CHAPTER 5

FRIEDEL CRAFTS
ACYLATION
AND
ALKYLATION

5.1 INTRODUCTION

Charles Friedel and James Crafts in 1877 developed a set of reactions popularly known today as Friedel-Crafts reactions, involving electrophilic aromatic substitution of two types, acylation and alkylation.

Friedel-Crafts acylation

Friedel-Crafts acylation (Figure 1) involves the reaction of an acyl chloride or acid anhydride with aromatic compounds in presence of a strong Lewis acid catalyst. Due to the electron-withdrawing effect of the carbonyl group, the ketone product is always less reactive than the original molecule, therefore multiple acylations do not occur, which is an advantage over the alkylation reaction (described later in the text).Also, there are no carbocation rearrangements, as the carbonium ion is stabilized by a resonance structure in which the positive charge is on the oxygen, inhibiting intra molecular reactions.

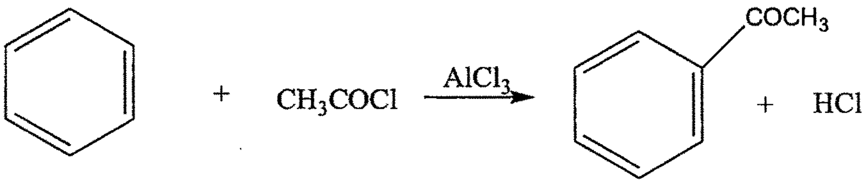

Figure 1 Reaction scheme for Friedel Crafts acylation

Mechanism for Friedel Crafts Acylation:

As seen from Figure 4, the first step consists of dissociation of a chlorine atom to form an acyl cation. This is followed by nucleophilic attack of the arene towards the acyl group. Finally, a chlorine atom reacts to form HCl, and the $AlCl_3$ catalyst is regenerated:

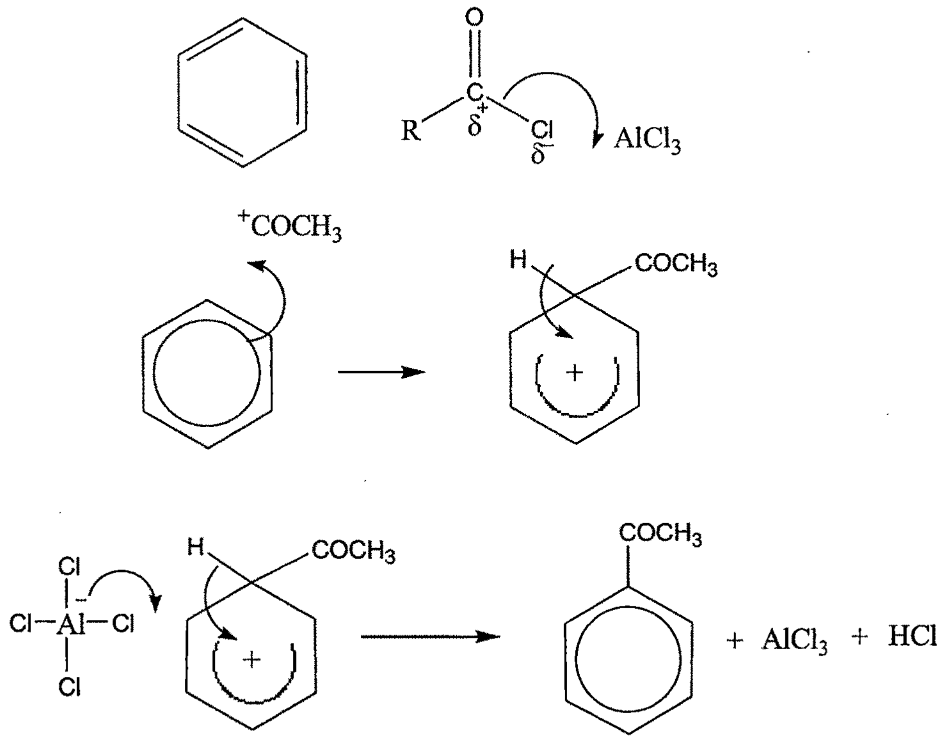

Figure 2 Reaction mechanism of Friedel Crafts acylation

The viability of the Friedel-Crafts acylation depends on the stability of the acyl chloride reagent. For example, in synthesis of benzaldehyde via the Friedel-Crafts pathway using formyl chloride as an acylating agent, since formyl chloride is too unstable to be isolated, formyl chloride has to be synthesized in situ. This is accomplished via the Gattermann-Koch reaction, accomplished by reacting benzene with carbon monoxide and hydrogen chloride under high pressure, catalyzed by a mixture of aluminium chloride and cuprous chloride.

Friedel–Crafts acylation of aromatic compounds and aromatic heterocyclic compounds is a ubiquitous reaction in the production of aromatic ketones, largely used as intermediates in the synthesis of pharmaceuticals, naproxen, dextromethorphan, ibuprofen and dyes, fragrances, and agrochemicals [1–6]. In particular, the synthesis of substituted acetophenones employing acylation is an important step for the production of a variety of precursors which find application in the production of pharmaceuticals, paint additives, photo initiators, fragrances, plasticizers, dyes and other commercial products[7-11].

Friedel-Crafts alkylation

Friedel-Crafts alkylation (Figure 3) involves the alkylation of an aromatic ring and an alkyl halide using a strong Lewis acid catalyst. With anhydrous aluminium chloride as a catalyst, the alkyl group substitutes the chloride ion.

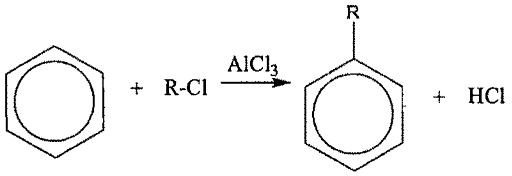

Figure 3 Reaction scheme for Friedel Crafts alkylation

Mechanism for Friedel Crafts Alkylation

As seen from Figure 4, the first step consists of dissociation of a chlorine atom to form an alkyl cation. This is followed by nucleophilic attack of the arene towards the alkyl group. Finally, a chlorine atom reacts to form HCl, and the $AlCl_3$ catalyst is regenerated

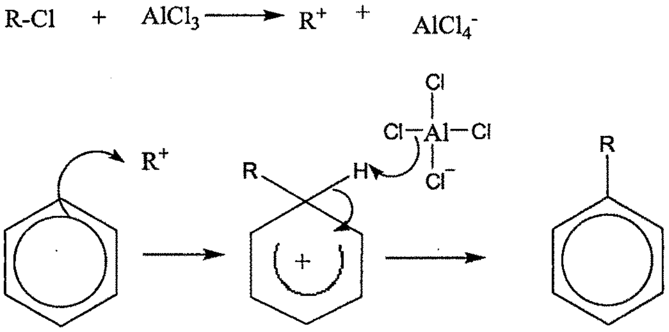

Figure 4 Reaction mechanism for Friedel Crafts alkylation

In this reaction, the product is more nucleophilic than the reactant due to the electron donating effect of alkyl-chain, therefore, another hydrogen is substituted with an alkyl-chain, which leads to overalkylation of the molecule. Further, if the chlorine is not on a tertiary carbon, carbocation rearrangement reaction occurs, attributed to the relative stability of the tertiary carbocation over the secondary and primary carbocations.Steric hindrance can be exploited to limit the number of alkylations, as in the tertiary butylation of 1,4-dimethoxybenzene.(Figure 5)

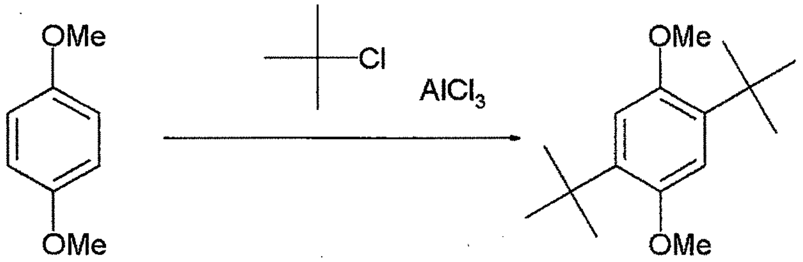

Figure 5 Reaction scheme for t-butylation of 1,4-dimethoxybenzene.

Alkylations are not limited to alkyl halides. Friedel-Crafts alkylation is possible with any carbocationic intermediate such as those derived from alkenes and a protic acid or lewis acid, enones and epoxides. In one study, the electrophile is a bromonium ion derived from an alkene and N-bromosuccinimide(NBS). In this reaction samarium(III) triflate is believed to activate the NBS halogen donor in halonium ion formation(Figure 6).

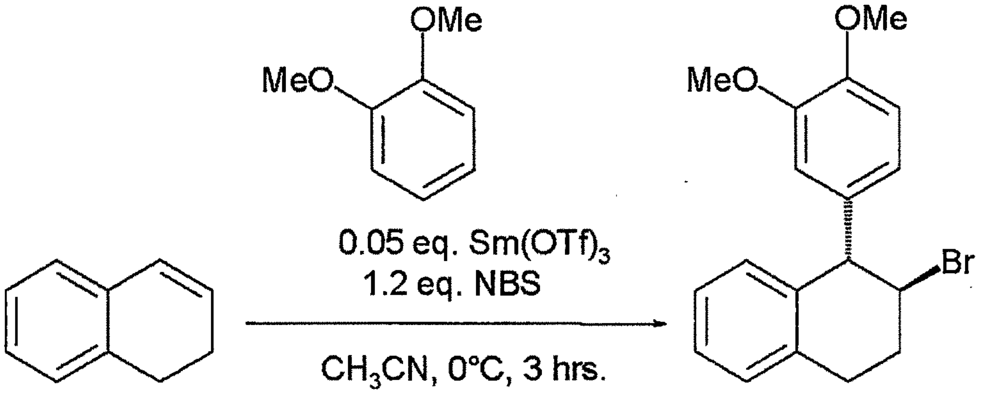

Figure 6 Reaction scheme for Friedel Crafts alkylation using bromonium ion as electrophile

The liquid phase benzylation of benzene and other aromatic compounds by benzyl chloride is important for the production of diphenylmethane and substituted diphenylmethanes which are industrially important compounds used as pharmaceutical intermediates and fine chemicals [12–15].

The use of acyl halides or anhydrides as acetylating agents and soluble Lewis acids as catalysts is polluting, expensive and difficult to work with. In normal practice, strong mineral acids, such as H_2SO_4, HF, or supported Lewis-acid catalysts like anhydrous $AlCl_3/SiO_2$ and BF_3/SiO_2, are used for such reactions. However, these Lewis acids are consumed in more than stoichiometric amounts due to the formation of 1:1 molar adduct with aromatic ketones and further, the subsequent separation of the product by hydrolysis is cumbersome and generates a large amount of environmentally hazardous and corrosive waste.

Friedel-Crafts alkylation reactions catalysed by homogeneous Lewis acid catalysts generally give complex reaction mixtures. The formation of reactant (and product) catalyst complexes, the increased tendency of alkylated products towards further alkylation and isomerization, coupled with the long contact of the reactant with the catalyst, result in decreased product selectivity.

Owing to stringent and growing environmental regulations world wide, there is a global effort to replace the conventional liquid acid catalysts by solid acids, which are less toxic, easily regenerable from the product, easy to handle and reuseable. In this context the focus has been towards design of processes to replace homogeneous Lewis acid catalysts with environmentally benign heterogeneous catalysts. The acid sites in solid acids being milder than the conventional lewis acids, would also inhibit side reactions such as polyalkylation, isomerization, transalkylation, dealkylation and polymerization that occur in traditional procedure. There is, therefore, substantial interest to carry out alkylation reactions with solid acid catalysts which decrease these side reactions.

5.2 LITERATURE SURVEY IN THE CURRENT AREA OF STUDY

Acylation/ alkylation of aromatic compounds have been reported using several solid acid catalysts in recent years. Kantam et al [16] have reported Friedel–Crafts acylation of aromatics and heteroaromatics using micro crystalline β zeolites with different acid anhydrides. The micronized β zeolite shows manifold activity over normal zeolite in acylation reactions of aromatics.

Deutsch et al [17] have reported acylation and benzoylation of various aromatics on sulfated zirconia and observed that the rate of acylation reactions is dependent on the nature of the respective aromatic compound. The application of sulfated zirconia as a catalyst for the acetylation of aromatics was only successful in case of anisole amongst various aromatic compounds used.

Kaur et al[18] have reported Friedel–Crafts acylation of anisole and toluene with acetic anhydride using heteropoly acid (HPA) supported on silica as catalyst as well as H-β Zeolite. In contrast to anisole, the acylation of toluene with HPA is far less efficient than that with H-β. The inhibited activity of HPA for toluene could be attributed to preferential adsorption of acetic anhydride on the catalyst.

Beers et al[19] have reported use of dealuminated β zeolites as solid acid catalyst for acylation of anisole with octanoic acid and proposed a structure–activity relation for the same. After dealumination, increased activity and selectivity were found in the acylation of anisole with octanoic acid. The enhanced activity is suggested to result from higher accessibility of the active sites associated with framework-connected aluminum atoms.

Bachiller-Baeza et al[20] have studied and compared the behaviours of HPA catalysts supported on a commercial silica and on a silica–zirconia mixed oxide for the acylation of anisole with acetic anhydride. The yields of p-methoxy acetophenone were highest for HPA/SiO_2.

Castro et al [21] have reported a mechanistic overview on the acylation reactions of anisole using α,β unsaturated organic acids as acylating agents and solid acids as catalysts. The mechanism of acylation of anisole with α,β unsaturated acids, i.e. acrylic, crotonic and methylcrotonic acid, have been investigated using phosphotungstic acid (PTA), PTA supported on SiO_2 and in the form of cesium salts as catalysts. Since α,β unsaturated acid can either alkylate and/or acylate the aromatic compound, the influence of the catalyst on the selectivity for these two competing reactions was studied. Analysis of products obtained on the acylation of aromatic compounds with α,β unsaturated acids shows that all the catalysts are more active for acylation than alkylation. Secondary products coming from intermolecular reactions of the acylated product with anisole as well as tertiary products coming from its further decomposition and recombination with another anisole molecule were observed. Heteropolyacids supported on silica were found to be more active and selective towards acylation reactions than zeolites HY and Hβ.

Melero et al [22] have reported Friedel Crafts acylation of aromatic compounds over arenesulfonic acid containing mesostructured SBA-15 materials. Arenesulfonic acid centers anchored on the pore surface of a mesostructured SBA-15 material show greater activity (normalised to the concentration of sulfonic groups) as compared to other homogeneous and heterogeneous sulfonated catalysts and even in solventless conditions. This high activity is accompanied with a remarkable thermal stability of the acid centers, without leaching of sulfur species during the reaction.

Cardoso et al [23] have reported silica supported heteropoly phosphotungstic acid catalyst for acylation of anisole using acetic anhydride as acylating agent. High conversions and very high *p*-selectivity were attained in the temperature range of 61–110 °C. However, deactivation was observed due to strong adsorption of the products.

Ma et al [24] have reported Friedel-Crafts acylation of anisole over Y-zeolite catalyst with alkanoic acids, anhydrides and substituted benzoic acids. When carboxylic acids were used as acylating agents, the activity of the Y zeolite increased with its Lewis acidity, showing that the Lewis acid sites were more active than the Bronsted acid sites. Further, the reaction mechanism was found to be similar to the homogeneous catalysis, that is, the electrophilic intermediate formed from the acylating agent over zeolite acid sites attacked the aromatic ring of anisole.

Gaare et al [25] have reported effect of Lanthanum ion exchange and Si/Al ratio of Y-zeolite on the Friedel-Crafts acylation of anisole by acetyl chloride and acetic anhydride. For the rare-earth modified zeolites, the activity was found to be dependent on the lanthanum content, and the yield increased with the level of lanthanum, even up to 93% exchange. Dealunminated Y-zeolites were also found to be very active, and an almost linear increase in the yield with decreasing aluminium fraction was found attributed to the increased hydrophobicity of dealuminated zeolites.

Heidekum et al [26] have reported use of Nafion/Silica composite materials as solid acid catalysts for acylation reactions and claimed that entrapping nanosized Nafion particles in a silica-matrix, effectively enhances the accessibility of the acid sites in comparison to the original material, Nafion resin.

Chaudhari et al [27] have reported $AlCl_x$-grafted Si-MCM-41 prepared by reacting anhydrous $AlCl_3$ with terminal Si–OH groups as an active and a reusable (if not exposed to atmosphere) mesoporous solid catalyst for the Friedel–Crafts benzylation and acylation reactions. However, like anhydrous $AlCl_3$, it is highly moisture sensitive and loses its activity on exposure to moist atmosphere. The active species on the catalyst are $(\text{–Si-O})_nAlCl_{3-n}$ (n = 1–3).

Cseri et al[28] have reported alkylation of benzene and toluene with benzyl chloride and benzyl alcohol over a series of clays obtained by exchanging the original cations of K10 by Ti^{4+}, Fe^{3+}, Zr^{4+}, Cu^{2+}, Zn^{2+}, Ce^{3+}, Cr^{3+} and Sn^{2+} cations. The acidity of these solids has been determined by infra red spectrometry using pyridine as molecular probe. The acidity of K1O clays can be changed to a great extent by cation exchange and by the thermal treatments applied to the solids. The rate of alkylation is roughly related to acidity when the substrate is benzyl alcohol, but not when benzyl chloride is used. In that case, the catalysts containing reducible cations (Fe^{3+}, Sn^{4+}, Cu^{2+}) exhibit high activities in spite of their low number of acid sites.

Bachari et al [29-31] have investigated benzylation of benzene and substituted benzenes, employing benzyl chloride as the alkylating agent over mesoporous silica with different Sn, Cu and Ga contents. The mechanism involves a redox step at the reaction initiation. The large pores of the mesoporous catalyst do not limit the size of the molecules that could be reacted.

Chaudhari et al[32] have investigated benzylation of benzene by benzyl chloride to diphenyl methane over $InCl_3$, $GaCl_3$, $FeCl_3$ and $ZnCl_2$ supported on commercial clays (viz. Montmorillonite-K10, Montmorillonite-KSF and Kaolin) or on high silica mesoporous MCM-41. The redox function created due to the impregnation of the clays or Si-MCM-41 by $InCl_3$, $GaCl_3$, $FeCl_3$ or $ZnCl_2$ seems to play a very important role in the benzylation process. Kinetics of the benzene benzylation (using excess of benzene) over the supported metal chloride catalysts have also been investigated and a plausible reaction mechanism for the benzylation over the supported metal chloride catalysts is proposed.

Silva et al [33] have evaluated catalytic activity of gel and macroreticular ion-exchange resins (Lewatit and Amberlyst-15) for the reaction of benzene with benzyl alcohol and benzyl chloride at 80°C in the liquid phase. With benzyl chloride, the monobenzylation product, diphenylmethane, was obtained in low yield, both with the gel and the macroreticular resins. Better results were obtained with benzyl alcohol as benzylation agent and the most active resin was Amberlyst-15, the conversion of benzyl alcohol being proportional to the concentration of acid sites on the resin.

Mantri et al [34] have investigated Friedel–Crafts alkylation of aromatics with benzyl alcohol as alkylating agent over rare earth metal triflates, Sc(OTf)3, $Hf(OTf)_4$, $La(OTf)_3$, and $Yb(OTf)_3$ supported on MCM-41. The catalytic activity of triflates, was enhanced after being loaded onto MCM-41 due to increased dispersion, and gave the benzylated product in high yield. The rate of the benzylation of benzene was accelerated by electron donating groups and retarded by electron withdrawing groups.

Narender et al [35] have studied benzylation of benzene and toluene with benzyl alcohol over a series of zeolites and metal modified β zeolites. A reaction mechanism has been proposed for formation of diphenylmethane and benzyl ether. Benzyl ether formation from benzyl alcohol is explained on the basis of the intermolecular reaction pathway, involving Bronsted acid sites of the zeolite.

Bachari et al [36] have reported benzylation of benzene by benzyl chloride to diphenylmethane over $FeCl_3$, $InCl_3$, $GaCl_3$, $ZnCl_2$, $CuCl_2$ and $NiCl_2$ supported on mesoporous SBA-15. Further it is claimed that the redox property due to the impregnation of the SBA-15 by transition metal chloride, seems to play a very important role in the benzene benzylation process.

Zhou et al [37] have reported silica-supported polytrifluoromethane sulfosiloxane (SiO_2–Si–SCF_3) catalyzed Friedel–Crafts benzylation of benzene and substituted benzenes. It was found that SiO_2–Si–SCF_3 could catalyze Friedel–Crafts benzylation of benzene and substituted benzenes with benzyl alcohol under relatively mild experimental conditions. Reactions are very clean and water is the only by-product of the reaction. The yields amounted to 97–100%.

Vinu et al [38] have reported benzylation of benzene and other aromatics by benzyl chloride over mesoporous Al SBA-15 catalysts.

In the present endeavour, we report the potential use of TMA salts, the M(IV) phosphates and tungstates as solid acid catalysts by studying Friedel crafts acylation of anisole and veratrole and alkylation of toluene using acetyl chloride and benzyl chloride as acylating and alkylating agents respectively as model reactions to synthesise methoxy acetophenone (4 MA) ,3,4 dimethoxy acetophenone (3,4DMA) and p-benzyl toluene (PBT) respectively under solvent free conditions. Further, in order to see the effect of crystallinity on the catalytic performance, crystalline M(IV)phosphates have been explored for Friedel Crafts acylation and alkylation reactions. The catalytic activity of amorphous and crystalline materials as well as phosphates and tungstates of TMA salts have been compared and correlated with surface properties of the materials.

5.3 EXPERIMENTAL

Catalyst Synthesis and Characterisation

Discussed in Chapter II.

Materials

Anisole, veratrole, benzyl chloride and toluene were procured from S.D. Fine chemicals.

Experimental setup:

The Friedel Crafts acylation and alkylation reactions were carried out in a two necked 50 ml round bottomed flask equipped with a magnetic stirrer under heating in an oil bath. In a typical set up, a mixture of anisole or veratrole (10 mmol) and acetyl chloride (15 mmol) for acylation and toluene (10 mmol) and benzyl chloride (15 mmol) for alkylation, along with the catalyst (0.15 g) were stirred in a round bottomed flask at 110°C for three hours. In all the reactions the substrates were used as solvents and hence the reaction temperature was kept at 110 °C (reflux temparature) for all the studies. Reaction parameters, mole ratio of reactants, time and catalyst amount have been optimized using SnP(Table 4.1). Using these optimized conditions the activity of the other catalysts have been explored (Table 4.2). The reactions were monitored by GC. After completion of reaction, the catalyst was separated by decantation, and reaction mixture was distilled to obtain the products 4 MA, 3,4DMA and PBT, the boiling points being ~273°C, 286°C and 300°C respectively. The catalyst was regenerated by refluxing in ethanol followed by drying and acid treated as described in Chapter 2, section 2.5.

5.4 RESULTS AND DISCUSSION

Catalytic activity of M (IV) Phosphates and Tungstates for Friedel Crafts acylation and alkylation have been presented in Table 4.1(optimization using SnP) and Table 4.2. Friedel crafts acylation of anisole and veratrole with acetyl chloride, gave selectively 4MA and 3,4 DMA respectively. Alkylation of toluene with benzyl chloride gave selectively PBT. It is observed that yield increases with reaction time until an equilibrium is reached within 3h. For the same reaction time, yield increases with increasing catalyst amount, since the number of active sites per gm of substrate increases.

It has been reported earlier that there is no significant effect of solvents in the acylation of anisole and veratrole and best results were obtained when aromatic ethers were used as self solvents [16]. In the present study therefore substrates have been used as solvents.

When comparison is made between anisole and veratrole the product yield and turn over number(TON) are higher for veratrole. The rate-determining step of the Friedel-Crafts acylation is the formation of the electrophilic intermediate. The presence of an additional electron donating methoxy group in veratrole makes it a more active compound for electrophilic substitution of acyl group in the para position than anisole due to an increased electron density at para position and resultant increased susceptibility for attack by the electrophile.

The proposed mechanism for the acylation and alkylation reaction on solid acid catalyst implies the formation of an adsorbed species by interaction of the acylating/alkylating agent with a Brønsted acid site [29,30](acyl/alkyl cation). The Bronsted acid site generates an acyl carbonium ion, which in turn affects the electrophilic substitution. A higher density of acid sites increases number of acyl cations enhancing activity of the reaction.

Based on the published literature, wherein it is reported that the mechanism for Friedel Crafts acylation and alkylation over solid acid catalysts is the same as homogeneous lewis acid caytalysts,[24,29,30] we propose the following mechanism for Friedel Crafts acylation and alkylation of aromatic compounds using TMA salts as solid acid catalyst.(Figure 7 & 8)

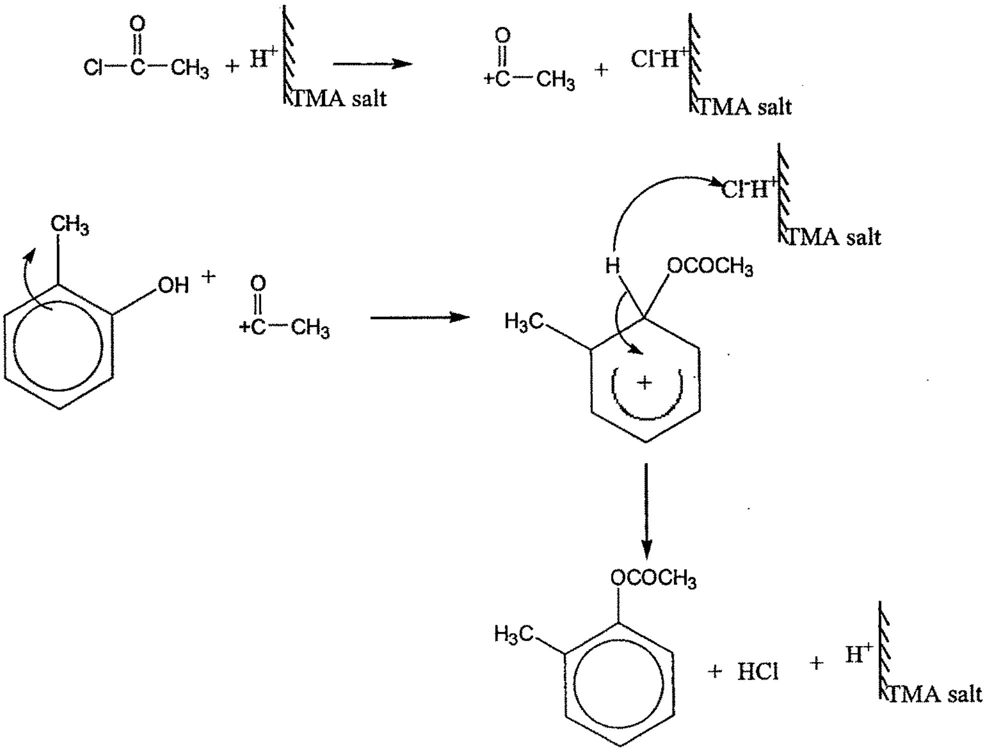

Figure 7 Reaction mechanism of Friedel Crafts acylation of anisole using TMA salts as solid acid catalyst

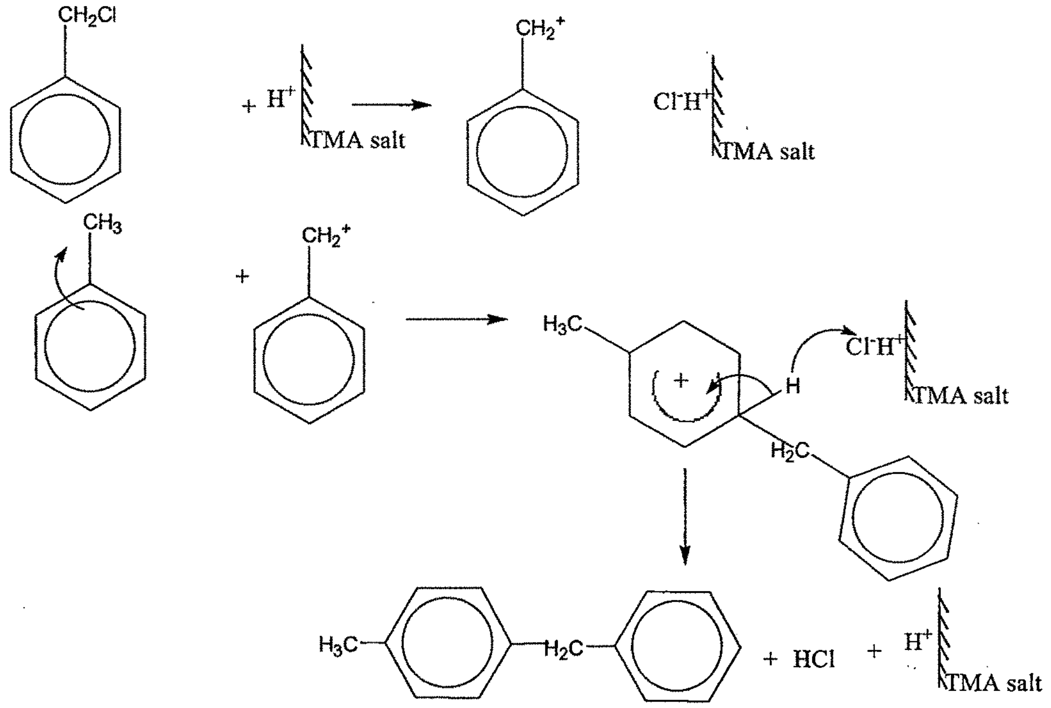

Figure 8 Reaction mechanism of Friedel Crafts alkylation of toluene using TMA salts as solid acid catalyst

Catalytic activity/TON is a function of number as well as type of acid sites present on the catalyst surface. The acylation and alkylation reactions are thus driven by the surface acidity of the catalyst and amongst amorphous M (IV) Phosphates, though surface acidity values are lower for TiP and SnP compared to ZrP, the catalytic activity is slightly higher. This could be explained on the basis of NH_3TPD patterns which indicate less acidity for TiP and SnP, but higher desorption temperature, indicating presence of very strong acid sites. Further, acidity of a cation and hence surface acidity, depends on the size and charge of the cation. In the materials under study Zr, Ti and Sn all being tetravalent as well as bearing a common anion phosphate/tungstate the size of the cation [Ti^{+4}(0.74 A°) ,Zr^{+4}(0.86 A°), Sn^{+4}(0.83 A°)] seems to play a dominant role[39]. In case of Ti^{+4} the ionic radius is small and hence the positive charge is concentrated in a small area, increasing the tendency to polarize the O–H bond in the hydroxyl group bonded to it.

Amongst tungstates, catalytic activity is highest for TiW compared to SnW and ZrW. This could be explained to be due to lower surface acidity and surface area values of SnW and ZrW. TiW posseses both a higher surface area as well as strong acid sites.

In case of crystalline materials, though surface area/surface acidity is less there is no decrease in the catalytic activity. This can be attributed to the fact that though the number of surface acid sites are less for crystalline materials, the desorption temperatures are higher indicating the presence of strong acidity/ active sites enhancing the catalytic activity. Amongst the crystalline M (IV) phosphates SnPcry exhibits the lowest acidity. However, the desorption temperature is higher indicating strong acid sites.

It is observed that the colour of the catalyst changes during the course of the reaction giving an indication that during the course of the reaction the reacting molecules come onto the surface of the catalyst. Some of them enter into reaction to give the product while a few of them remain adsorbed on the surface. The fact that the reactant molecules are weakly adsorbed is evident from the catalyst regaining its original colour, when treated with ethanol. The possibility of molecules entering interstices cannot be ruled out. This is observed from the fact that the yields go down by 10% after every regeneration. The deactivation of the catalyst might be due to the strongly adsorbed acetic acid and the product on the acid sites. It is known that acetic acid is generally strongly absorbed on the acidic sites. The study shows that M(IV) phosphates and tungstates are insoluble during the reaction, are recoverable by simple filtration, and can be reused without significant loss in catalytic activity.

Table 5.1 Optimisation of reaction conditions for Friedel Crafts acylation and alkylation using SnP:

Substrates (Mole ratio)	A	B	% Yield
A+AC(1:1)	0.05	2	17.2
A+AC (1:1)	0.10	2	23.1
A+AC (1:1)	0.15	2	32.4
A+AC (1:1.5)	0.15	2	39.8
A+AC (1:1.5)	0.15	3	40.1
A+AC (1:1.5)	0.15	4	40.2

A = anisole, AC=acetyl chloride ,

A=Catalyst amount (gm),B=Reaction time(hours),

Table 5.2 Friedel Crafts acylation and alkylation using TMA salts

Substrates (Mole ratio)	**Catalyst**	**% Yield**	**TON**
A+AC (1:1.5)	ZrP	39.4	4.90
A+AC (1:1.5)	TiP	43.7	5.44
A+AC (1:1)	SnW	34.0	4.23
A+AC (1:1)	ZrW	1.0	0.12
A+AC (1:1)	TiW	33.9	4.22
A+AC (1:1.5)	SnPcry	40.0	4.98
V+AC (1:1.5)	ZrPcry	37.3	5.39
V+AC (1:1.5)	TiPcry	42.1	6.08
V+AC (1:1.5)	SnP	58.9	8.51
V+AC (1:1.5)	ZrP	47.7	6.89
V+AC (1:1.5)	TiP	53.5	7.73
V+AC (1:1.5)	SnW	31.7	4.58
V+AC (1:1.5)	ZrW	21.5	3.11
V+AC (1:1.5)	TiW	19.3	2.79
V+AC (1:1.5)	SnPcry	56.0	8.09
V+AC (1:1.5)	ZrPcry	45.0	6.50
V+AC (1:1.5)	TiPcry	53.1	7.67
T+BC (1:1.5)	SnP	56.0	8.17
T+BC (1:1.5)	ZrP	49.3	7.19
T+BC (1:1.5)	TiP	57.0	8.31
T+BC (1:1.5)	SnW	50.0	7.29
T+BC (1:1.5)	ZrW	44.7	6.52
T+BC (1:1.5)	TiW	50.0	7.29
T+BC (1:1.5)	SnPcry	56.0	8.17
T+BC (1:1.5)	ZrPcry	49.0	7.14
T+BC (1:1.5)	TiPcry	56.8	8.28

A= anisole, AC=acetyl chloride, V= veratrole, T= toluene, BC=benzyl chloride
Catalyst amount = 0.15g, Reaction time=3 h, Reaction temperature=110°C

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M(IV) PHOSPHATES
AND
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