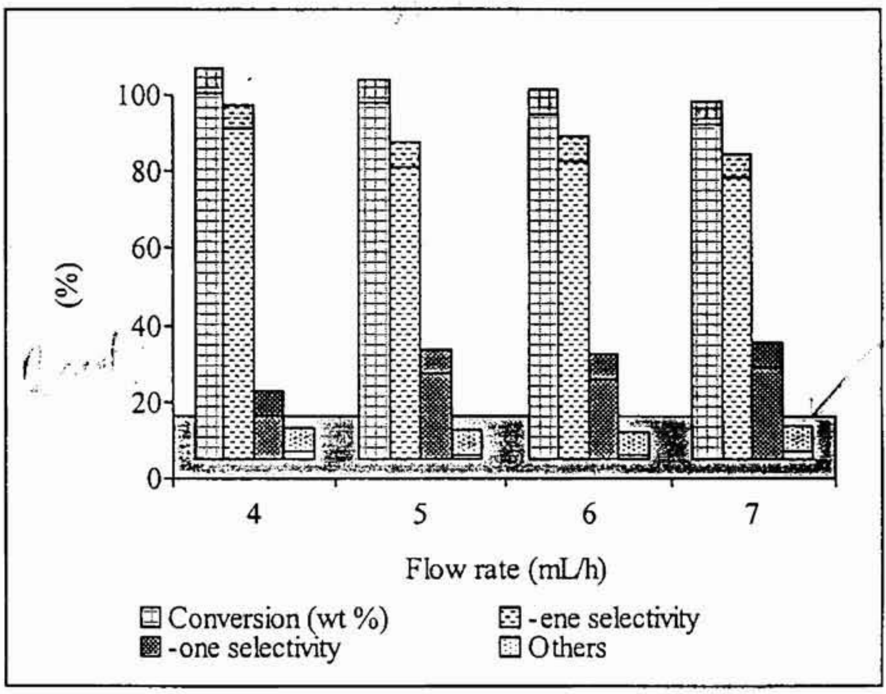


Figure 3.15 Catalytic activity variation with flow rate for cyclohexanol Decomposition

Reaction conditions: 0.5 g M_8 activated at 700°C, Reaction temperature-275°C, Duration – 2 h.

ii) Influence of reaction temperature

Figure 3.16 shows the temperature influence on cyclohexanol decomposition carried out over M_8 system. As temperature was increased from 250°C to 275°C, the conversion increased considerably from 79.96% to 95.54%. Further increase in temperature does not have much effect on the activity, whereas the selectivity towards different products changed considerably. At 250°C the selectivity to –ene was only 75%, but at 275°C selectivity increased to about 85% and a further increase in temperature had a negative influence on –ene selectivity and it decreased to 59% at 375°C. At the same time cyclohexanone selectivity also showed a decrease with increase in temperature. At high temperatures the amount of other products such as benzene, methylcyclopentene, etc. increased to a considerable proportion.

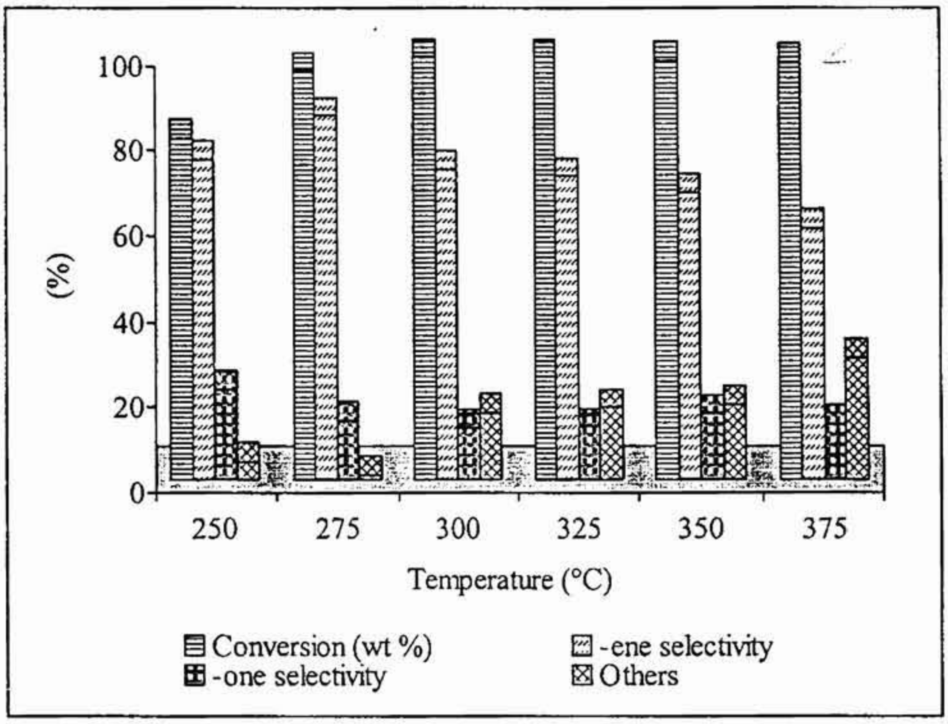


Figure 3.16 Influence of temperature on catalytic activity and selectivity for cyclohexanol decomposition

Reaction conditions: 0.5 g M_8 activated at 700°C, Flow rate- 4 mL/h, Duration – 2 h

iii) Influence of time on stream - Deactivation studies

The stability of the catalyst system was checked by carrying out the reaction for 5 h. Figure 3.17 represents the results of deactivation studies. The conversion decreases with time and –ene selectivity also showed some decrease with time, whereas the amount of cyclohexanone is slightly enhanced as the time passes by. This indicates that there is some decrease in the acidity of catalyst with time.

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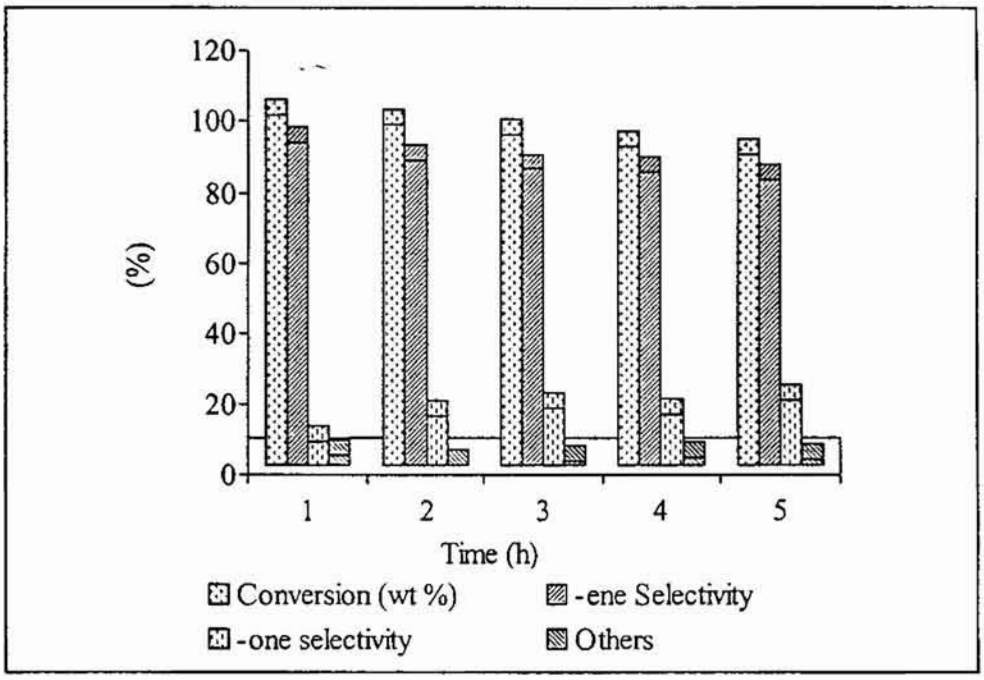

Figure 3.17 Variation of activity and selectivity with time for cyclohexanol decomposition

Reaction conditions: 0.5 g M_8 activated at 700°C, Reaction temperature- 275°C, Duration – 2 h, Flow rate- 4 mL/h

iv) Catalyst Comparison

The results for cyclohexanol decomposition over the three systems are given in Tables 3.18 - 3.20. All the systems including pure tin oxide showed a conversion of above 90%. Hence the activity of these systems could be in no way compared with their acidity. But selectivity showed considerable variation. A different pattern of selectivity was shown by each series. Pure tin oxide showed almost equal selectivity towards cyclohexene and cyclohexanone, which may be due to amphoteric nature of tin oxide. Sulphate doping slightly enhanced the selectivity for cyclohexene, which can be attributed to an increase in acidity after sulphation.

Table 3.18 Influence of molybdenum oxide loading on cyclohexanol decomposition reaction

Systems	Conversion (wt %)	Selectivity (%)		
		Cyclohexene	Cyclohexanone	Others
S	90.16	48.07	51.92	-
SS	89.84	58.08	49.11	0.79
M_4	96.96	85.02	13.74	1.24
M_8	95.54	86.17	11.59	2.23
M_{12}	98.83	87.29	11.60	1.08
M_{16}	94.26	92.70	6.18	1.11
M_{20}	94.67	98.43	0.99	0.58
M_{24}	93.23	85.67	9.98	4.35

Reaction conditions: 0.5 g catalyst activated at 700°C, Reaction temperature-275°C, Flow rate-4 mL/h, Duration-2 h

Molybdenum and tungsten systems showed high –ene selectivity, the maximum was shown by molybdenum series; all the systems in this series exhibited more than 85% selectivity towards cyclohexene. This may be due to the high acidity of these samples as evident from results of TPD and thermodesorption of pyridine. Tungsten systems also have high –ene selectivity but the values were not as high as molybdenum systems. The high activity in the formation of cyclohexene may be due to the weak and medium acid centres on the catalyst surface (38), which is apparent from TPD measurements (Figures 3.18 and

3.19). The considerably small amount of other products like benzene, methylcyclopentene and cyclohexane points to the absence of strong acid sites on the catalyst surface.

Table 3.19 Catalytic activity of tungsten systems for cyclohexanol decomposition

Systems	Conversion (wt %)	Selectivity (%)		
		Cyclohexene	Cyclohexanone	Others
S	90.16	48.07	51.92	-
SS	89.84	58.08	49.11	0.79
W_4	98.15	80.58	19.93	0.50
W_8	98.95	83.04	14.39	1.58
W_{12}	98.80	88.26	10.32	1.47
W_{16}	98.50	91.97	7.40	0.62
W_{20}	97.54	93.01	6.12	0.79
W_{24}	94.12	86.86	11.75	1.39

Reaction conditions: 0.5 g catalyst activated at 700°C, Reaction temperature-275°C, Flow rate-4 mL/h, Duration-2 h

Iron systems behave in a slightly different manner. In these systems, the –ene selectivity was only around 70-75%. These catalysts showed a selectivity of around 15-20% for cyclohexanone, which is a high value compared to that observed for the other two series. It is also observed from TPD and perylene studies that iron systems are comparatively less acidic than molybdenum and tungsten systems. The formation of cyclohexanone over any catalyst indicates the presence of strong and medium basic centres. From all these analyses it was assumed that iron systems retained some basicity of pure tin oxide. The selectivity in the alcohol decomposition is mainly controlled by the acid-base properties (39). Variation in the dehydrogenation and dehydration selectivity for the catalyst systems suggests that acidic and basic properties of sulphated tin oxide vary with incorporation of different transition metal oxides.

Table 3.20 Data for cyclohexanol decomposition over tungsten oxide loaded sulphated tin oxide

Systems	Conversion (wt %)	Selectivity (%)		
		Cyclohexene	Cyclohexanone	Others
S	90.16	48.07	51.92	-
SS	89.84	58.08	49.11	0.79
F_4	94.00	68.32	30.12	1.56
F_8	91.86	71.42	28.57	-
F_{12}	90.16	71.37	28.63	-
F_{16}	95.38	76.32	23.34	0.35
F_{20}	94.04	75.83	24.17	-
F_{24}	91.89	65.16	34.84	-

Reaction conditions: 0.5 g catalyst activated at 550°C, Reaction temperature-275°C, Flow rate-4 mL/h, Duration-2 h

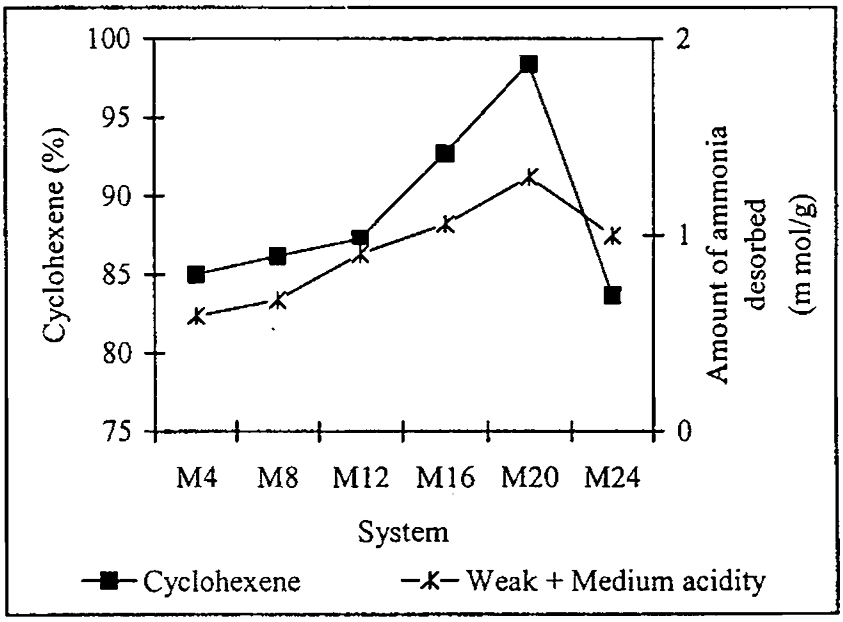

Figure 3.18 Correlation of cyclohexene selectivity with weak + medium acidity for molybdenum series

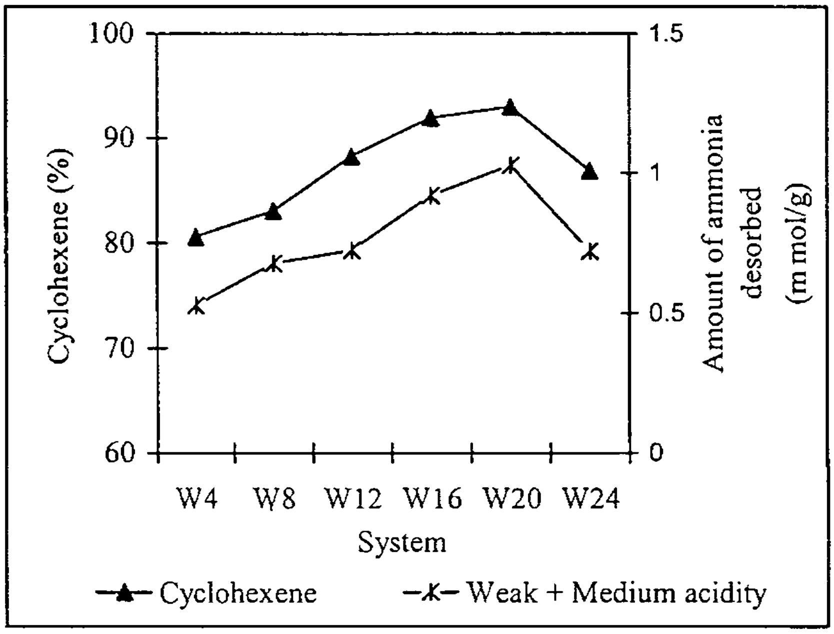

Figure 3.19 Correlation of cyclohexene selectivity with weak + medium acidity for tungsten series

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4

FRIEDEL-CRAFTS REACTIONS

FRIEDEL – CRAFTS BENZYLATION AND BENZOYLATION

4.1 INTRODUCTION

Friedel-Crafts reactions are of great interest due to their importance and widespread use in synthetic and industrial chemistry. Liquid phase alkylation and acylation of aromatic compounds using homogeneous catalysts are the commonly practised Friedel-Crafts reactions (1,2). However, conventionally used homogeneous acid catalysts *viz.* $AlCl_3$, BF_3, H_2SO_4, etc. pose several environmental and technological problems like difficulty in separation and recovery of desired product, disposal of spent catalyst, corrosion, high toxicity, etc. Also these catalysts are highly moisture sensitive and hence demand moisture free reagents and dry atmosphere for their handling. In addition to this, degradation, polymerisation and isomerisation of products arising due to the high acidic nature of these catalysts causes a significant reduction in the expected primary product yield (3-5). In view of this, active research has been directed at substituting the traditional homogeneous catalysts with environment friendly heterogeneous acid catalysts such as clay minerals and zeolites. Development of reusable acid catalysts which show high activity for Friedel–Crafts reaction is thus of great practical importance (6,7).

An acidic surface is required to catalyse alkylation and acylation reactions. Eco-friendly solid acids like zeolites (8,9), acid treated clays, pillared clays (10), Keggin type heteropoly acids (11), etc. are found to have acidity close to the traditional mineral acid solutions. These systems are now widely tested for the alkylation and acylation reactions.

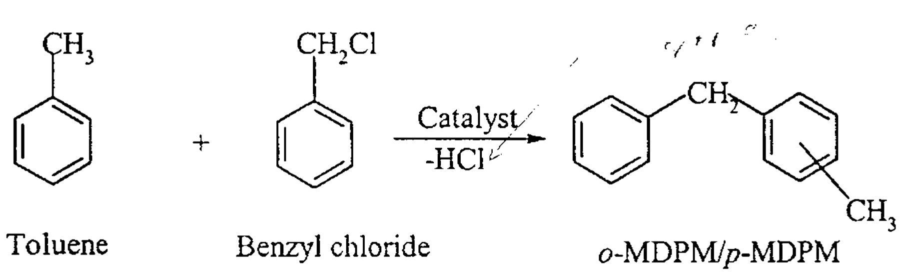
Clays are highly acidic and Clark *et al.* reported that montmorillonite supported zinc (clayzic) and nickel chlorides are highly active and selective catalysts for Friedel-Crafts alkylation (12-14). Rhodes *et al.* showed that high activity is shown by only those clayzic samples with pore diameter (10-12 nm) (15). Lenardo *et al.* investigated the catalytic activity of montmorillonite pillared with Al or Al/Ga polyoxy cation and their repillared derivatives for the alkylation of benzene with ethylene (16). In the past 15 years, Friedel-Crafts alkylations have been extensively studied over K10 montmorillonite modified with various metal ions (17-22). It has been found that benzylation of benzene and toluene with benzyl chloride and benzyl alcohol proceeded efficiently over cation exchanged K10 (17,23). In benzylation using benzyl alcohol, catalytic activity is not much influenced by the metal cation used for the exchange, but when benzyl chloride is used as the benzylating agent, K10 modified with Cu(II) and Fe(III) showed a worth while increase in the catalytic activity. Iron pillared clays are also found to be efficient catalysts for Friedel-Crafts reactions as reported by Choudary *et al.* (24). This high activity is attributed to the highly reducible nature of these cations.

Al- impregnated MCM-41, MCM-48, etc. are found to be excellent catalysts for the alkylation of benzene, toluene and *m*-xylene using benzyl alcohol (7). Basic and amphoteric Ga_2O_3 and In_2O_3 supported on mesoporous Si-MCM-41 are active for the benzylation and acylation of benzene and other aromatic compounds, even in the presence of moisture and also exhibited excellent reusability. These metal oxides also showed high catalytic activity even when they are supported on other non-acidic micro or macro porous materials (25). He *et al.* studied the alkylation of benzene with benzyl chloride over iron supported mesoporous materials (26). HCl-gas treated Ga-Mg hydrotalcite anionic clay showed high catalytic activity for the benzylation and acylation of toluene and benzene and these catalysts are also found to be moisture insensitive and highly reusable (27). Zeolites are also well tested for Friedel- Crafts reactions due to their shape selective properties, easy separation from reaction medium, regeneration and thermal stability (28-32). Specifically medium- and large- pore zeolites have been projected as excellent catalysts for the production of aromatic ketones. H-ZSM-5 have been generally used in the acylation of less substituted aromatic molecules like benzene, phenol and toluene (33-36), while zeolites with larger pores such as H-Beta and HY have been extensively used for the acylation of arylethers such as anisole and polysubstituted aromatics such as xylenes and mesitylenes (8,28,29,33,37). Benzoylation of chlorobenzene with 4-chlorobenzoyl chloride over H-beta was studied by Venketesan *et al.* They also examined the influence of reaction temperature, catalyst concentration, molar ratio of the reactants and recycling of H-beta on the conversion of 4-chlorobenzoyl chloride (38). Sugunan and co-workers investigated the catalytic performance of H-ZSM-5, H-beta, H-mordenite, H-Y, etc. for the benzylation and benzoylation of *o*-xylene with benzyl chloride (39,40). Alkylation of benzene and ethylbenzene with butyl halides proceeded efficiently over iron exchanged zeolites under mild conditions (41). But rapid deactivation of the catalysts by coke deposition within the pores limits the use of zeolite materials.

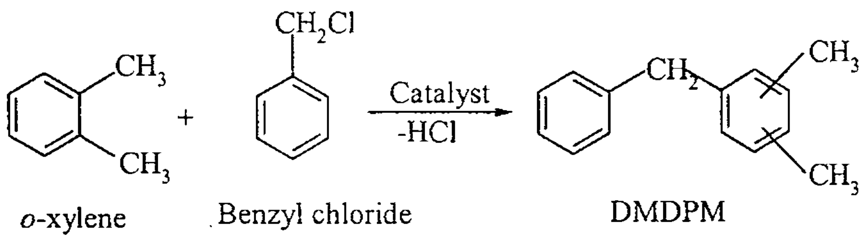
It is well established that sulphation enhances the surface acidity of the metal oxides. Due to this enhanced acidity sulphated metal oxides could be used as solid acid catalysts. More recently, increasing applications of these sulphated metal oxide solid acids are being found in heterogeneous catalysis for a wide variety of reactions such as hydrocarbon isomerisation (42-44), nitration (45), reduction (46), cracking (47), etc. Catalytic activity of the sulphated metal oxides towards Friedel-Crafts reaction was not much explored earlier. Recently, there are reports regarding the utility of these systems towards alkylation (48) and acylation (49). Catalytic activity of titania sulphated by different agents for the gas phase alkylation of benzene and substituted benzenes using isopropanol was investigated by Samantaray *et al.* (50). Sulphated zirconia is found to be an efficient catalyst for acylation reactions (51). Solid super acids like sulphated alumina and zirconia showed high catalytic activity for benzoylation of toluene at temperatures even below the reflux temperature of the reaction mixture (52,53). Tungsten and molybdenum oxides supported on zirconia, titania and tin oxide also showed super acidity and are found to be active for the acylation reactions (54,55).

4.2 BENZYLATION OF TOLUENE AND O-XYLENE

Friedel-Crafts benzylation introduces a benzyl moiety to an aromatic ring. Benzylation of toluene ring can be represented as in Scheme 4.1. Benzyl entity will be either introduced at the *ortho* or *para* positions to give *o*-/*p*-methyldiphenylmethane (*o*-MDPM /*p*-MDPM). In the case of *o*-xylene (Scheme 4.2) benzylation gives dimethyl diphenyl methane (DMDPM).



Scheme 4.1 Benzylation of toluene



Scheme 4.2 Benzylation of *o*-xylene

4.2.1 PROCESS OPTIMISATION

Generally in any reaction, yield and selectivity to a desired product depends on reaction parameters such as temperature at which the reaction is carried out, molar ratio of the reactants, reaction time, etc. So before testing the catalytic activity of the various systems prepared, it becomes really essential to optimise the reaction parameters. For this purpose, we have studied the influence of temperature, molar ratio, presence of moisture, effect of metal leaching, etc. on the benzylation reaction, carried out over the present systems.

i) Influence of temperature

The temperature at which a reaction is performed is an important factor in determining the yield and selectivity of that particular reaction. Most reactions possess an optimum temperature below which the yield will be very low. In order to fix the optimum temperature the reactions were carried out for a range of temperature keeping all other parameters fixed. The results are given in Table 4.1 and 4.2.

A significant increase in the conversion of benzyl chloride was observed with an increase in reaction temperature, and at temperatures above100°C the reaction attained 100% conversion in a short interval of time for both substrates.

Table 4.1 Influence of temperature on the catalytic activity for the benzylation of toluene

Temperature (°C)	Time (min)	Conversion (wt %)	Selectivity (%)	
			MAP	DAP
70	60	21.78	100	-
80	60	67.83	100	-
90	60	98.34	100	-
100	30	100	90.02	9.98
110	30	100	87.68	12.32

Reaction conditions: 0.1 g of M_{20} activated at 700°C, Molar ratio- (toluene/benzyl chloride)- 10:1

Another observation was that low temperatures favour monoalkylated products in the case of toluene (Table 4.1). As the temperature was increased some amount of dialkylated products were also produced and the percentage of dialkylated products formed increased with increase in the temperature. Thus temperature seems to have a noteworthy influence on selectivity of the reaction when toluene was used as the substrate. But for xylene, only monoalkylated product was observed even at high reaction temperatures, this may be due to the steric hindrance offered by the two methyl groups (Table 4.2).

Table 4.2 Effect of temperature in the benzylation of *o*-xylene with benzyl chloride

Temperature (°C)	Time (min)	Conversion (wt %)
50	30	9.59
60	30	24.74
70	30	40.22
80	30	98.67
90	15	100
100	10	100
110	10	100

Reaction conditions: 0.1 g M_{20} activated at 700°C, Molar ratio- (xylene/benzyl chloride)- 10:1

ii) Influence of molar ratio

The stoichiometric ratio between substrate and benzyl chloride also influences the conversion and selectivity. To investigate the influence of molar ratio, we studied the benzylation of toluene at various molar ratios over the M_{20} system. The result is shown in Figure 4.1. As toluene to benzyl chloride molar ratio was increased from 5 to 10, a significant increase in the conversion of benzyl chloride was observed; a further increase in the amount of toluene led to a decrease in the yield. Low product yield at lower toluene concentration may be due to the polycondensation of benzyl chloride over the catalyst at high benzyl chloride concentration as reported by Arata *et al.* (56) in the case of calcined iron sulphates.

When the ratio of toluene was increased from 5 to 10, the effective concentration of benzyl chloride may not be sufficient enough to cause polymerisation. Further increase in molar ratio decreases the yield. This may be due to the fact that as the concentration of toluene was increased there will be a decrease in the effective concentration of benzyl chloride. In all these cases there was 100% selectivity towards the monoalkylated product.

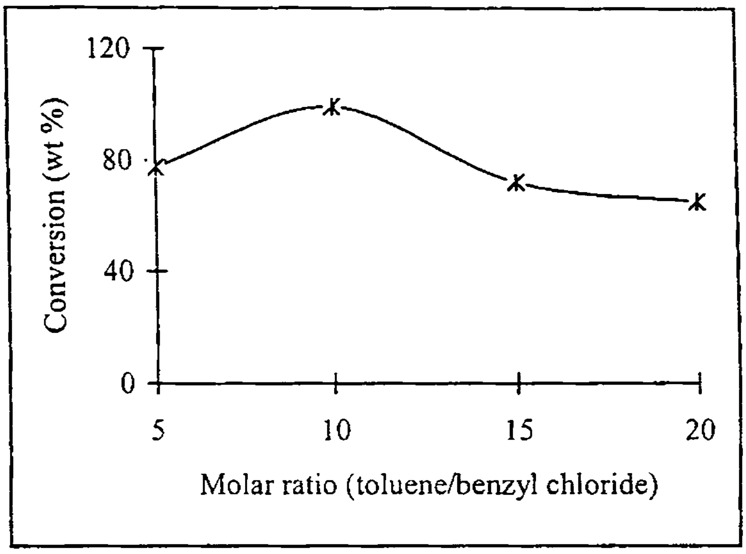


Figure 4.1 Variation of catalytic activity with molar ratio in the benzylation of toluene

Reaction conditions: 0.1 g M_{20} activated at 700°C, Reaction temperature- 80°C, Duration-3 h

iii) Influence of substrate

Catalytic activity is largely dependent on the substrates used. Variation of reactivity with substrate was studied by carrying out the reaction using benzene, toluene and *o*-xylene over the same catalyst under the same conditions. Table 4.3 illustrates the influence of substrate on the catalytic activity for benzylation reaction. For *o*-xylene, the yield was nearly 100% in 30 minutes, toluene showed a conversion of above 95% in 3 hours, but for benzene the yield was less than 20% in 3 hours. So the reactivity is in order *o*-xylene> toluene>benzene.

$-CH_3$ being an electron-donating group, will increase the electron density on the benzene ring and makes it more vulnerable to the attack by an electrophile. Thus it is worth mentioning that the reactivity of aromatic nucleus increases with the number of electron donating groups attached to the aromatic ring. Hence xylene, which has two methyl groups, reacts more easily than toluene with only one methyl group. Benzene, since it possesses no substituent methyl groups, is much less reactive than *o*-xylene and toluene (57).

Table 4.3 Influence of substrate on catalytic activity

Substrate	Time (min)	Conversion (wt %)	Selectivity (%)	
			MAP*	DAP*
Benzene	180	18.79	100	-
Toluene	180	98.89	100	-
o-Xylene	30	98.67	100	-

Reaction conditions: 0.1 g M_{20} activated at 700°C, Molar ratio- (substrate/benzyl chloride)- 10:1, Reaction temperature- 80°C (MAP*- monoalkylated product and DAP*- dialkylated product)

iv) Influence of moisture

Normally used homogeneous Friedel-Crafts catalysts suffer an inherent drawback of high moisture sensitivity. This makes the handling of these systems very difficult (58). Thus it becomes essential to test the moisture sensitivity of the catalyst system prepared. To study the influence of moisture two parallel runs were carried out, one using the fresh activated catalyst and another with the catalyst adsorbed with moisture. To prepare the catalyst adsorbed with moisture, the catalyst was first activated and then kept in a dessicator containing water for forty eight hours.

The reaction was carried out using fresh and moisture adsorbed catalyst simultaneously and the reaction mixtures were analysed at definite time intervals. Figure 4.2 illustrates the results. In the case of fresh samples the reaction commenced quickly, but for the moisture adsorbed sample, conversion remained very low even after one hour. After one and a half hours, catalytic activity of moisture adsorbed samples showed an increase and as the time progressed the catalytic conversion of benzyl chloride over moisture adsorbed system increased and became the same as that given by the fresh catalyst.

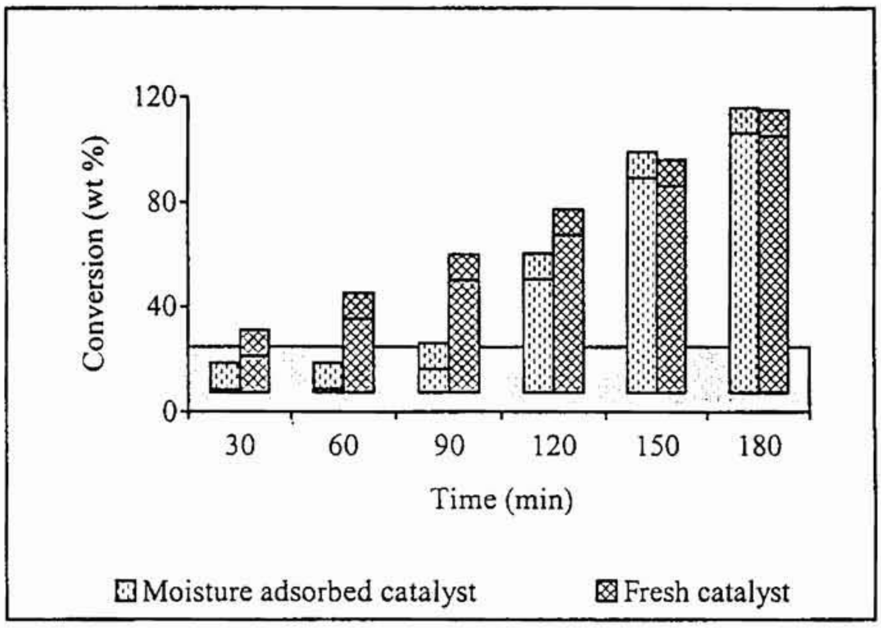


Figure 4.2 Catalytic activity for benzylation in the presence and absence of moisture

Reaction conditions: 0.1 g M_{20} activated at 700°C, Molar ratio- (toluene/benzyl chloride)- 10:1, Reaction temperature- 80°C

Thus it is evident that presence of moisture developed an induction period for the reaction, but in no way influenced the catalytic activity of the system. The observation of induction period may be due to the adsorption of water molecules on the active sites of the catalyst and as a consequence of which the benzyl chloride molecules take some time to replace this water molecules from the catalyst surface. Once these water molecules are removed, reaction proceeds at the same rate as that of the fresh catalyst.

v) Influence of time

Analysing the reaction mixture at different time intervals monitored the variation of catalytic conversion with time. Figure 4.3 depicts the variation in catalytic activity with time for the benzylation of toluene over M_{20} system. There was an increase in the conversion as time proceeds, but the selectivity remained constant throughout the course of the reaction, i.e., 100% selectivity towards mono alkylated product.

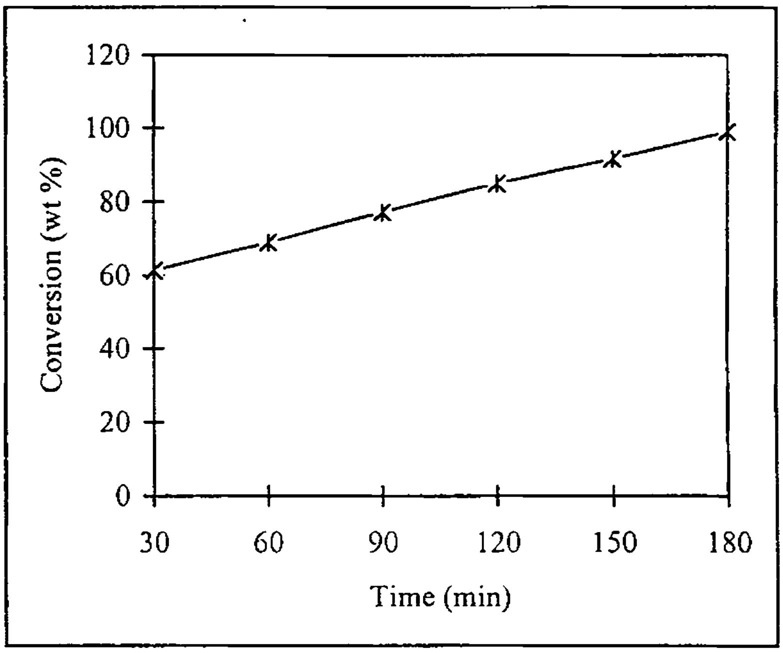


Figure 4.3 Change in conversion with time for the benzylation of toluene with benzyl chloride

Reaction conditions: 0.1 g M_{20} activated at 700°C, Reaction temperature- 80°C, Molar ratio- (toluene/benzyl chloride)- 10:1

vi) Metal leaching studies

For any catalyst, chemical stability is an essential requirement in addition to thermal stability. The leaching of metal ions from the catalyst during the course of the reaction may alter its crystal structure. HCl is evolved in the case of alkylation reaction using alkyl chlorides and if the metals ions leached out are Fe^{3+}, Al^{3+}, Sn^{4+}, etc. these ions can react with HCl producing Lewis acids like $FeCl_3$, $AlCl_3$, $SnCl_4$, etc. These Lewis acids can catalyse the reaction homogeneously, and then the reaction becomes partially heterogeneous. The catalyst systems selected for the present study have tin oxide as the base material, and hence leaching studies become highly relevant in this context.

For leaching studies, benzylation reaction was carried out for three hours, after which the catalyst was filtered out from the reaction mixture and then the reaction was carried out using the filtrate for another one hour. The result of the analysis is given in Table 4.4. Not much increase in the conversion was noticed after the removal of the catalyst. The filtrate was tested for any metal ion (Sn^{4+}) and confirmed its absence. Both these observations imply that the reaction is 100% heterogeneously catalysed.

Table 4.4 Metal leaching for the benzylation of toluene

Time (h)	3	3.5	4
Conversion over M_{24}	71.71	72.66	73.35
Conversion over W_{24}	55.69	56.37	57.13

Reaction conditions: 0.1 g M_{20} activated at 700°C, Molar ratio- (toluene/benzyl chloride)- 10:1, Reaction temperature- 80°C

4.2.2 CATALYST COMPARISON

i) Iron oxide loaded systems

After optimisation studies, catalytic activity of all the systems were evaluated at a reaction temperature of 80°C and a molar ratio of 10:1 was selected for both *o*-xylene and toluene. In the case of iron systems an interesting observation was, that these systems exhibited an induction period and after that the reaction attained 100% conversion in no time. This high activity of the iron loaded systems could not be explained on the basis of their Lewis acidity. The results for the two substrates are given in Table 4.5 & 4.6.

In order to account for this abnormal behaviour shown by the iron loaded systems the influence of both time and temperature on the catalytic activity of these systems was studied. Analyses of influence of temperature and time on the activity of a representative system (F_{16}) was carried out using both *o*-xylene and toluene and the results for the variation of catalytic activity with time and temperature are given in Tables 4.7 and 4.8 respectively.

Table 4.5 Influence of iron loading in the benzylation of *o*-xylene

Systems	Conversion (wt %)	Selectivity (%)	
		DMDPM	Others
S	-	-	-
SS	1.5	100	-
F_4	100	89.66	10.34
F_8	100	88.89	11.11
F_{12}	100	88.14	11.86
F_{16}	100	88.68	11.32
F_{20}	100	89.13	10.87
F_{24}	100	87.99	12.01

Table 4.6 Variation of catalytic activity with iron loading in the benzylation of toluene

Systems	Conversion (wt %)	Selectivity (%)	
		MAP	DAP
S	-	-	-
SS	-	-	-
F_4	100	91.85	8.15
F_8	100	89.68	10.32
F_{12}	100	88.33	11.67
F_{16}	100	89.85	10.15
F_{20}	100	88.66	11.34
F_{24}	100	88.18	11.82

Reaction conditions: 0.1 g of catalyst activated at 550°C, Duration- 10 min for xylene & 20 min for toluene, Molar ratio- (substrate/benzylchloride)- 10:1 Reaction temperature- 80°C

Evaluation of the catalytic activity of F_{16} for benzylation of toluene with time revealed that there was no conversion at all up to 15 minutes and at 20 minutes the reaction attained 100% conversion. In the case of xylene the duration of induction period was reduced to 5 minutes. Some amount of dialkylated products was also formed in the case of both the substrates. The temperature study conducted for benzylation also gave interesting results. The reaction was carried out over a range of temperature from 40-80°C. For temperatures up to 70°C there was no conversion even after 2 hours, but as the temperature was increased from 70 to 80°C the reaction attained 100% conversion within 20 minutes. This anomalous hike in the catalytic activity points to the fact that benzylation activity of the iron loaded systems cannot be explained on the basis of the usual carbo-cation mechanism for alkylation reactions.

The temperature effect and the existence of an induction period point to the operation of redox or free radical mechanism in the case of iron loaded systems. It is reported that catalysts containing reducible cations like Fe^{3+}, Sn^{4+}, Cu^{2+}, Sb^{3+}, etc. exhibit high alkylation activity regardless of their low Lewis acidities (22-24). When the redox mechanism is operating there will a homolytic rupture of the carbon-chlorine bond of the alkylating agent (benzyl chloride). The radicals so formed are powerful reductants, which would be readily oxidised to carbocations in the presence of reducible metallic ions such as Fe^{3+}. The mechanism is depicted in Figure 4.4.

Tables 4.7 Catalytic activity as a function of time for iron systems in the benzylation of toluene

Time (min)	Conversion (wt %)	Selectivity (%)	
		MAP	DAP
5	-	-	-
10	-	-	-
15	-		
20	100	89.85	10.15

Reaction conditions: 0.1 g of F_{16} activated at 550° C, Reaction temperature- 80°C, Molar ratio- (toluene/benzyl chloride)- 10:1

Table 4.8 Influence of temperature on the catalytic activity of iron systems in the benzylation of toluene

Temperature (°C)	Time (min)	Conversion (wt %)	Selectivity (%)	
			MAP	DAP
40	120	-	-	-
50	120	-	-	-
60	120	-	-	-
70	120	-	-	-
80	20	100	89.85	10.15

Reaction conditions:0.1 g of F_{16} activated at 550°C, Molar ratio- (toluene/benzyl chloride)-10:1

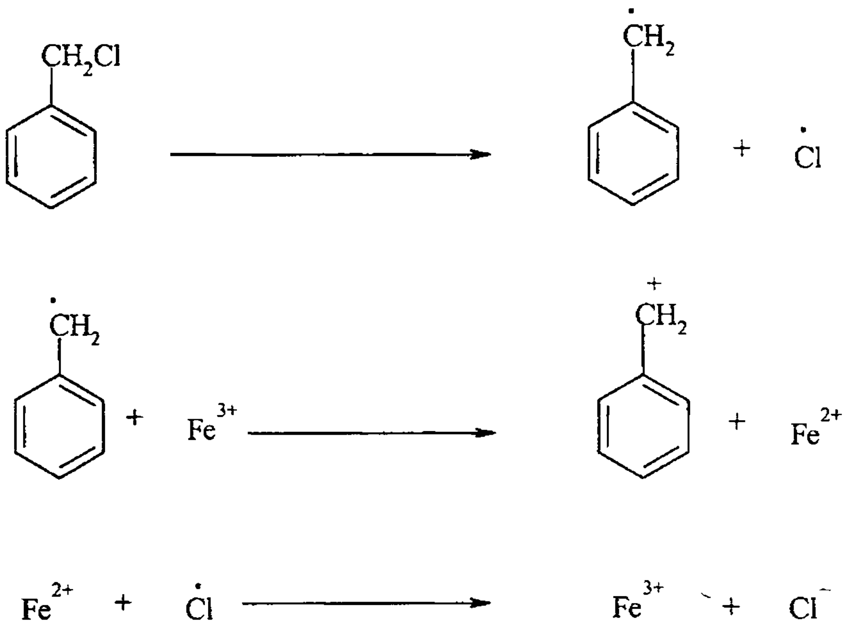


Figure 4.4 Formation of benzyl carbocation by free radical mechanism

It may be assumed that below 80°C, the activation energy for the homolytic rupture of carbon–chlorine bond may not be attained and therefore no reaction occurs (26). This could be the reason for no conversion at temperatures below 80°C.

ii) Molybdenum oxide loaded systems

Catalytic activity of all the systems were analysed at a reaction temperature 80°C and the molar ratio used was 10:1 for both toluene and *o*-xylene. Duration of the reaction was different for the two substrates; for toluene it was three hours and xylene required only half an hour. Table 4.9 and 4.10 show the catalytic activity data of the molybdenum oxide modified system for the benzylation of toluene and *o*-xylene respectively.

Table 4.9 Effect of molybdenum oxide loading on catalytic activity for benzylation of toluene

Systems	Conversion (wt %)
S	-
SS	19.08
M_4	30.48
M_8	44.36
M_{12}	63.38
M_{16}	80.19
M_{20}	99.27
M_{24}	71.71

Reaction conditions: 0.1 g of catalyst activated at 700°C, Molar ratio- (toluene/benzyl chloride)- 10:1, Reaction temperature- 80°C, Duration- 3 h

From the data it is clear that pure tin oxide does not show any activity for benzylation and sulphation causes a slight increase in the activity. But when pure tin oxide was sulphated and loaded with molybdenum oxide good yield for methyldiphenylmethane was observed. The yield increased with an increase in the molybdenum oxide content up to 20% loading and further increase in the concentration of molybdenum oxide resulted in a decrease in the conversion.

When *o*-xylene was used as the substrate, catalytic activity followed the same trend as in the case for toluene. Only monoalkylated products were obtained in the case of both xylene and toluene, unlike the iron loaded systems where some amount of dialkylated products were also obtained. Another interesting observation was that benzylation of toluene gave only a single product.

Table 4.10 Influence of molybdenum oxide loading on benzylation of *o*-xylene

Systems	Conversion (wt %)
S	-
SS	11.75
M_4	28.32
M_8	42.80
M_{12}	65.88
M_{16}	87.69
M_{20}	98.67
M_{24}	81.84

Reaction conditions: 0.1 g of catalyst activated at 700°C, Reaction temperature- 80°C, Molar ratio- (*o*-xylene/benzyl chloride)- 10:1, Duration- 30 min

The results of benzylation reaction using both the substrates were compared with the acidity determined by different methods such as the total acidity determined by TPD method and thermodesorption of pyridine, the Lewis acidity determined by perylene adsorption studies and the results obtained for the two test reactions. A rough correlation was observed between total acidity obtained by TPD measurements and activity. The activities also well correlated with the Lewis acidity obtained by the perylene adsorption in the case of both these substrates. (Figures 4.6 & 4.7 for toluene and *o*-xylene respectively). The catalytic activity of the systems also showed a correlation with α-methylstyrene selectivity for cumene cracking, which in turn is a measure of the Lewis acidity of the catalytic systems (Figures 4.8 & 4.9 for toluene and *o*-xylene respectively).

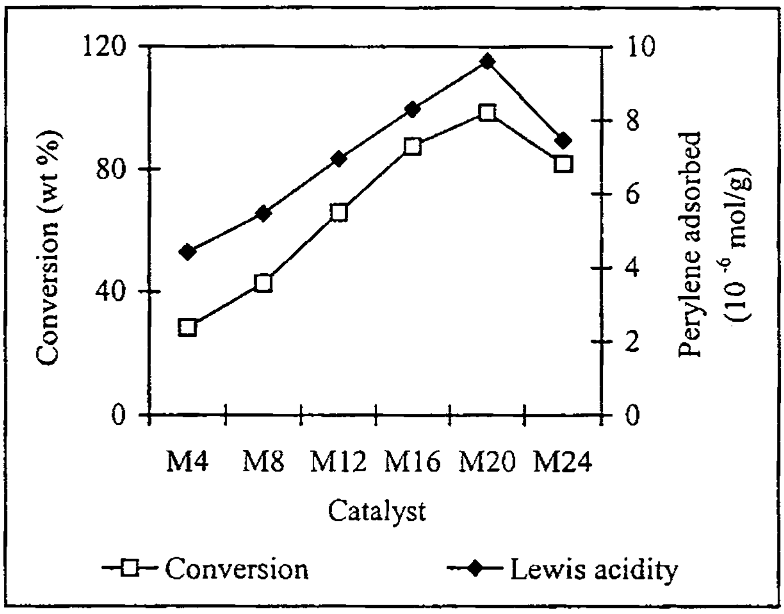


Figure 4.6 Correlation of benzylation activity for toluene with Lewis acidity

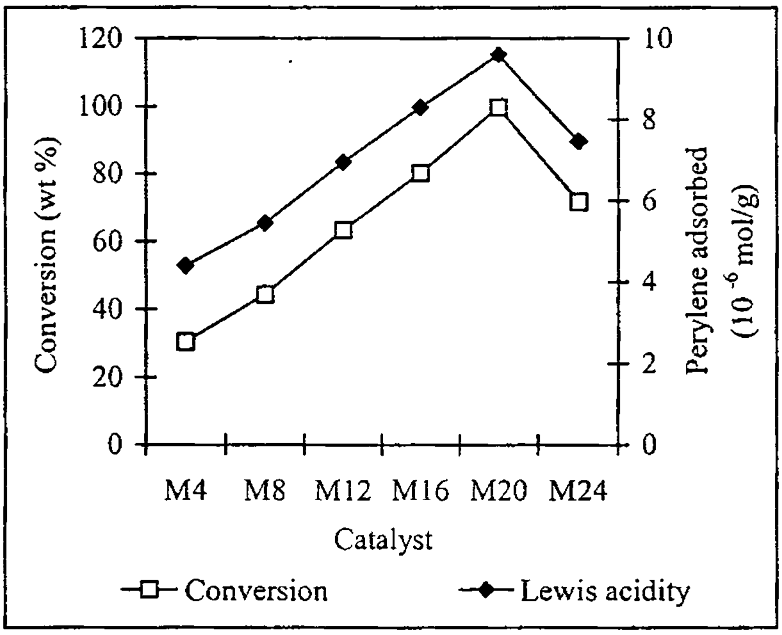


Figure 4.7 Correlation of benzylation activity for *o*-xylene with Lewis acidity

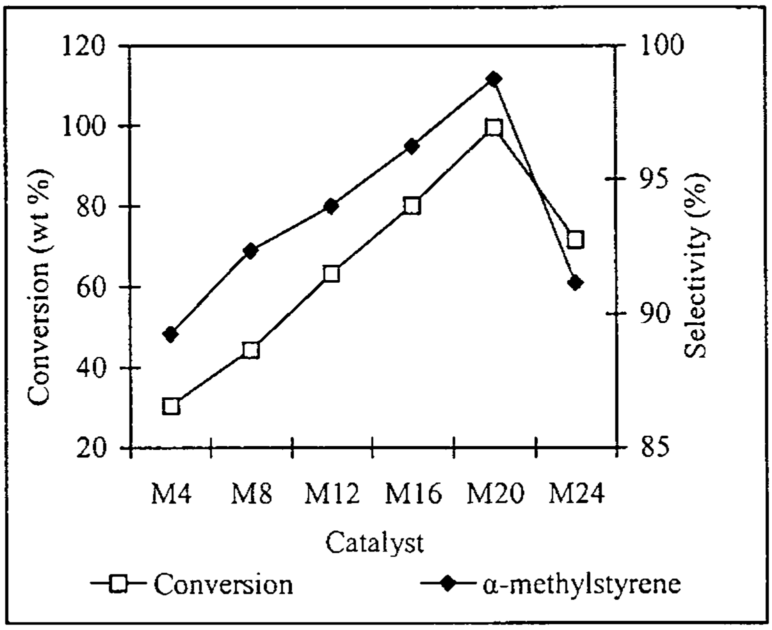


Figure 4.8 Correlation of benzylation activity for toluene with α-methylstyrene selectivity.

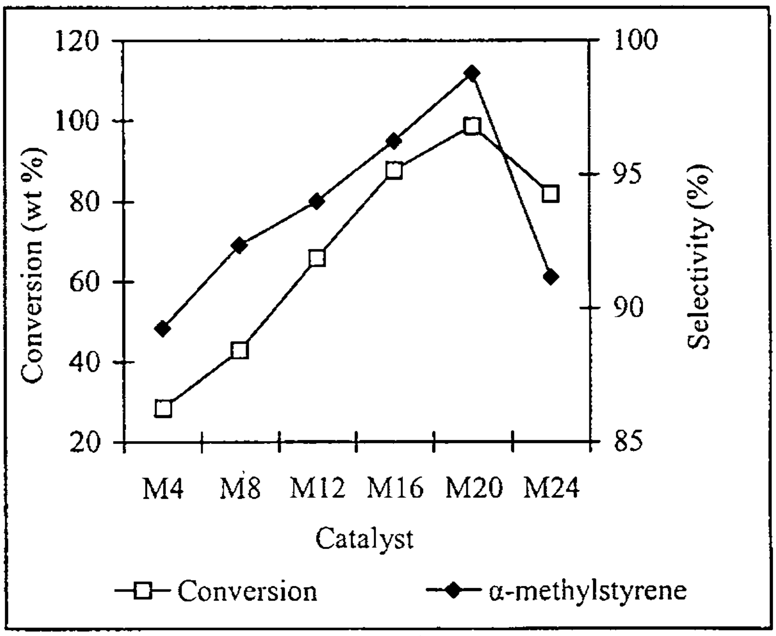


Figure 4.9 Correlation of benzylation activity for *o*-xylene with α-methylstyrene selectivity

iii) Tungsten oxide loaded systems

Table 4.11 and 4.12 illustrates the results for the benzylation of toluene and *o*-xylene over the various tungsten oxide loaded systems.

Table 4.11 Catalytic activity of tungsten oxide loaded systems for benzylation of toluene

Systems	Conversion (wt %)
S	-
SS	19.08
W_4	26.44
W_8	34.92
W_{12}	40.51
W_{16}	54.51
W_{20}	50.49
W_{24}	55.69

Reaction conditions: 0.1 g of catalyst activated at 700°C, Reaction temperature-80°C, Duration- 3 h, Molar ratio- (substrate/benzyl chloride)- 10:1

It is concluded that in the case of iron oxide loaded systems benzylation activity is not at all influenced by the Lewis acidity of the catalyst. The reducible nature of the Fe^{3+} ion is the key factor in determining the catalytic activity of iron systems, but in the case of molybdenum and tungsten oxide modified systems a good correlation between the catalytic activity and Lewis acidity was observed. The low activity of the tungsten oxide modified systems in comparison with molybdenum systems may be explained on the basis of their low Lewis acidity. Figure 4.10 and 4.11 gives the correlation of the benzylation activity with Lewis acidity of the tungsten systems determined by perylene adsorption for *o*-xylene and toluene respectively. The correlation of the catalytic activity with α-methylstyrene selectivity for cumene cracking is given in Figures 4.12 (toluene) and 4.13 (*o*-xylene).

Table 4.12 Effect of tungsten oxide loading on benzylation of *o*-xylene

Systems	Conversion (wt %)
S	-
SS	11.75
W_4	19.49
W_8	35.94
W_{12}	57.15
W_{16}	70.16
W_{20}	58.36
W_{24}	64.54

Reaction conditions: 0.1 g of catalyst activated at 700°C, Reaction temperature- 80°C, Molar ratio- (*o*-xylene/benzyl chloride)-10:1, Duration- 30 min

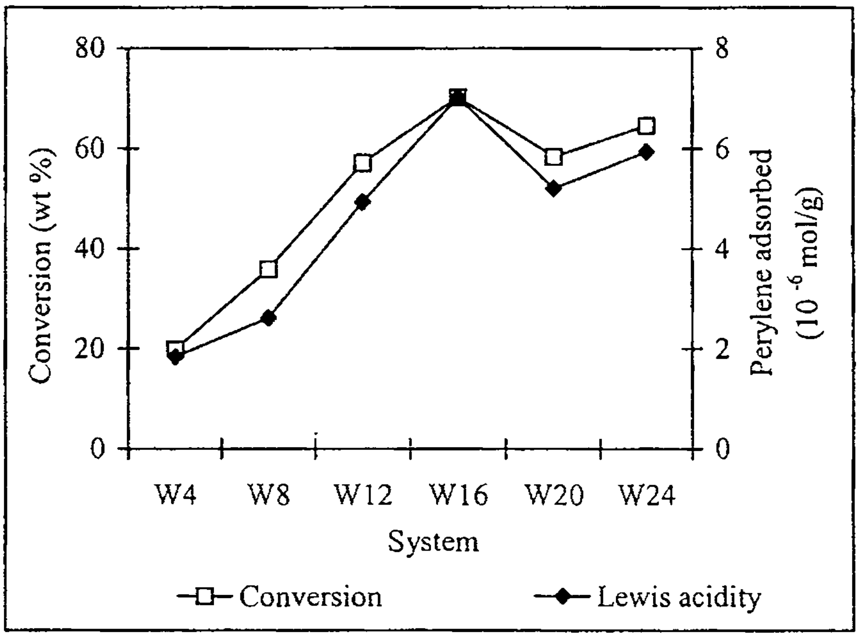


Figure 4.10 Correlation of benzylation activity for *o*-xylene with Lewis acidity

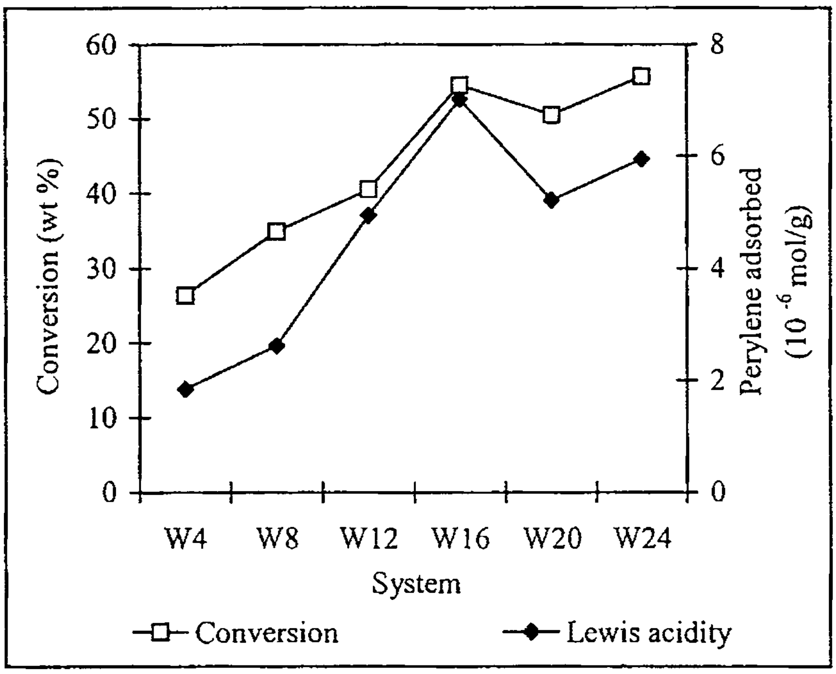


Figure 4.11 Correlation of benzylation activity for toluene with Lewis acidity

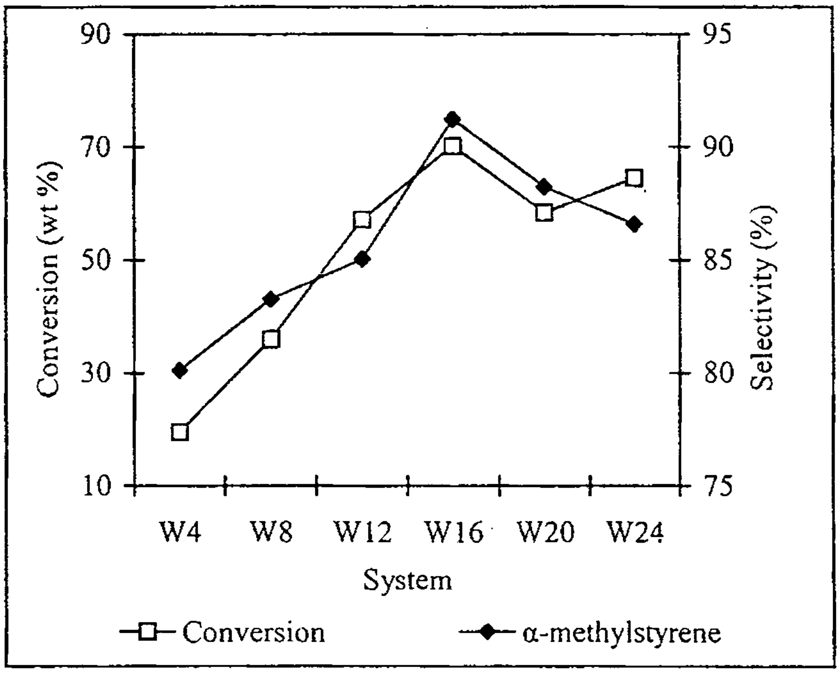


Figure 4.12 Correlation of benzylation activity for *o*-xylene with α-methylstyrene selectivity

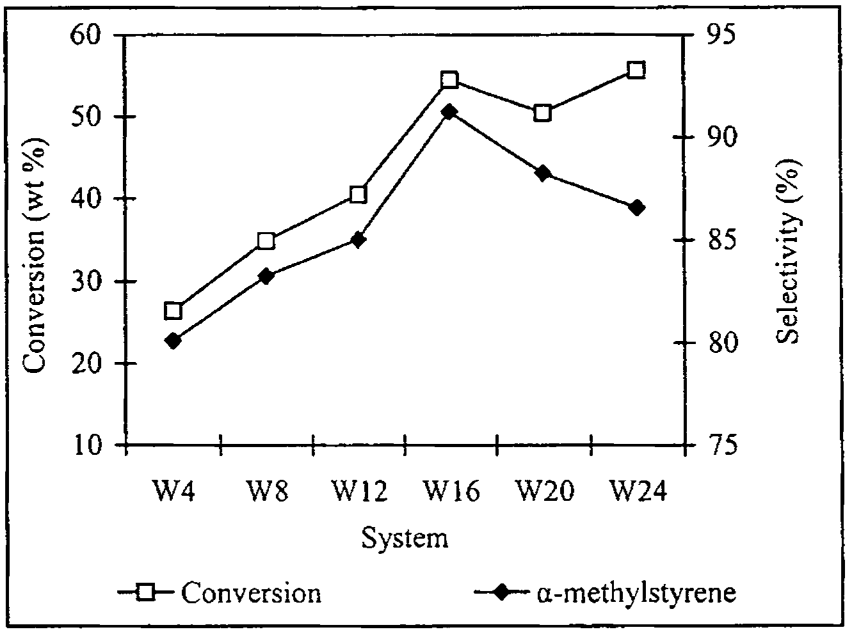


Figure 4.13 Correlation of benzylation activity for toluene with α-methylstyrene selectivity

4.2.3 MECHANISM FOR BENZYLATION REACTION

Friedel-Crafts alkylations are aromatic electrophilic substitution reactions in which the carbocation intermediate is produced by complexation between the alkyl halide and catalyst i.e., the alkyl halide is polarised over the acidic sites of the catalyst. The carbocation then attacks the aromatic substrate giving the product. Formation of carbocation is thus an important step in the reaction mechanism. It can be formed by the polarisation of benzyl chloride at Lewis or Brönsted acid sites.

Mechanism operating in a particular reaction is largely dependent on the catalyst selected. Among the three series of catalyst systems studied, it was observed that for the molybdenum and tungsten systems the catalytic activity could be directly correlated to the Lewis acidity (Figures 4.6-4.13). This implies that the benzyl chloride molecule may be polarised over the Lewis acid sites on the catalyst. A plausible mechanism for benzylation of toluene involving the Lewis acid sites is depicted in Figure 4.14. The high activity of iron systems, in spite of its low total and Lewis acidity can be attributed to the redox or free radical mechanism (Figure 4.5) operating in such systems.

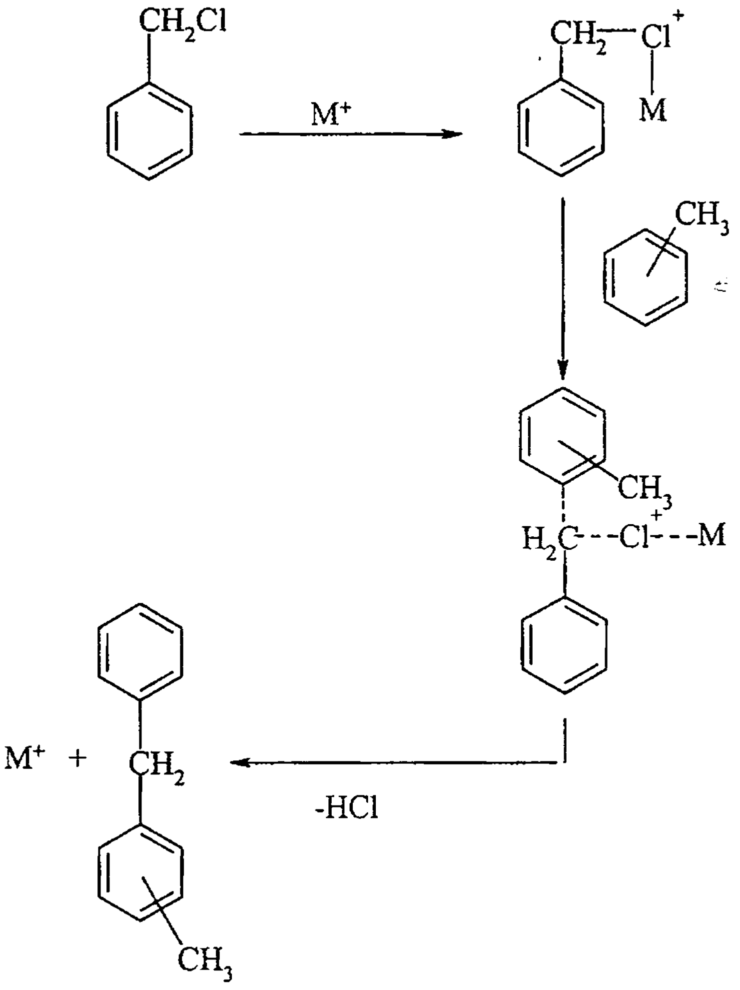
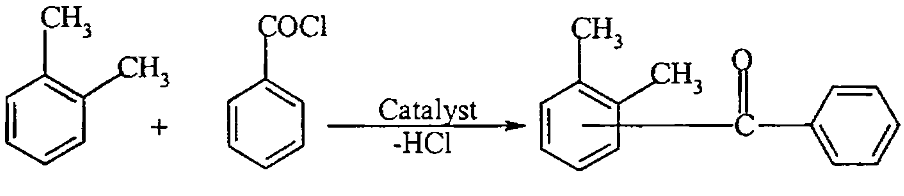


Figure 4.14 A plausible mechanism for benzylation of toluene involving the Lewis acid sites of the catalyst

4.3 BENZOYLATION OF O-XYLENE

Friedel-Crafts acylations are generally used for the synthesis of aryl ketones. Aryl ketones are of great importance for the production of fine chemicals such as drugs, fragrances, dyes and pesticides. Benzoylation of *o*-xylene is schematically represented in Scheme 4.3.



2,3-DMBP/3,4-DMBP

Scheme 4.3 Benzoylation of *o*-xylene

4.3.1 PROCESS OPTIMISATION

The reaction parameters were first optimised by analysing the influence of temperature, molar ratio and the effect of metal leaching on the activity and selectivity of a chosen catalyst.

i) Influence of temperature

The reaction was carried out over a range of temperatures using a selected catalyst in order to analyse the dependence of catalytic activity on temperature. The results are illustrated in Figure 4.15.

From the figure it is clear that as the temperature was increased the conversion increased. Maximum conversion was obtained at refluxing temperature of the reaction mixture. But the fact to be noticed is that at lower temperatures there was high selectivity for the *para* isomer, and as the reaction temperature was increased from 100 to 140°C the selectivity to the *para* isomer decreased from 97.48 % to 88.19 %.

ii) Influence of molar ratio

Benzoylation of *o*-xylene at different molar ratios was carried over the M_{20} system and the result is depicted in Figure 4.16. From the figure, it is clear that the catalytic activity is highly dependent on the molar ratio. As the amount of xylene was increased there was considerable decrease in the yield. The decrease in the catalytic activity with molar ratio may be either due to the dilution effect or due to the adsorption of xylene on the active sites of catalyst at high xylene concentration. But xylene being a non-polar molecule will not be adsorbed to the catalyst surface. So the decline in percentage conversion may be solely due to decrease in the effective concentration of benzoyl chloride in the reaction mixture.

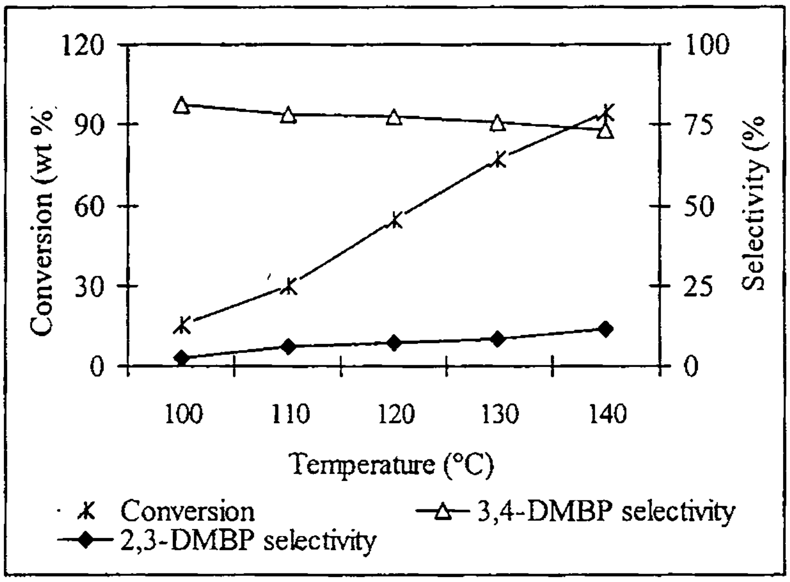


Figure 4.15 Catalytic activity as function of temperature for benzoylation of *o*-xylene

0.1 g M_{20} activated at 700°C, Molar ratio- (xylene/benzoyl chloride): 5:1, Duration-2 h

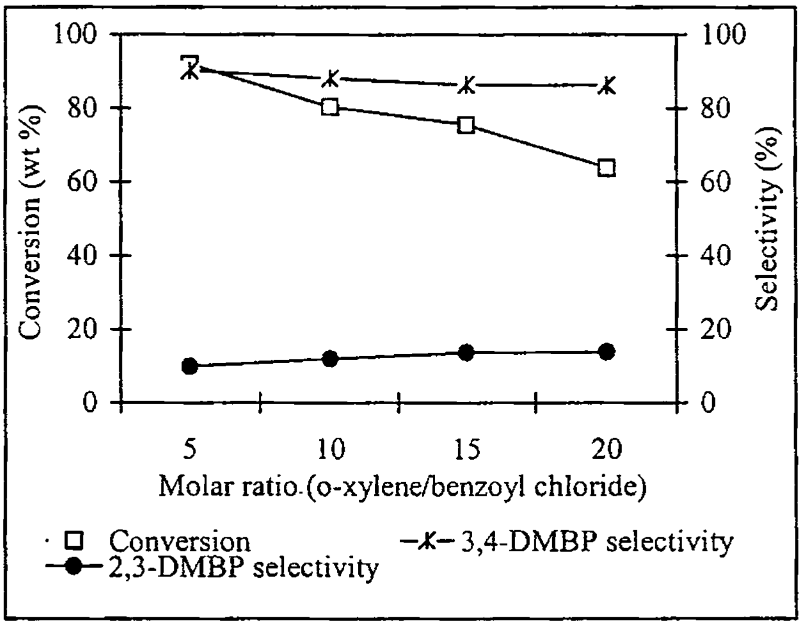


Figure 4.16 Dependence of catalytic activity and selectivity on molar ratio for benzoylation

Reaction temperature-140°C, 0.1 g M_{20} activated at 700°C, Duration-2 h.

iii) Metal leaching studies

In the case of heterogeneous catalyst systems metal leaching studies are essential because in some systems metal ions will leach out from the crystal lattice of catalyst and will homogeneously catalyse the reaction. For the leaching studies, the reaction was carried out for a particular time and after that the catalyst was filtered off and reaction was continued for another one hour using this filtrate. The results for leaching studies over M_{24}, W_{24} and F_{24} are given in Table 4.13.

From the data in the table it becomes clear that there was not much leaching for the M_{24}, W_{24} systems. In both these cases conversion was not increased to a great extent even when the reaction was continued for one hour after filtering off the catalyst. But for F_{24}, the case was different and conversion increased by more than 10% in one hour even when there was no catalyst in the reaction system. The reaction mixture was tested for presence of Fe^{3+} ion. The thiocyanate test gave a positive result, confirming our suggestion of a partly homogeneous reaction mechanism. So among the three series of catalysts studied, catalytic reaction took place partially homogeneously for iron systems.

Table 4.13 Data for the metal leaching studies for benzoylation over various systems

Time (h)	Conversion (wt %)		
	M_{24}	W_{24}	F_{24}
1	78.39	62.74	79.18
1.5	79.56	63.21	85.78
2	80.03	64.01	92.83

Reaction conditions: 0.1 g M_{24}, W_{24} activated at 700°C and F_{24} activated at 550°C, Reaction temperature-140°C for M_{24}, W_{24} and 100°C for F_{24}, Molar ratio- (xylene /benzoyl chloride)- 5:1

iv) Influence of substrate

The results for the benzoylation using various substrates are given in Table 4.14. The reaction was carried out at the refluxing temperature of each substrate. The activity varies in the order *o*-xylene> toluene > benzene. In the benzoylation reaction the substrate is attacked by an active electrophile. The tendency of an electrophile will be to attack the aromatic ring with higher electron density. Since the $-CH_3$ group is an electron donating one, the substrate that contains the maximum number of $-CH_3$ groups, will be more active towards the benzoylation reaction. This explains the high activity of xylene towards the benzoylation reaction.

Table 4.14 Influence of substrate on catalytic activity

Substrate	Time (h)	Conversion (wt %)
Benzene	3	18.79
Toluene	3	64.14
o-xylene	2	91.93

Reaction conditions: 0.1 g M_{20} activated at 700°C, Molar ratio- (substrate /benzoyl chloride)- 5:1

4.3.2 CATALYST COMPARISON

Benzoylation of iron oxide modified systems was carried out at 100°C for two hours, whereas for molybdenum and tungsten modified systems 140°C was found to be the optimum temperature, and molar ratio (xylene/benzoyl chloride) used for all these systems was 5:1. The data for catalytic activity of these systems are given in Tables 4.15-4.17. Pure tin oxide and sulphated analogue were not much active towards benzoylation. Metal oxide loading seemed to enhance the catalytic activity of sulphated tin oxide.

Among the three series of metal oxide modified systems prepared, iron oxide modified systems showed highest catalytic activity. From the results for the benzoylation over the iron oxide systems (Table 4.15), it is well evident that the catalytic activity increased with increase in iron oxide loading, maximum activity being exhibited by the F_{24} system. In molybdenum series, it was M_{20}, which gave the maximum conversion (Table 4.16). For the tungsten series, the reactivity increased with increase in metal oxide loading till W_{16}; further increase in the tungsten oxide percentage did not have a significant effect on reactivity.

Table 4.15 Catalytic activity and selectivity of iron oxide systems for benzoylation of *o*-xylene

Systems	Conversion (wt %)	Selectivity (%)	
		2,3-DMBP	3,4-DMBP
S	-	-	-
SS	6.54	11.13	88.87
F_4	38.94	6.67	93.33
F_8	51.85	7.08	92.92
F_{12}	68.11	7.75	92.25
F_{16}	79.24	7.26	92.74
F_{20}	89.13	8.15	91.85
F_{24}	96.91	10.00	90.00

Reaction Conditions: 0.1 g activated at 550°C, Reaction temperature-100°C, Duration- 2 h, Molar ratio - (*o*-xylene/benzoyl chloride) - 5:1

The catalytic activity and selectivity shown by the metal oxide systems are largely dependent on their acidic and basic properties. In the case of Friedel-Crafts reactions, acidity seems to be the determining factor. Molybdenum based systems exhibited high values for acidity by TPD, thermodesorption of pyridine and Lewis acidity determined by perylene adsorption. Though iron based systems gave the lowest values in all these analyses they were showing high yields for benzoylation reaction even at lower reaction temperature compared to the molybdenum and tungsten oxide systems (Table 4.16 and 4.17 respectively). Hence it was concluded that for iron systems, acidity was not the influential factor in determining their catalytic activity. From metal leaching studies it was clear that there was Fe^{3+} ions in the reaction mixture, so these ions may combine with the HCl formed during the reaction to give $FeCl_3$. It is the $FeCl_3$ that was formed in the reaction mixture, which homogenously catalyse the reaction. Thus due to the leaching of ions from the crystal structure the iron oxide systems gave good results for xylene benzoylation even at 100°C.

For both molybdenum and tungsten oxide systems the reactivity could be well correlated with Lewis acidity values obtained by the perylene adsorption analysis (Figures 4.17 and 4.18 respectively) and α-methylstyrene selectivity for the cumene cracking reaction (Figures 4.19 and 4.20 respectively)

Table 4.16 Data for the benzoylation of o-xylene over molybdenum oxide modified systems

Systems	Conversion (wt %)	Selectivity (%)	
		2,3-DMBP	3,4-DMBP
S	-	-	-
SS	15.39	10.77	89.23
M_4	33.13	11.34	88.66
M_8	48.43	10.54	89.46
M_{12}	60.67	9.28	90.72
M_{16}	79.52	10.01	89.99
M_{20}	91.93	9.81	90.19
M_{24}	77.34	13.16	86.84

Reaction Conditions: 0.1 g catalyst activated at 700°C, Reaction temperature - 140°C, Duration- 2 h, Molar ratio - (*o*-xylene/benzoyl chloride) - 5:1

Table 4.17 Effect of tungsten oxide loading on benzoylation of *o*-xylene

Systems	Conversion (wt %)	Selectivity (%)	
		2,3-DMBP	3,4-DMBP
S	-	-	-
SS	15.39	10.77	89.23
W_4	24.23	11.73	88.27
W_8	40.14	11.18	88.86
W_{12}	58.73	12.02	87.98
W_{16}	79.82	12.57	87.43
W_{20}	73.28	10.19	89.89
W_{24}	75.59	11.83	88.17

Reaction Conditions: 0.1 g catalyst activated at 700°C, Reaction temperature-140°C, Duration- 2 h, Molar ratio- (*o*-xylene/benzoyl chloride) - 5:1

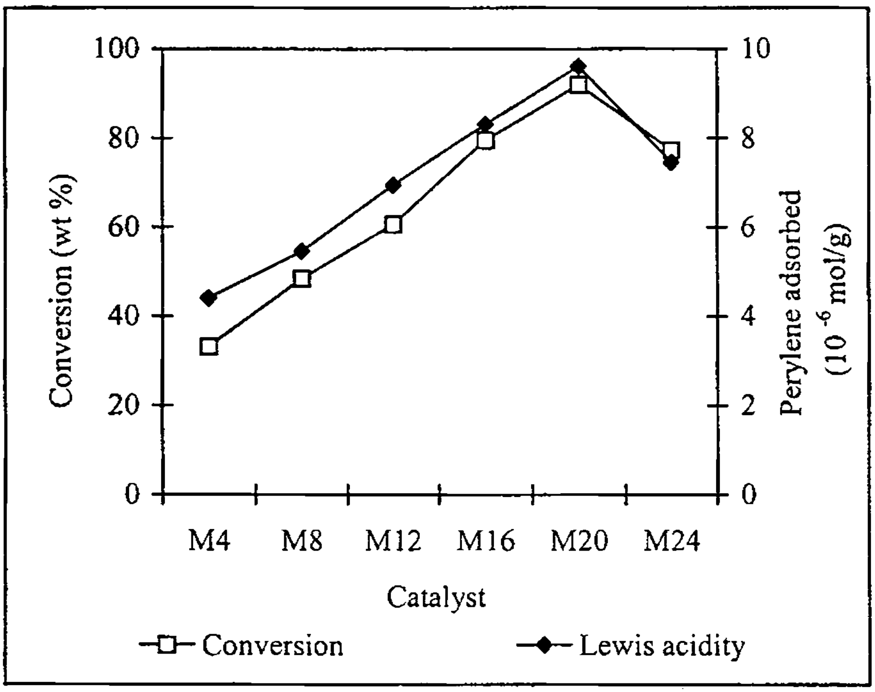


Figure 4.17 Correlation of the benzoylation activity of molybdenum series with Lewis acidity

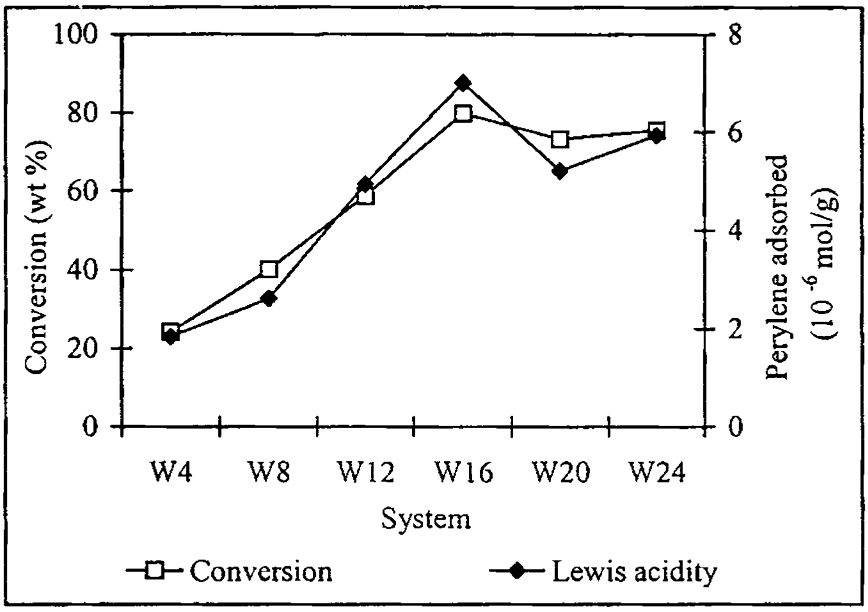


Figure 4.18 Correlation of the benzoylation activity of tungsten series with Lewis acidity

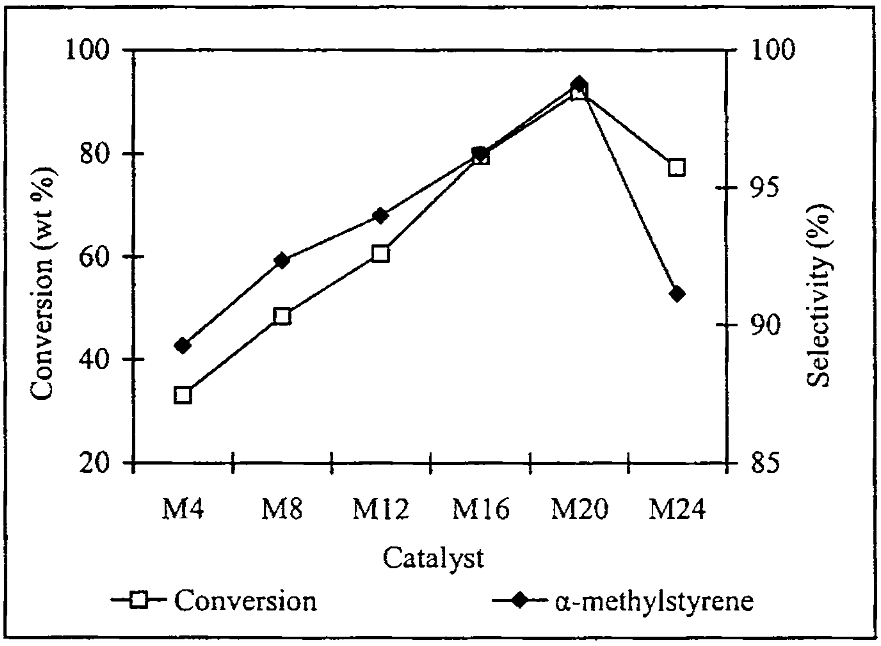


Figure 4.19 Correlation of the benzoylation activity of molybdenum series with α-methylstyrene selectivity

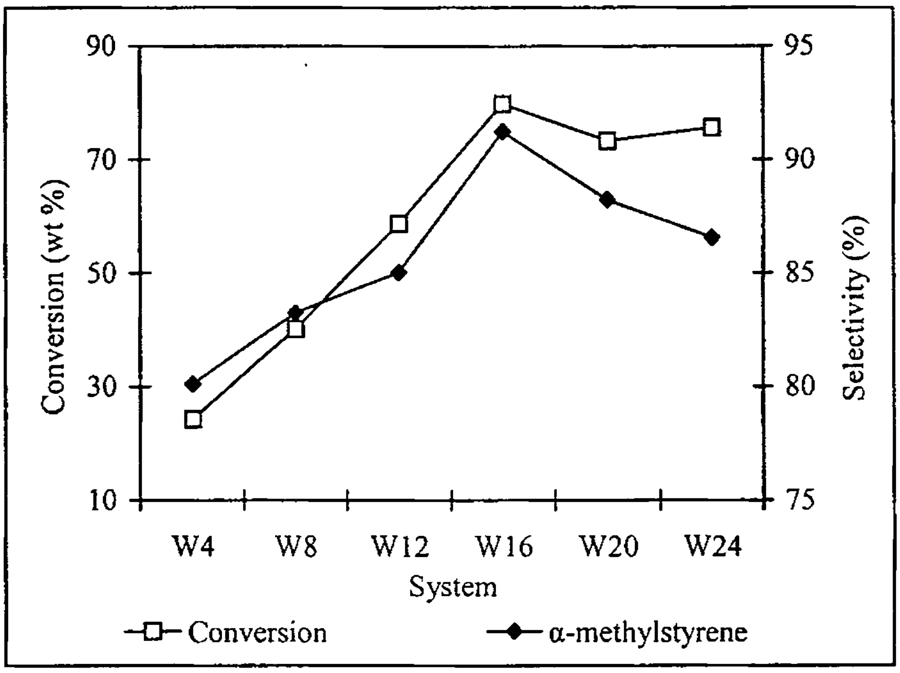


Figure 4.20 Correlation of the benzoylation activity of tungsten series with α-methylstyrene selectivity

4.3.3 MECHANISM OF BENZOYLATION REACTION

Friedel-Crafts acylation under homogeneous conditions requires the presence of stoichiometric amount of Lewis acids. It is well established that benzoylation of *o*-xylene proceeds though electrophilic substitution (29,59). The active electrophile can be either a complex formed between the catalyst and the carbonyl group of the acyl halide or an acylium ion. In the case of solid acids, there are reports regarding the involvement of both Lewis and Brönsted acid sites for the acylation reactions. The mechanism involves polarisation of the acyl chloride at the Lewis or Brönsted sites over the catalyst surface, the polarised acyl chloride molecule then acts as the electrophile and attacks the substrate.

Among the three series studied, molybdenum and tungsten based systems showed correlation between the Lewis acidity and benzoylation activity. But for the iron systems no such correlation existed, it was the Fe^{3+} that leached out that was catalysing the reaction homogenously. So on the basis of these results a plausible mechanism for benzoylation involving the Lewis acid sites for tungsten and molybdenum based systems is given in Figure 4.21

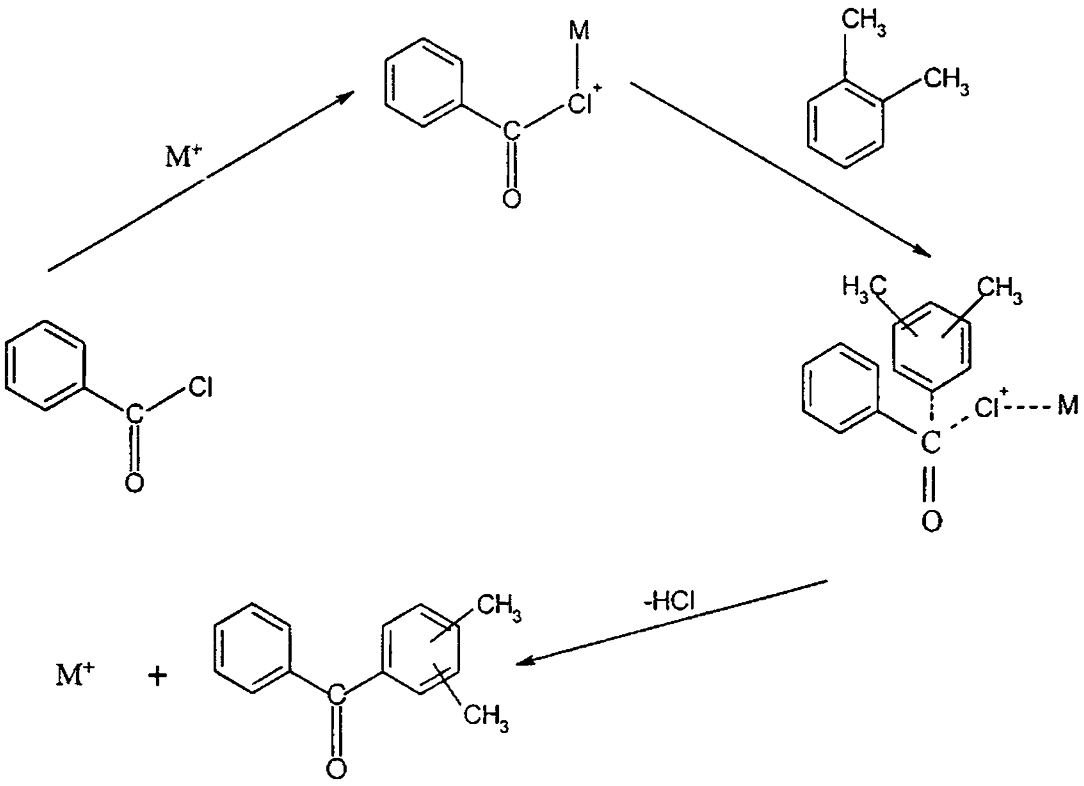
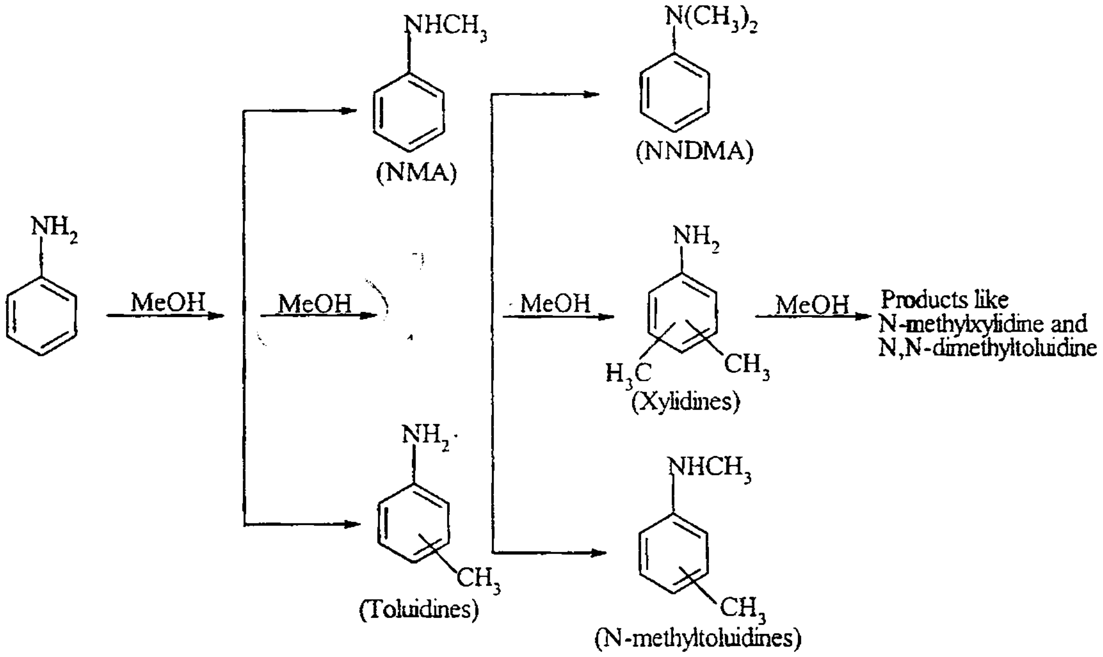


Figure 4.21 A plausible mechanism for benzoylation of *o*-xylene involving the Lewis acid sites of the catalyst

4.4 VAPOUR PHASE METHYLATION OF ANILINE

Methylation of aniline is an industrially important process aimed at the synthesis of N-methylaniline, N,N-dimethylaniline and toluidines, which are useful raw materials for organic synthesis, and essential intermediates in dye stuff production and in the pharmaceutical and agrochemical industries. The methylation of aniline is represented in Scheme 4.4. Until now, the industrial process leading to these products is based on the application of corrosive liquid acids as catalysts (60,61). Continuous efforts have been made to replace the traditional Friedel-Crafts type systems due to the inherent drawbacks associated with the process. A broad range of solid acid catalyst systems has been studied due to their eco friendly nature and their potential to replace the conventional Friedel-Crafts type systems (62-68). The toxic alkylating agents are now replaced by non-toxic agents such as methanol and dimethyl carbonate. By performing the alkylation in the vapour phase, the tedious and expensive procedures associated with liquid phase reactions can be avoided.



Scheme 4.4 Different pathways for the methylation of aniline

The vapour phase methylation was initially studied by Hill *et al.* (68). Recently, a wide variety of catalysts have been tested for alkylation of aniline with methanol and some of them became viable alternative to the conventional homogeneous systems. Different systems studied include zeolites (69-75), clays and metal oxides such as Al_2O_3 (61), MgO (63,64), etc. Studies showed that the major factors influencing the activity and selectivity of gas phase alkylation of aniline are the acid- base properties and shape selectivity of the solid acids.

Zeolites and alumino-phosphate based molecular sieves were extensively studied for the vapour phase alkylation of aniline (70,71,76,77). Chen *et al.* (78) reported selective formation of N,N-dimethylaniline over H-ZSM-5 zeolite modified by alkali metal species. Ione and Kikhtyanin (73) studied the dependence of product selectivity for aniline methylation on chemical composition of zeolite, reaction temperature and feed rate. Modified ZSM-5 was found to exhibit high activity for aniline methylation. But they gave some amount of C-alkylated products also and the activity was directly dependent on the catalyst acidity. It was also confirmed that alkylation of aniline may take place on acidic as well as basic zeolites and this reaction was even performed on zeolites with redox properties (79,77). The basic zeolites were found to favour the formation of N-alkylated products and zeolites with acidic cations caused C-alkylation. Ethylation of aniline with ethanol and diethyl carbonate over alkali and alkaline earth metal exchanged zeolite Y and β were investigated by Yuvraj *et al.* (80). Zeolites K-EMT and K-Y were found to be good catalysts for N-methylation (81,82) whereas alkaline earth metal exchanged X- zeolite showed high selectivity for N, N- dialkylated products.

Woo *et al.* used borosilicates for alkylation of aniline (83) and correlated selectivity of methylated anilines with catalyst's acidity. In methylation of aniline over AlPO-5, Prasad and Rao (67) found that N-methylaniline and N,N- dimethylaniline were formed consecutively and N,N-dimethylaniline isomerised to N-methyltoluidine at temperatures above 325°C. Burgoyne *et al.* already reported that low temperatures favour N-alkylation and high temperatures favour ring alkylation by Hoffmann-Martius rearrangement (84). Elangovan *et al.* investigated the catalytic activity of AFI and AEL type molecular sieves for the methylation of aniline and found that the product distribution was influenced by the reaction temperature and molar ratio between methanol and aniline. Another observation was that the catalytic activity was dependent on the acidity of the systems (85).

Santhalakshmi and Raja observed that calcined layered double hydroxides of Mg^{II}-Al^{III} (LDH) with various atomic ratios for Mg:Al showed absolute selectivity for N-methylaniline (86). Aramendia *et al.* have investigated the methylation of aniline over magnesium phosphates and found that these catalysts gave only the N-alkylated products. But these catalysts deactivated rapidly at high temperatures. Na_2CO_3 impregnation on magnesium phosphate decreased the amount of coke formation on the catalyst surface and thus the deactivation of the catalyst was reduced to a considerable extent (87,88). Alkylation of aniline proceeded efficiently over alumina and silica-alumina catalysts.

Bautista *et al.* reported the alkylation of aniline over systems like $AlPO_4$-Al_2O_3 and $CrPO_4$-$AlPO_4$ (66,67).

Metal oxides were reported to show better selectivity for N-alkylation over C-alkylation, but many such systems cause both mono and disubstitution on nitrogen leading to poor selectivity for synthetically important monosubstituted product. Sreekumar *et al.* have found that ferrospinels are excellent catalysts for N-monoalkylation of aniline using methanol. Their observation was that Lewis acid sites were required for good catalytic performance. In spinels acid base properties are highly influenced by the distribution of cations in the crystal lattice. Thus it is the cationic distribution, which is the determining factor in the catalytic activity of spinel systems (89,90).

4.4.1 PROCESS OPTIMISATION

i) Influence of temperature

The reactivity and product distribution of any reaction is largely dependent on the reaction temperature. Methylation of aniline was carried out over M_{20} system at various temperatures to study the temperature influence on the reaction. It was found that as temperature was increased the yield also increased steadily (Figure 4.22). The increase in the percentage conversion was more prominent when the temperature was changed from 300 to 350°C. Further increase in temperature caused a decrease in the conversion. A considerable decrease in conversion at higher temperatures may be due to the side reactions of methanol leading to alkenes and other polymeric aromatics (91). Coke formed from the alkenes will get deposited on the active sites of the catalyst, leading to the decrease in the number of active sites available for the reaction (92). The selectivity to different products was also highly influenced by the reaction temperature. At low temperature, there was high selectivity towards the N-mono alkylated product and as the temperature was increased N,N-dimethyl aniline was formed in a greater extent. The results were in very good agreement with the literature reports (67). At all these temperatures only N-alkylated products were observed.

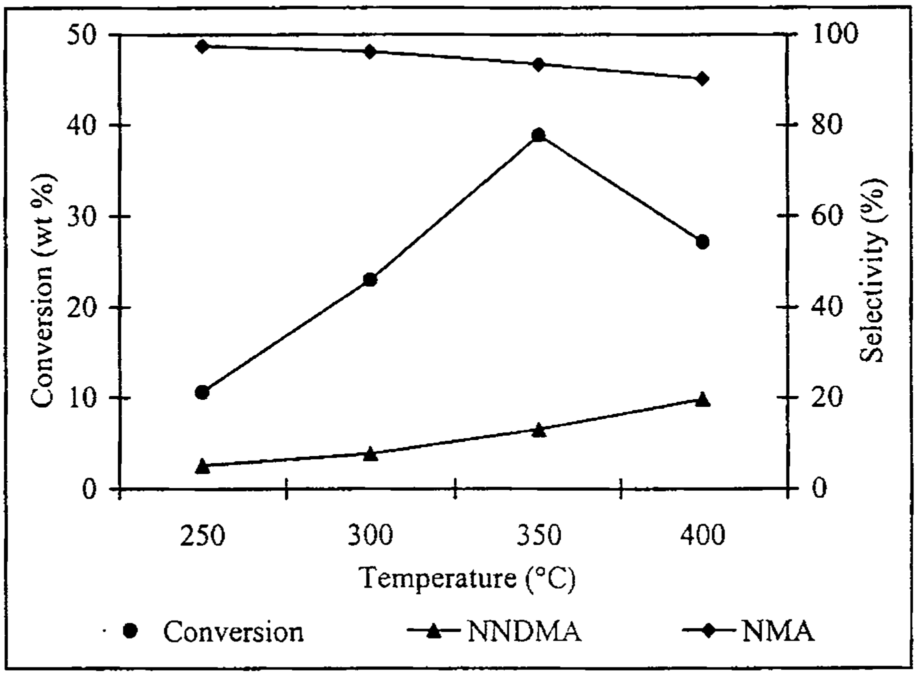


Figure 4.22 Catalytic activity for methylation of aniline as a function of temperature

Reaction Conditions: 0.5 g M_{20} activated at 700°C, Duration- 2 h, Flow rate- 6 mL/h, Molar ratio- (aniline/ methanol)- 1:7

ii) Influence of molar ratio

Molar ratio between aniline and methanol is another factor that influences the conversion and product selectivity. To fix the optimum molar ratio, a series of reactions were performed at 350°C with different molar ratios of methanol to aniline over M_{20} at a flow rate of 5 mL/h (Figure 4.23). An increase in conversion was observed with the increase in the molar ratio of the reactants. This increase was observed up to a molar ratio of 7. However, further increase in the molar ratio had an adverse effect on the conversion, which may be credited to the competitive adsorption of methanol. This prevents aniline from getting adsorbed on the active sites and the low concentration of aniline on the active sites may contribute to the decrease in overall conversion. The selectivity was also highly altered by the variation in molar ratio. Increase in the concentration of methanol caused a reduction in the N-methylaniline selectivity. As the selectivity of N-methyl aniline was decreased there was a corresponding increase in the percentage of N,N-dimethylaniline.

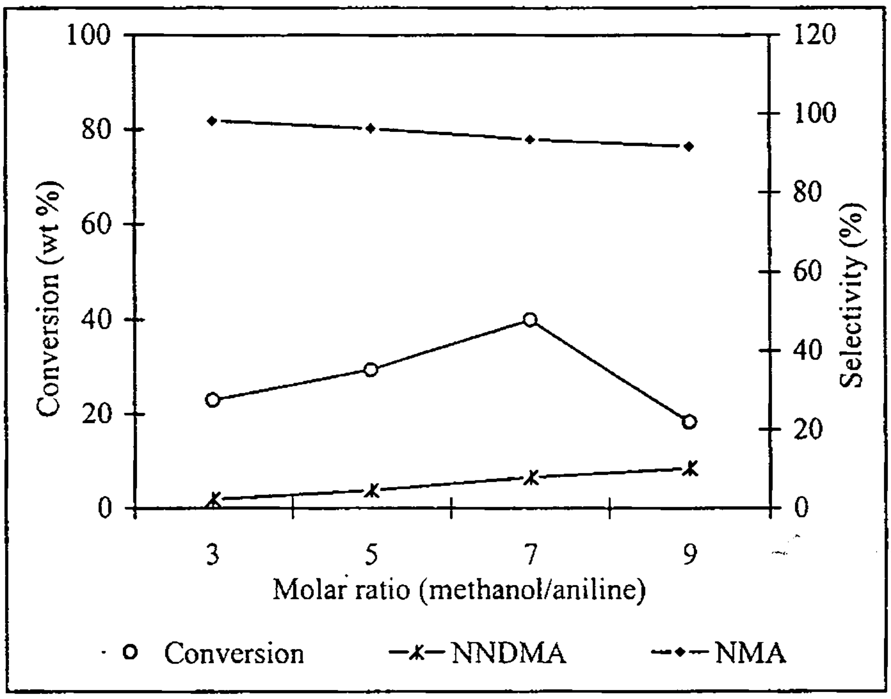


Figure 4.23 Influence of molar ratio for methylation of aniline

Reaction Conditions: 0.5 g M_{20} activated at 700°C. Reaction temperature-350°C, Duration- 2 h, Flow rate-6 mL/h

iii) Influence of flow rate

In gas phase reactions contact time between the reactants and catalyst is significant in determining the reactivity and selectivity; hence flow rate study becomes highly essential. In order to find the optimal feed rate, a series of reactions were performed over M_{20} system by varying the flow rates (4, 5 and 6 mL/h) at a fixed temperature (350°C) and molar ratio (7:1). Figure 4.24 shows the effect of flow rate on aniline conversion, NMA and NNDMA selectivity. At a lower feed rate of 4 mL/h conversion was high, this may be due to the fact that at a high contact time the reactants would get enough time on the catalyst surface to get converted to the products. As the feed rate was increased from 4 mL/h to 6 mL/h there was a considerable decrease in the conversion. But high selectivity to the NMA was shown at the flow rate of 6 mL/h. At lower flow rates NMA will remain adsorbed on the catalyst surface and gets successively alkylated to NNDMA.

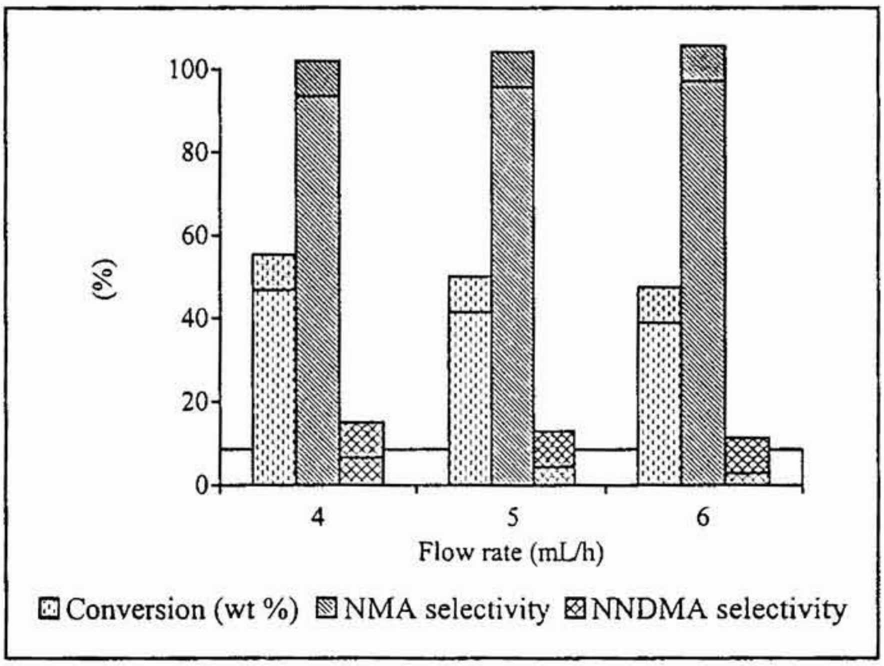


Figure 4.24 Variation of catalytic activity and selectivity with flow rate

Reaction Conditions: 0.5 g M_{20} activated at700°C, Reaction temperature-350°C, Duration- 2 h, Molar ratio- (methanol/aniline)- 7:1

iv) Influence of time on stream - Deactivation studies

An efficient catalyst is one, which retains its catalytic activity even after continuous usage. The performance of the present catalysts was tested by carrying out the methylation reaction over a selected catalyst for 5 h. Reaction was performed at 350°C using the molar ratio selected was 7:1 and the product analysis was done at regular intervals of 1 h. The results for the deactivation study are depicted in Figure 4.25. It is well evident from the figure that the conversion decreases with time. But the selectivity towards NMA remained almost the same after 5 h. The decrease in the conversion may be due to the coke deposition on the catalyst surface, thus reducing the number of active sites available for the adsorption of aniline and methanol.

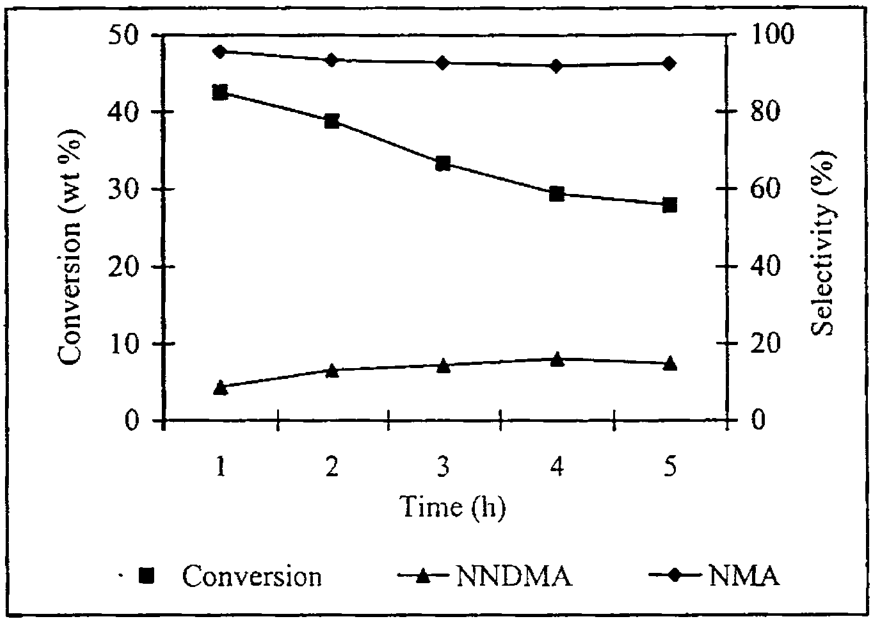


Figure 4.25 Deactivation study for aniline methylation

Reaction Conditions: 0.5 g M_{20} activated at 700°C, Reaction temperature-350°C, Molar ratio- (aniline/ methanol)- 1:7, Flow rate-6 mL/h

4.4.2 CATALYST COMPARISON

After analysing the optimisation results, catalytic activity of the systems were studied by carrying out the reaction at 350°C, using a molar ratio of 7:1 and a flow rate of 6mL/h. The results for the three series are given in Tables 4.18- 4.20. Metal oxide loading and sulphation improved the methylation activity of tin oxide to a considerable extent.

An important observation was that only N-alkylated products were formed in the case of all the three systems. Moreover, they showed high selectivity towards the NMA. It was reported that weak and medium acid sites results in N-alkylation and strong acid sites are responsible for C-alkylation and the latter can enhance the successive alkylation of the monoalkylated product. TPD results show that these catalyst systems possessed mainly weak and medium acidic sites. The amount of strong acid sites was comparatively much lesser than the weak and medium sites. Thus all these systems, which have mainly weak and moderate acidity, gave high percentage of NMA.

Table 4.18 gives the aniline methylation data for the molybdenum systems. The tungsten series (Table 4.19) exhibited lower activity than molybdenum oxide modified systems and iron series (Table 4.20) have the lowest reactivity. Aniline methylation being considered as an acid catalysed reaction, an attempt was made to obtain a correlation between the acidity and the conversion. Total acidity for the three series, as determined by TPD method was also in the order of the series molybdenum > tungsten >iron. There was no such regular trend for the conversion within a series. From the comparison it was obvious that the most acidic and the least acidic systems showed low activity in comparison with the intermediate ones (M_{12}, M_{24}, and W_{20}).

Table 4.18 Catalytic activity of molybdenum systems for methylation of aniline

Systems	Conversion (wt %)	Selectivity (%)	
		NMA	NNDMA
S	-	-	-
SS	7.89	100	-
M_4	27.92	94.38	5.62
M_8	33.78	95.35	4.65
M_{12}	44.94	93.44	6.56
M_{16}	40.53	92.77	7.23
M_{20}	38.89	95.16	4.84
M_{24}	47.80	92.26	7.74

Reaction Conditions: 0.5 g activated at 700°C, Molar ratio- (aniline/ methanol)- 1:7, Reaction temperature- 350°C, Duration- 2 h, Flow rate-6 mL/h

Table 4.19 Data for the methylation of aniline over tungsten oxide loaded systems

Systems	Conversion (wt %)	Selectivity (%)	
		NMA	NNDMA
S	-	-	-
SS	7.89	100	-
W_4	18.77	94.58	5.42
W_8	23.38	95.23	4.77
W_{12}	28.68	93.79	6.21
W_{16}	34.47	94.57	5.43
W_{20}	41.53	91.97	8.03
W_{24}	30.51	93.63	6.37

Reaction Conditions: 0.5 g activated at 700°C, Molar ratio- (aniline/ methanol)- 1:7, Reaction temperature-350°C, Duration- 2 h, Flow rate-6 mL/h

Table 4.20 Methylation of aniline over iron oxide modified systems

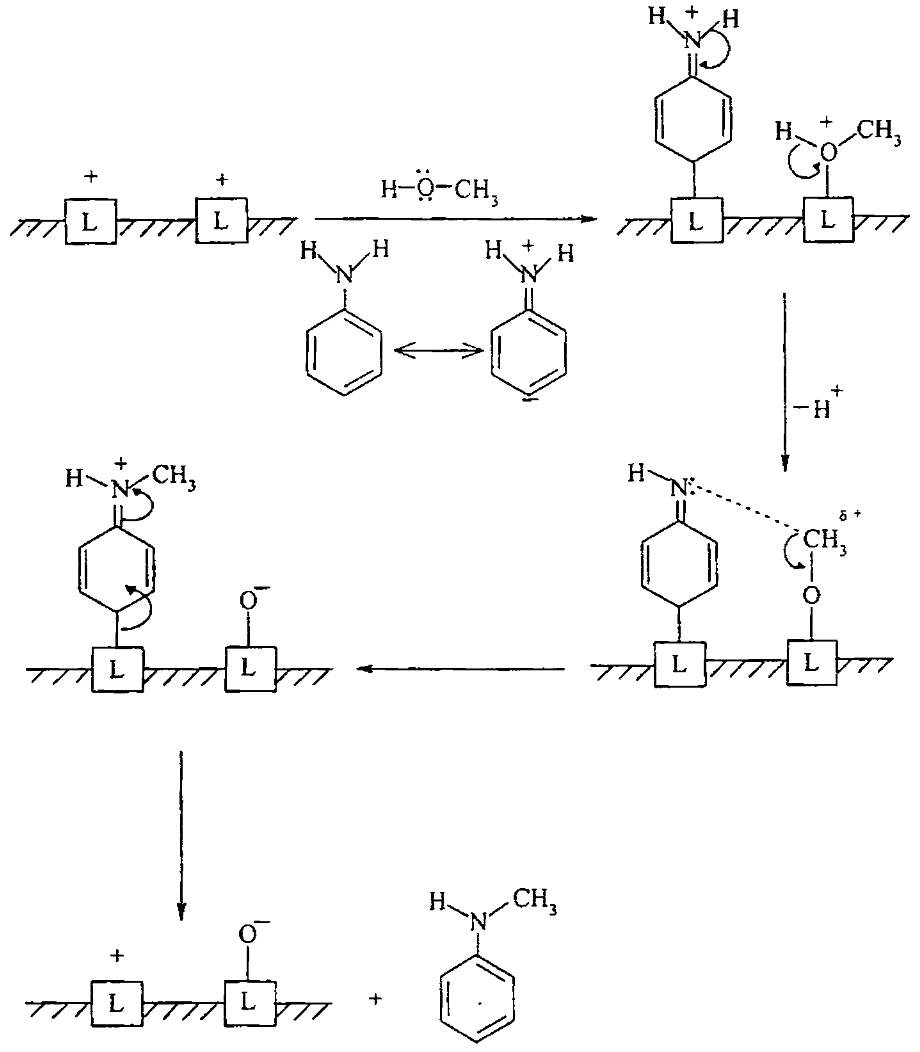
Systems	Conversion (wt %)	Selectivity (%)	
		NMA	NNDMA
S	-	-	-
SS	7.89	100	-
F_4	15.83	94.31	5.69
F_8	17.21	94.29	5.71
F_{12}	22.38	89.29	10.71
F_{16}	28.96	90.82	9.18
F_{20}	32.14	88.74	11.26
F_{24}	19.76	92.37	7.73

Reaction Conditions: 0.5 g activated at 700°C, Molar ratio (aniline/ methanol)- 1:7, Reaction temperature-350°C, Duration- 2 h, Flow rate- 6 mL/h

4.4.3 MECHANISM FOR ANILINE METHYLATION

Several mechanisms were proposed for the methylation of aniline involving Lewis and Brönsted acid sites and Lewis basic sites. The mechanism of aniline alkylation reaction established by Ko *et al.* (64) involve the adsorption of methanol to the Lewis acid sites i.e., the methoxy species is co-ordinatively bonded to these sites and the hydrogen atoms of the undissociated hydroxyl groups interact with the Lewis basic sites. Adsorption of aniline also follows a similar pattern. Electrophilic attack of methyl group of the methanol on the nitrogen atom of adsorbed aniline leads to NMA, which on subsequent methylation leads to NNMA. The mechanism accounts for the need of moderate amounts of both acidic and basic Lewis sites for the system. A different mechanism was proposed by Rao and coworkers (67) for ALPO and SAPO, in which the adsorption and subsequent polarisation of the substrates is mainly caused by the Brönsted acidity on the catalyst surface. Ivanova *et al.* also suggested that the Brönted acid sites are playing an important role in the methylation of aniline over zeolite H-Y (93). The rate of the reaction mainly depends on the probability that aniline and methanol molecules are adsorbed on adjacent sites. The activity and selectivity of the catalysts will be significantly influenced by any variation in acidity or basicity.

The experimental observations failed to give any proper correlation between the surface acidic properties. In general, the weak and medium acidity of the systems may be considered to play an important role in the relatively high selectivity towards NMA. It is well agreed that strong acidic sites favour C-alkylation in preference to N-alkylation and even when taking the case of N-alkylation, successive alkylation is greatly facilitated by the strong acid sites [94-97,70,79]. Similarly no correlation could be observed between the Lewis acidity of the samples and the conversions and product selectivities. Thus, we assume that a combined effect of the acidic sites along with the other surface properties may be the factor that influences the catalytic activity of the systems for methylation of aniline. Based on these considerations, a general mechanism involving Lewis acidic sites may be proposed for the reaction (Figure 4.26).



L-Lewis site

Figure 4.26 A plausible mechanism for methylation of aniline involving Lewis acid sites

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5

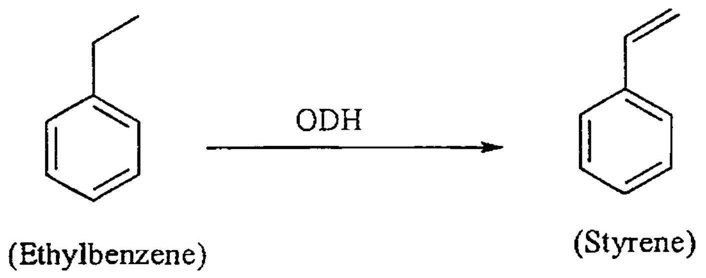
OXIDATIVE DEHYDROGENATION OF ETHYLBENZENE

5.1 INTRODUCTION

Styrene is an important monomer used for industrial production of many synthetic polymers. It is commercially manufactured by the catalytic dehydrogenation of ethylbenzene (1,2). This classical thermal dehydrogenation of paraffins to give the corresponding olefins and H_2 is a strongly endothermic process, which has to be carried out at temperatures above 600°C and its conversion is limited by thermodynamic equilibrium (3). Such high reaction temperatures lead to unwanted side reactions producing coke and smaller hydrocarbons. Hence, a continuous catalyst mediated oxidative dehydrogenation appears to be more promising compared to simple dehydrogenation (4-7). Oxidative dehydrogenation involves the removal of hydrogen from the reactant molecules by oxygen from the feed to form the corresponding olefins without parallel or consecutive oxidation reactions giving carbon monoxide or dioxide as non-selective products. Air is the most economically preferred oxidant as it can maintain high selectivity. The formation of H_2O as by product for the ODH reaction makes the process endothermic and the conversion becomes significant at much lower temperature. Generally the oxidative dehydrogenation of alkanes produces a considerable amount of carbon oxides reducing the selectivity of catalyst employed. Thus the key aspect of technology is development of catalysts capable of activating only the C-H bonds of the alkane molecule in a flow of oxygen.

Dehydrogenation of ethylbenzene was carried out over a variety of catalysts and reaction conditions of temperature, diluents, and catalyst promoter. Many catalysts such as cobalt, copper, iron and zinc oxide have been studied, with and without promoters (8) When promoted with potassium, all these catalysts exhibited enhanced activity, but maximum activity was shown by the iron system. Further studies showed that the active phase in potassium promoted iron oxide catalyst is potassium ferrite $KFeO_2$ (9,10).

Most works on the oxydehydrogenation of ethylbenzene (Scheme 5.1) has been devoted to the selection of suitable catalyst and appropriate reaction conditions for improved styrene yield and selectivity. The general catalysts reported for the ODH of ethylbenzene includes metal oxide (11-16), phosphates (7,17-19) and organic polymers (20,21).



Scheme 5.1 Oxidative dehydrogenation of ethylbenzene to styrene

The oxydehydrogenation activity of various acidic catalysts has received increasing attention in recent years. Tagawa *et al.* (4,6,17,22,23) after examining the catalytic activity of tin oxides and phosphates concluded that moderate acid strength is the key factor in deciding the reactivity. Removal of strong acid sites by addition of sodium acetate improved the selectivity, but excessive sodium deactivated the catalyst. Fiedorow *et al.* (24) also obtained similar results with alumina where small amounts of sodium did not affect activity even though strong acid sites would have been removed. Echigoya *et al.* (25) found that introducing acidity into silica by addition of either magnesium or zirconium correlated well with oxydehydrogenation activity. Alumina is reported to be an active catalyst for oxidative dehydrogenation of ethylbenzene and other alkylbenzenes (26-28). Alumina when treated with mineral acids showed an enhancement in activity (29,30). Kania *et al.* (31) investigated the effect of incorporation of Fe_2O_3, Cr_2O_3, NiO, MoO_3 and MgO on the oxydehydrogenation activity of γ- alumina and observed that introduction of Fe_2O_3 and Cr_2O_3 leads to a considerable increase in the catalytic activity.

Catalysts based on phosphates of nickel-zirconium, aluminium, cerium and calcium have also been reported to be active for the oxidative dehydrogenation reactions (32,33). In the pulse reaction of ethylbenzene over SnO_2 catalyst, non-selective oxidation proceeded. But the addition of phosphorus to SnO_2 suppressed the total oxidation reaction and enhanced the formation of styrene. This suggests the cooperative effect of acid base properties of the catalyst in influencing the reaction. It was also shown that mixed metal phosphates such as Zr-Sn and Sn-Ge systems display improved catalytic performances with respect to the single phosphates (34,35). High selectivity of about 97% to styrene was reported on Sn-Ge mixed phosphate (35). Among different condensed phosphates, the pyrophosphate group showed superior activity than the orthophosphates or oxides towards the oxydehydrogenation of ethylbenzene (18).

Jyothi *et al.* investigated the catalytic activity of rare earth promoted sulphated tin oxide for the oxidative dehydrogenation of ethylbenzene and found that these systems exhibit better oxidation activity when compared to the non-sulphated analogues and sulphated tin oxide (36). Kim *et al.* (37) studied the influence of incorporation of lanthana, ceria, praseodymia and neodymia on the activity of molybdena-alumina systems and among the four lanthanides used, praseodymia showed the maximum promoting effect.

5.2 PROCESS OPTIMISATION

For any reaction, conversion and product selectivity is influenced not only by the catalyst composition, but also by the reaction conditions like temperature, time on stream, feed rate, etc. So before carrying out the reaction over all the catalyst systems for comparing the catalytic activity of these prepared systems, it becomes highly essential to fix the optimum parameters for the reaction.

i) Influence of reaction temperature

In order to study the temperature influence on the ODH of ethylbenzene to styrene, the reaction was performed over a selected catalyst system at various temperatures such as 400, 450, 500 and 550°C. The reactant feed rate and air flow rate were maintained at 4 mL/h and 15 mL/h respectively. The results depicted in Figure 5.1 points to the fact that as temperature increases the conversion of ethylbenzene increases, but this hike in conversion is at the cost of decrease in the selectivity of styrene. As the temperature was raised in steps from 450 to 550°C, selectivity for styrene falls from 86% to 64% and the amount of benzene, toluene and C-oxides formed showed an enhancement. The overall conversion of ethylbenzene showed a leap after 500°C. This may be due to the excessive cracking of ethylbenzene to toluene and benzene at high temperatures.

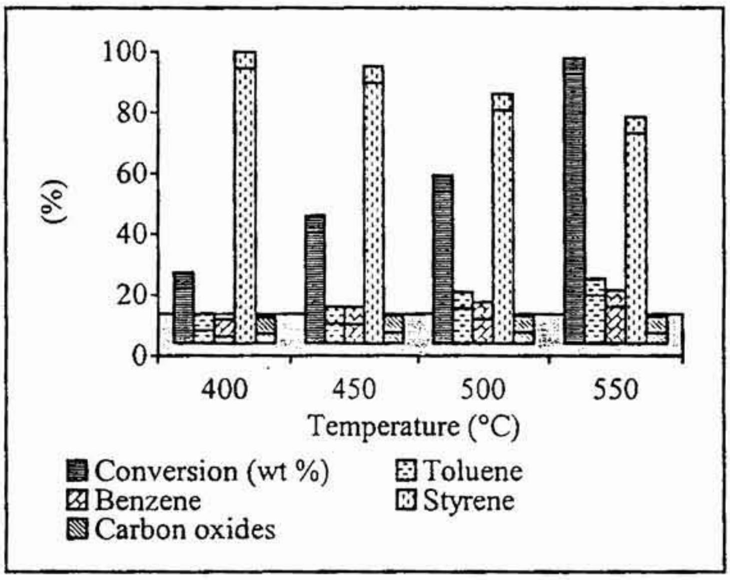


Figure 5.1 Influence of temperature on the activity and selectivity for oxidative dehydrogenation of ethylbenzene

Reaction conditions: 0.5 g M_{24} activated at 700°C, Flow rate- 4 mL/h, Duration –2 h

ii) Influence of flow rate

Flow rate is another important parameter that influences the reactivity in the case of gas phase reactions. The feed rates examined for this reaction were 4, 5, 6 and 7 mL/h. The reaction was carried out over M_{24} system at 450°C and at an air flow rate of 15 mL/h. The reaction mixture was analysed after 2h. The conversion was found to be higher at lower flow rates and it was adversely affected by the increase in flow rate (Figure 5.2). This may be due to the fact that with an increase in flow rate, the reactants will spend less time on the catalyst surface, leading to the decrease in the contact time between the reactants and catalyst. At higher feed rates reactants will not get enough time to get adsorbed on the catalyst surface for the reaction to take place. Thus the increase in flow rate has a negative effect on the conversion. However, high selectivity for styrene was observed at a feed rate of 7 mL/h, which might be due to the prevention of re-adsorption of styrene on catalyst surface to get converted into unwanted products.

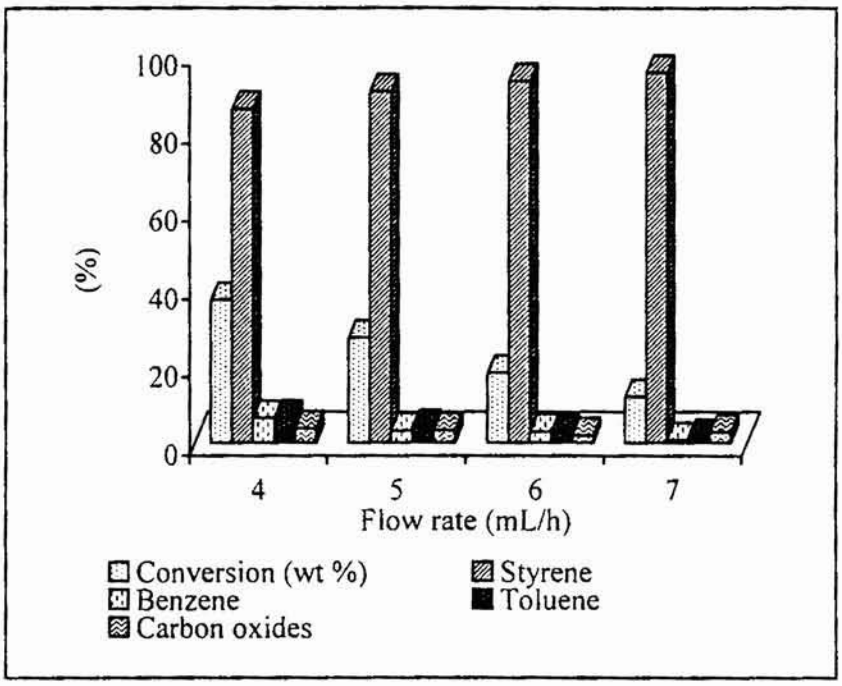


Figure 5.2 Variation of catalytic activity with flow rate for the oxidative dehydrogenation of ethylbenzene

Reaction conditions: 0.5 g M_{24} activated at 700°C, Duration – 2 h
Reaction temperature-450°C

iii) Influence of time on stream – Deactivation studies

An excellent catalyst is one that retains its catalytic activity and selectivity even after repeated runs. In order to test the deactivation of the prepared systems, the reaction was carried out continuously for 5 hours and the reaction mixture was analysed after every one hour. The results depicted in Table 5.1 shows that the reactivity of the catalyst system decreases to some extent in the first thee hours and after that the conversion remains more or less constant. Another important observation was that the selectivity towards styrene remained almost the same even after 5 h.

Table 5.1 Deactivation studies in the oxidative dehydrogenation of ethylbenzene to styrene

Time (h)	Conversion (wt %)	Selectivity (%)			
		Benzene	Toluene	Styrene	Carbon oxides
1	40.83	4.68	4.73	86.92	3.67
2	37.53	6.29	5.43	85.63	3.65
3	35.89	6.32	5.37	84.78	3.53
4	33.75	5.08	6.52	85.63	2.97
5	32.18	4.78	7.58	84.57	3.27

Reaction conditions: 0.5 g M_{24} activated at 700°C, Reaction temperature-450°C, Flow rate- 4 mL/h

5.3 CATALYST COMPARISON

In order to determine the effect of catalyst composition on the catalytic activity for the ODH of ethylbenzene, we carried out the reaction under optimised conditions over the prepared systems. All the catalysts gave styrene as the selective product and toluene, benzene and carbon oxides as non-selective products. Sulphate modification and incorporation of three different transition metal oxides had a positive influence on the catalytic activity of tin oxide towards the reaction.

In the case of all three systems studied catalytic activity and selectivity for styrene increased to a maximum until a certain percentage loading, and further addition of metal oxides decreased the activity and selectivity. Molybdenum oxide systems showed the least activity (Table 5.2) in spite of the fact that these systems were the most acidic among the three series. Acidity determination using different independent methods showed that addition of molybdenum oxide enhances the acidity of the catalyst systems, concomitantly reducing the basicity as evident from the cyclohexanol decomposition reaction. Tagawa *et al.* has showed that both acidic and basic sites are required for the oxidative dehydrogenation reactions (5). Thus lack of enough number of surface basic sites may be the cause for the low activity of the molybdenum oxide systems.

Table 5.2 Effect of molybdenum oxide loading on the oxidative dehydrogenation of ethylbenzene to styrene

Systems	Conversion (wt %)	Selectivity (%)			
		Benzene	Toluene	Styrene	Carbon oxides
S	15.55	7.97	3.62	70.50	17.91
SS	21.65	3.18	5.86	79.91	11.05
M_4	34.07	5.36	6.13	86.95	1.56
M_8	35.94	4.15	3.76	90.57	1.78
M_{12}	37.36	3.66	3.22	91.68	1.44
M_{16}	39.73	2.88	2.82	92.80	1.51
M_{20}	33.59	4.25	4.44	89.67	1.63
M_{24}	29.83	5.33	4.50	88.23	1.94

Reaction conditions: 0.5 g catalyst activated at 700°C, Reaction temperature-450°C, Flow rate- 4 mL/h, Duration – 2 h.

Among the molybdenum, tungsten and iron systems studied, iron oxide loaded systems showed the maximum catalytic activity and selectivity (Table 5.3) compared to tungsten and molybdenum oxide modified systems. Iron loaded systems showed only a slight enhancement in acidity than the pure and sulphated tin oxide when compared to the other two metal oxide loaded systems. Cyclohexanol decomposition studies showed that iron systems have both dehydration (acidic sites) and dehydrogenation (basic sites) activity indicating the presence of both acidic and basic sites in iron oxide modified sulphated tin oxide systems. There are many reports suggesting that both acidic and basic sites are required for the oxidative dehydrogenation. So maximum activity for this reaction will be obtained over those catalysts, which have a perfect balance between the acidic and basic sites.

Table 5.3 Catalytic activity and selectivity for the iron oxide systems in the oxidative dehydrogenation of ethylbenzene to styrene

Systems	Conversion (wt %)	Selectivity (%)			
		Benzene	Toluene	Styrene	Carbon oxides
S	15.55	7.97	3.62	70.50	17.91
SS	21.65	3.18	5.86	79.91	11.05
F_4	33.59	4.71	3.78	89.41	2.11
F_8	41.09	2.67	4.18	92.15	1.00
F_{12}	52.83	0.99	1.23	95.87	1.91
F_{16}	40.10	3.36	6.31	87.85	2.24
F_{20}	43.12	2.92	3.56	91.16	2.36
F_{24}	35.23	3.16	4.59	90.35	1.92

Reaction conditions: 0.5 g catalyst activated at 550°C, Reaction temperature- 450°C, Flow rate- 4 mL/h, Duration – 2 h.

In the case of tungsten modified systems ethylbenzene conversion and styrene selectivity improved with increase in the tungsten oxide loading, up to W_{16} system and then it showed a decline (Table 5.4). The catalytic activity enhancement for tungsten oxide systems is higher when compared with the molybdenum systems. From the acidity values determined by TPD measurement and thermodesorption of pyridine, it can be observed that these systems are less acidic than the molybdenum systems. That may be the reason for the better activity of these systems.

Table 5.4 Variation of catalytic activity with tungsten oxide loading in the oxidative dehydrogenation of ethylbenzene to styrene

Systems	Conversion (wt %)	Selectivity (%)			
		Benzene	Toluene	Styrene	Carbon oxides
S	15.55	7.97	3.62	70.50	17.91
SS	21.65	3.18	5.86	79.91	11.05
W_4	35.22	4.97	4.52	85.60	4.99
W_8	38.35	6.55	4.49	87.87	1.58
W_{12}	40.83	4.24	5.68	88.03	2.06
W_{16}	43.83	3.12	3.04	91.86	1.98
W_{20}	32.24	6.44	4.43	87.06	2.07
W_{24}	36.53	4.29	5.43	85.63	1.92

Reaction conditions: 0.5 g catalyst activated at 700°C, Reaction temperature-450°C, Flow rate-4 mL/h, Duration – 2 h

5.4 MECHANISM OF OXYDEHYDROGENATION REACTION

A redox reaction was proposed as a possible mechanism for oxydehydrogenation in many literatures (4,17,38). In the oxidative dehydrogenation of ethylbenzene the most probable mechanism is the one, which involves the abstraction of hydrogen from ethylbenzene by lattice oxygen on the surface to form styrene though a л- allyl intermediate, and the reoxidation of the catalyst by gas phase oxygen. A л- allyl mechanism is generally accepted in the oxidation of olefins. The following sequences involve the redox cycle of adsorbed ethylbenzene on the catalyst surface, as suggested by Hanuza and co-workers (39).

$$\mathrm{EB} + [\mathrm{O}] \longrightarrow \mathrm{ST} + [\ ]$$

$$[\ ] + \tfrac{1}{2}\,\mathrm{O}_2 \longrightarrow [\mathrm{O}]$$

where [ ] is the anion vacancy and [O] is the lattice oxygen. Schalter and DeBoer have reported that the rate-determining step of propylene oxidation is the dissociative adsorption of propylene by the cleavage of the C-H bond in the methyl group of propylene in ^{14}C tracer studies. Moreover, the competitive reaction of ethylbenzene with other aromatic hydrocarbons over SnO_2-P_2O_5 catalysts suggests that ethylbenzene is adsorbed by the abstraction of α-hydrogen on the catalyst (4). Tagawa *et al.* showed that the β-hydrogen of the terminal CH_3- group of ethylbenzene molecule is unexchangeable; but the α-hydrogen and the hydrogen in the benzene ring are exchangeable. However, the exchange on the α-hydrogen is predominant to that on the aromatic ring. Thus, the adsorbed species can be regarded as being dissociated reversibly at the α-position of ethylbenzene. The basic site i.e., -OH group adjacent to the acidic site will abstract α-hydrogen and acts as the adsorption site for ethylbenzene (22). It was also concluded from the quantum calculations that the acid sites withdraw the electrons to reduce the electron density of the aromatic ring and enhances the acidic property of the α-hydrogen and it then interact with the -OH group near the acidic site (40). Grunewald *et al.* showed that catalysts based on pyrolysed systems also function *via.* a hydrogen abstraction mechanism. It is difficult to conclusively decide whether this was hydrogen atom or hydride abstraction. Most likely it is a concerted process, as proposed by both the Emig and Cadus groups (7,41). In this process the hydrogenated catalyst was then returned to its original state by reaction with air to produce H_2O.

Several literatures give strong evidence that surface acidity of the catalyst plays a direct (24,22) or an indirect (18,34) role in the oxydehydrogenation. It has been proposed that the selectivity of a catalyst during the oxidative dehydrogenation can be related to the oxidation degree of the surface (42). This implies that the acid base character of the catalyst surface oxygens must play an important role for the oxidative dehydrogenation of alkanes (43-46). Various studies on oxidation reactions suggest the participation of acidic sites (47,48) and basic sites (49) in the partial oxidation reactions. Tagawa *et al.* (22) investigated the oxidative dehydrogenation ethylbenzene over SnO_2-P_2O_5 and other solid acid catalysts and concluded that acid-base sites with suitable strength ranges are essential sites for oxidative dehydrogenation. Alkhasov *et al.* assumed that in the oxidative dehydrogenation, ethylbenzene is first adsorbed on acid sites of the catalyst surface. They claimed that the reaction pathway depends on the strength of the adsorption; the stronger the adsorption the greater is the conversion of ethylbenzene (including the formation of carbon oxides). In this process, base centres of the catalyst surface also play an important role as they activate the oxygen from the gas phase which take part in this reaction. Oxygen activated on strong base centers at high temperature was found to be responsible for the total oxidation of hydrocarbons. Therefore, a catalyst which has acid and base centres of moderate or weak strength, is most suitable for the oxidative dehydrogenation of ethylbenzene. Base sites of higher strength activate the adsorbed molecular oxygen to the form O_2^- and O^-, which at higher temperatures oxidise the hydrocarbons to carbon dioxides. SnO_2-P_2O_5 and SnO_2-SiO_2 catalysts exhibited high selectivity to styrene, which may be due to the remarkable suppression of complete oxidation. Tagawa *et al.*, suggested that acid site of H_0 between 1.5 and –5.6 are proven to be the active sites, which could adsorb ethylbenzene reversibly, whose oxidation on the other hand occurs by the intervention of strong basic sites.

For nickel phosphate systems, a decrease in styrene yield was observed with the increase in surface Brönsted site concentration. A probable explanation of this fact is that a very high concentration of protons on the catalyst surface can diminish the rates of adsorption or the styrene formation steps either by screening the ethylbenzene molecule from coordination to hydrogen abstraction centres on the catalyst surface or by lowering the concentration of the ethylbenzene available. (50). In the case of Fe_2O_3-Al_2O_3 and Cr_2O_3-Al_2O_3 systems the amount of acid and base centres of moderate and weaker strength increases, which can be assumed to be the reason for the increase in the activity of these catalysts in the oxidative dehydrogenation of ethylbenzene (31). The improvement in the partial oxidation activity of rare earth modified systems can be attributed to the fact that the highly mobile oxygen species generated by the rare earth species can migrate to the surface of SnO_2 and regenerate the active sites by the reoxidation (remote control mechanism) (36).

A plausible mechanism for the oxidative dehydrogenation of ethylbenzene over the metal oxide modified sulphate tin oxide systems involving the adjacent acidic and basic sites are depicted in Figure 5.3.

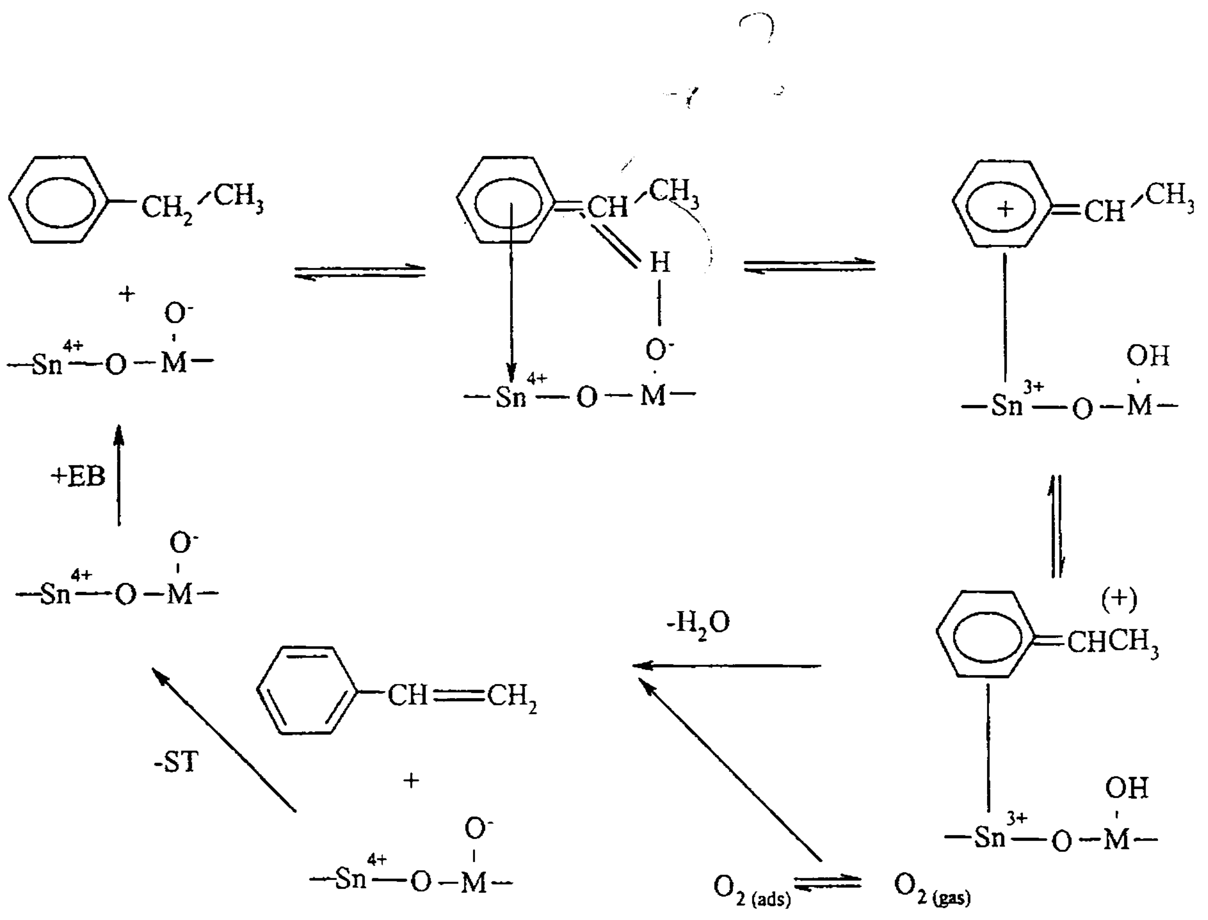


Figure 5.3 A plausible mechanism for the oxidative dehydrogenation of ethylbenzene over transition metal oxide modified sulphated tin oxide catalyst.

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6

SUMMARY AND CONCLUSIONS

6.1 SUMMARY

The thesis evaluates the effect of sulphate modification and transition metal oxide (Fe_2O_3, MoO_3 and WO_3) loading on the physico–chemical characteristics and catalytic activity of tin oxide. Sulphated tin oxide was prepared by impregnation method using 1N H_2SO_4 solution. To obtain the metal oxide loaded samples, single step impregnation technique was employed, utilising an appropriate metal salt solution. Sulphation and transition metal oxide incorporation do have positive influence on the acidity and catalytic activity of tin oxide. The samples were characterised by techniques like XRD, FTIR, EDX, SEM, TG, surface area and pore volume measurements. NH_3 TPD and thermodesorption of pyridine determined the surface acid site distribution. The surface electron accepting property (Lewis acidity) was determined by perylene adsorption. Vapour phase cumene cracking was done as a test reaction for acidity and the activity and selectivity in the cyclohexanol decomposition reaction helped to correlate the acid–base properties of the catalyst systems. The catalytic activity of the prepared systems was analysed by performing some industrially important reactions such as Friedel–Crafts reactions (liquid phase benzylation and benzoylation and vapour phase methylation of aniline) and oxidative dehydrogenation of ethylbenzene over them.

The chapter-wise depiction of the thesis is

Chapter I presents a brief literature review on the properties and catalytic activity of tin, iron, molybdenum and tungsten oxide based systems. This chapter also covers the surface properties and the acidity generation of sulphated metal oxide systems.

Chapter II focuses on the different materials used for the preparation and characteristion of the catalyst systems. This also includes the detailed procedure used for the preparation of the catalysts. It also gives a brief description about the various techniques used for the physico–chemical characterisation. The experimental procedures used to analyse the catalytic activity are also incorporated in this chapter.

Chapter III narrates the physico-chemical characteristics of the prepared catalysts. The sulphated mixed oxide structure was identified from the detailed study of XRD patterns, FTIR, EDX and SEM measurements. Acidity measurements (by TPD of ammonia and thermodesorption of pyridine), electron accepting property studies and surface area-pore volume analysis gave a detailed account of the surface properties. The thermal stability of the systems was determined by thermogravimetric analysis. Vapour phase cumene cracking and cyclohexanol decomposition were performed as test reactions for acidity. Cumene cracking was done to determine the amount of Lewis and Brönsted sites, and the latter reaction to correlate the acid – base sites of the systems.

Chapter IV explains the utility of the catalysts prepared for Friedel-Crafts reactions. This includes the benzoylation of *o*-xylene using benzoyl chloride and benzylation of toluene and *o*-xylene by benzyl chloride in the liquid phase. For both the reactions, the influence of reaction parameters such as temperature, molar ratio, time, etc. on the activity and selectivity are studied in detail. Description of methylation of aniline performed in vapour phase and the change in the catalytic activity and selectivity with reaction parameters are also included in this chapter. In the case of all these reactions, an attempt was made to correlate the catalytic activity with the surface acidity determined by different methods, and on the basis of these observations plausible mechanism is proposed for each reaction.

Chapter V discusses the application of the prepared catalyst systems for the oxidative dehydrogenation of ethylbenzene to styrene. The influence of various reaction parameters such as feed rate, reaction temperature and time on stream is also explained. A plausible reaction mechanism is also suggested based on the experimental results.

Chapter VI describes the summary and conclusion of the work.

6.2 CONCLUSIONS

The following are the conclusions elucidated from the present study.

- Sulphation and metal oxide modification improves the physico-chemical properties of pure tin oxide. The major outcomes include enhancement of surface area and stabilisation of the catalytically active tetragonal phase. Sulphate doping considerably improves the surface acidic properties.

- As the metal oxide loading increases the surface area increases to a maximum value and then decreases; the decrease is pronounced in the case of iron oxide loaded systems.

- Vapour phase cumene conversion reactions worked out as a test reaction for surface acidity. Good correlation was obtained between cumene conversion and the total acidity. Dehydrogenation product selectivity could be correlated with the Lewis acidity of the systems.

- Cyclohexanol decomposition reaction provided a good correlation between the acidity and basicity of the systems. This reaction proceeded efficiently over all the systems. Tungsten and molybdenum oxide modified systems showed high selectivity towards cyclohexene whereas iron systems gave considerable amounts of cyclohexanone, which is formed on the basic sites. The high cyclohexene selectivity in the case of these systems can be correlated to the weak and medium acidity of these systems.

- Transition metal oxide modified sulphated tin systems exhibited improved catalytic activity for the benzoylation of *o*-xylene compared with pure SnO_2 and simple sulphated tin oxide. Molybdenum oxide modification was found to be the most effective for this reaction. In all the cases, *para* isomer was formed preferentially with around 80-84% selectivity. The reaction seemed to be driven by the Lewis acidic sites. In the case of iron oxide modified systems the reaction may be considered to be partially homogeneous, as evident from metal leaching studies.

- Metal oxide modified sulphated tin systems were found to be efficient for the benzylation of toluene and *o*-xylene, the most efficient being the molybdenum oxide modified systems. Investigations on temperature influence showed that high reaction temperature favours dialkylation. Exceptionally high activity in the case of iron systems leads us to propose the operation of a free radical mechanism, which was confirmed, by the temperature influence studies as well as the appearance of an induction period for the reaction.

- Vapour phase methylation of aniline over sulphated tin oxide systems gave predominantly N-alkylated products. Parameters like reaction temperature, molar ratio, feed rate, etc. profoundly influenced the catalytic activity and product selectivity. All the metal oxide modified systems showed high selectivity for the N-methylaniline.

- Transition metal oxide modified sulphated tin systems proved to be efficient catalysts for oxidative dehydrogenation of ethylbenzene to styrene. All the systems showed high selectivity towards styrene. Among the three systems, iron modified systems showed maximum conversion and styrene selectivity, which might be due to the presence of both acidic and basic sites on these systems in appropriate proportions.

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