Single pot benzylation of *o*-xylene with benzyl chloride and benzyl alcohol over pillared montmorillonites

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Improvement of product selectivity is a major concern of the day. Presence of a coreactant can alter the rate as well as product selectivity of many key reactions like Friedel-Crafts benzylation. Single pot benzylation of o-xylene with benzyl chloride and benzyl alcohol was studied over transition metal exchanged pillared clay catalysts. Complete conversion of benzyl alcohol occured within one hour with 100% monoalkylated product selectivity. The reaction of o-xylene with benzyl alcohol was found to proceed fast in presence of benzyl chloride in single pot, than when present alone as the benzylating species. This enhancement occurs at the expense of no reaction of benzyl chloride, which when present alone reacts faster than benzyl alcohol. Existence of a second transition metal exchanged between the pillars increased the rate of the reaction. A detailed investigation of the reaction variables suggested preferential adsorption of benzyl alcohol to catalyst active sites as the reason.

Keywords: Friedel-Crafts benzylation, single pot benzylation, pillared clays.

INTRODUCTION

The development of cutting edge and cleaner processes is of topical interest to meet global competition and conform to stringent environmental specifications. When more than one reaction occurs in a single pot, the relative rates as well as product selectivities for the reactions can vary, than when they occur seperately. Potential applications of such reversals in reaction rates as well as product selectivities are numerous. Very high selectivities could be achieved without time consuming, costly and wasteful separations. Laszlo et.al documented first such a switch in relative reactivities when a substrate is reacted alone or in tandem with a co-reactant[1]. The reversal in reaction rate was attributed to the pore structural effects that appeared in microreactors capable of dynamic sieving[2]. However, there are not much reports devoted to this aspect in the recent literature.

Intercalation of clays via exchange of cations located in their interlayer space with hydroxy metal cations, followed by thermal treatment is an effective approach to obtain catalysts, catalyst supports, sensors and adsorbents. The materials thus prepared are referred to as pillar inter-layered clays (PILCs). By varying the size, charge and shape of the entering ions, a homogenous network of micropores can be obtained with pore openings ranging in size from 16–30 Å. Pillared clays have been the subject of recurrent research owing to interesting properties like high surface area, regular porous structure, appreciable thermal stability and substantial Lewis and Brönsted acidity[3–6]. Insertion of a second metal in the exchanged form substantially improves the textural, surface and catalytic properties of pillared clays[7, 8].

Friedel-Crafts alkylation is an important tool for introducing alkyl substituents into the aromatic ring system[9–12]. Benzylation of *o*-xylene is an important reaction as the products of the reaction viz.; dimethyldiphenylmethanes (DMDPMs) are significant synthetic intermediates used as heat transfer fluids, aromatic solvents, fragrances and monomers for polycarbonate resins[13]. Different benzylating agents including benzyl chloride and benzyl alcohol can be used for the reaction. Generally benzyl chloride brings about the reaction to completion much faster than benzyl alcohol when used alone. Nevertheless, when a combination of the two reagents is used, benzyl alcohol reacts first and benzyl chloride starts reacting only after the complete consumption of the alcohol. Also presence of benzyl chloride increases the reaction rate than when benzyl alcohol is present alone. The reaction has been studied extensively using iron and mixed iron aluminium pillared montmorillonites exchanged with transition metals of the first series.

EXPERIMENTAL

Aluminium(II) nitrate, iron(III) nitrate, manganese(II) nitrate, cobalt(II) nitrate, nickel(II) nitrate, copper(II) nitrate, zinc(II) nitrate, sodium carbonate and ammonium metavanadate supplied by Merck, India was used. Montmorillonite KSF was supplied by Aldrich Chemicals. Iron pillared montmorillonite was synthesised by partial hydrolysis method and the experimental procedure has been described in our previous publications[14–16]. The prepared systems were notated as X/Z PM where X is the exchanged metal and Z is pillared metal.

The single pot benzylation of *o*-xylene with a combination of benzyl alcohol and benzyl chloride was carried out in a closed 50 mL round bottomed glass flask equipped with reflux condenser and magnetic stirrer. In a typical run, appropriate amounts of *o*-xylene, benzyl chloride, benzyl alcohol and catalyst were allowed to react at specified temperatures under magnetic stirring. Reaction mixture was withdrawn at specific intervals and was analysed using Chemito 8610 Gas Chromatograph equipped with Flame Ionisation Detector and SE -30 coloumn.

RESULTS AND DISCUSSION

Physicochemical characterisation

The pillared clay catalysts for the present study have been well characterised with various physicochemical techniques and have been reported elsewhere[14–16]. EDX

analysis of the prepared samples showed that increase in amount of pillared metal is at the expense of exchangeable cations. 1–3% of transition metals were incorporated on exchange. Surface area and pore volume increased substantially upon pillaring. 60–70% of the total surface area can be attributed to micropores. Transition metal exchange decreased the surface area, especially the external surface area. X-ray diffraction peaks suggested shifting of 2θ values implying expansion of clay layer during pillaring process. Presence of Fe substituted Al_{13} like polymers were detected in the mixed pillared system. Insertion of the second metal after the formation of stable pillars did not destabilise the porous network. IR spectra of the various samples could be assigned properly. The vibrations on the framework region did not change on pillaring, indicating the structural integrity of the clay layers. For iron pillared systems, ^{27}Al NMR peaks were broader due to relaxation effects of the paramagnetic centres. The structure of mixed pillared systems was similar to Al polymeric species. Incorporation of transition metals did not affect the structural stability of the layers and pillars. ^{29}Si NMR spectra revealed that majority of the silicon tetrahedra is linked to 3 Si atoms and one Al atom. The distribution of silicon tetrahedra into various environments was not affected by pillaring. The strain in local environment of the Si atoms was proportional to the size of intercalated species. The thermal stability of the pillared clays was in the order FeAl PM > Fe PM. UV- DRS supported the presence of the Keggin cation in mixed pillared systems. The spectrum showed a band that could be assigned to the polyoxoiron complexes. Surface acidity as determined by cumene cracking test reaction shows a greater percentage of Lewis acid sites on the exchanged systems.

Single pot benzylation of *o*-xylene

Catalytic activity of various transition metal doped pillared clays were tested for single pot benzylation of *o*-xylene using benzyl chloride and benzyl alcohol under optimised conditions. Conversion of benzyl alcohol takes place at faster rate even at low temperatures in presence of benzyl chloride, than when present alone. Fe PM shows good activity towards the reaction with almost equal selectivity towards isomeric monoalkylated products (Table 1). Absence of polyalkylated products and dibenzyl ether are commendable observations for

the reaction. When reactants are constrained to diffuse in a porous solid, which has a layered structure like clays, their encounter frequencies increase. Also, organic molecules congregate in the compartment like structures of the clay matrix. Pores locally increase the interaction between reactants and hence the increase in reaction rate. Selective formation of monoalkylated products can be assigned to the shape selective nature of the pillared clay, restricting further alkylation of the product. Transition metal incorporation improves the catalytic activity greatly (almost fivefold enhancement), the effect being minimum for vanadium exchanged species. From the table it is evident that the ascend in activity comes mainly from increase in *p*- product concentration.

The scheme of the Friedel-Crafts benzylation of *o*-xylene is given in Figure 2. The generally accepted mechanism for this reaction is that the benzyl carbocation formed first by the interaction with catalyst surface attacks the unadsorbed substrate molecules, forming product. Owing to steric factors, 3,4-DMDPM formation is thus much easier in Friedel-Crafts alkylations. Hence, increased activity of the catalyst results in enhanced 3,4-DMDPM concentrations. In the mixed pillared series, FeAl PM shows a conversion of 30.2% with almost equal selectivity for the isomeric monobenzylated products. Incorporation of transition metals increase the catalytic activity as well as 3,4-DMDPM selectivity. Thus, V/FeAl PM and Zn/FeAl PM act as the best catalysts in the series with cent percent conversion of benzyl alcohol and predominant selectivity towards 3,4-DMDPM. 2,3-DMDPM is produced by the adsorption of substrate to catalyst acid site[17]. As time goes by, as Friedel-Crafts reactions generally prefers, 3,4-DMDPM concentration increases.

Structural stabilty of the catalysts

Deteriorations can occur in catalyst structure due to several reasons like thermal sintering, pore blocking due to coke deposition, poisoning by products and phase changes of active phase. The stability of prepared catalysts was checked against metal leaching as well as moisture adsorption by taking FeAl PM as reference at standard conditions. The reference catalyst contains iron in the pillars that has every chance of combining with Cl- ions from benzyl chloride forming $FeCl_3$, the traditional Friedel-Crafts catalyst. Thus, there is a chance of the reaction becoming partly homogeneous in natu-

Table 1. Activity of the prepared systems towards single pot benzylation of *o*-xylene

Catalyst	Conversion [%]	Selectivity [%][a]	
		2,3-DMDPM	3,4-DMDPM
V/Fe PM	58.9 (27.8)	39.2 (24.3)	60.8 (75.7)
Mn/Fe PM	71.4 (38.5)	25.1 (27.1)	74.9 (72.9)
Ni/Fe PM	98.4 (42.9)	1.6 (3.8)	98.4 (96.2)
Co/Fe PM	96.6 (41.7)	2.9 (17.7)	97.1 (82.3)
Cu/Fe PM	71.9 (33.9)	16.0 (15.6)	84.0 (84.4)
Zn/Fe PM	100 (51.2)	2.5 (3.7)	97.5 (96.3)
Fe PM	16.5 (10.5)	56.2 (44.7)	43.4 (55.3)
V/FeAl PM	100 (58.9)	4.7 (14.3)	95.3 (85.7)
Mn/FeAl PM	48.4 (24.9)	28.9 (17.1)	71.1 (72.9)
Co/FeAl PM	59.8 (29.1)	22.3 (23.8)	77.7 (76.2)
Ni/FeAl PM	42.4 (26.2)	24.4 (17.7)	75.6 (82.3)
Cu/FeAl PM	47.0 (25.3)	32.0 (35.6)	68.0 (64.4)
Zn/FeAl PM	100 (56.2)	3.7 (3.7)	96.3 (96.3)
FeAl PM	30.2 (10.1)	56.8 (44.7)	43.2 (55.3)

o-xylene/BA – 10, temperature – 120°C, time – 30 minutes, catalyst/BA – 0.0859, BA/BC – 2,
[a] Selectivities are expressed in weight % values in parantheses give the activities and selectivities in the absence of benzyl chloride.

re[18]. The possibility of leached out iron was checked by two methods 1) by continuing the reaction for further 30 minutes after filtering off the catalyst at 30 minutes 2) testing the presence of iron in the reaction mixture with thiocyanate ions. On continuing the reaction for further 30 minutes after filtering off the catalyst, almost same activity and product selectivity pattern is noticed (Table 2). Addition of thiocyanate ions to the reaction mixture gives no blood red colour, characteristic of Fe^{3+} ions. Thus, leaching of iron from the catalyst does not occur and a completely heterogeneous mechanism can be envisaged for the reaction. Further, this gives proof to the preferential adsorption mechanism of benzyl alcohol to catalyst active sites. Benzyl chloride, preferentially adsorbed to the catalyst active site, would have leached out iron from the surface, thus increasing the reaction rate after filtering off the catalyst.

Table 2. Stability of the prepared systems towards single pot benzylation of *o*-xylene

Time [minutes]	Conversion [%]	Selectivity [%]^a	
		2,3-DMDPM	3,4-DMDPM
30	62.5	72.9	27.1
30*	63.9	71.5	28.5

Catalyst – FeAl PM, *o*-xylene/BA – 10, temperature – 130°C, time – 30 minutes, catalyst/BA – 0.0859, BA/BC – 2 (*after filtering off the catalyst),
^{a} Selectivities are expressed in weight %.

Conventional Friedel-Crafts catalysts are extremely moisture sensitive. Moisture sensitivity of the catalysts was checked by saturating the catalyst and substrate with moisture in a dessicator and conducting the reaction as usual. The observations are presented in Figure 1. Presence of benzyl chloride makes the catalyst indifferent to moisture. Percentage conversion does not alter much but product selectivity changes. Initial formation of 3,4-DMDPM increases in presence of moisture. However, 3,4-DMDPM selectivity at complete conversion of benzyl alcohol is much low in presence of moisture, than in its absence. The mo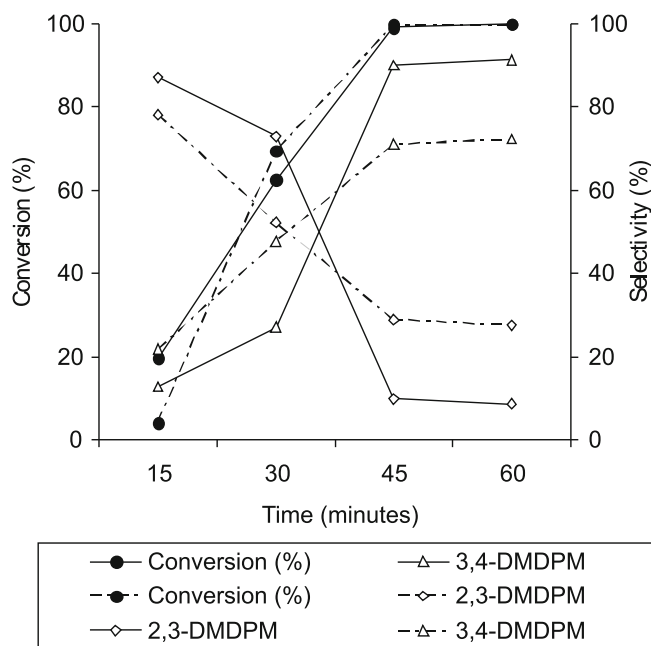isture sensitivity studies give further confirmation to preferential adsorption of benzyl alcohol to catalyst active sites. Moisture, which gets adsorbed to catalyst active site is displaced by benzyl alcohol and benzyl chloride. In the absence of benzyl chloride, benzyl alcohol alone is present in the catalyst active sites and hence the increased activity in the absence of benzyl chloride. Friedel-Crafts alkylations generally prefer the *p*- product considering the steric factors. 2,3-DMDPM formation occurs by a different mechanism. *O*-xylene has two electron releasing groups and this causes an accumulation of a slight negative charge in the ring. Thus, *o*-xylene gets adsorbed to acidic sites on the catalyst surface, preferably at *para* position, considering steric factors. The *p*- position being blocked, the benzyl cation attacks the *o*-position[17]. Moisture present in active sites prevent the interaction of substrate molecules with catalyst and hence increased 3,4-DMDPM selectivity at initial stages. As time goes by, substrate molecules displace the water molecules present in active sites and hence the better selectivity to 2,3-DMDPM.

Effect of reaction variables

Important conclusions on reaction mechanism can be obtained by a systematic study of various reaction variables. A thorough scrutiny of parameters like temperature, reactant molar ratio, catalyst concentration, benzylating agent ratio etc was undertaken with FeAl PM as the reference catalyst (Table 3). Increase in reaction temperature has a boosting effect on catalytic efficiency. Complete conversion of benzyl alcohol is obtained in 30 minutes on gentle reflux. The 3,4-DMDPM selectivity decreases with increase in temperature. The linear increase in catalytic activity with temperature can be assigned to speedy desorption of the benzylated product from the catalyst surface at high temperatures. This facilitates further adsorption of reactant molecules, resulting in enhanced conversion of benzyl alcohol. The increase in activity can also be ascribed to increase in intrinsic activity of the bare catalyst surface. 2,3-DMDPM formation occurs by the adsorption of both substrate and benzyl alcohol to the catalyst active site[17]. This rate will be increased at high temperatures due to speedy desorption of product molecules and hence increased selectivity to *o*-DMDPM.

Reaction rate increases linearly with time ascertaining the heterogeneity of the reaction. The 3,4-DMDPM selectivity though negligible initially, picks up with time. It seems that 3,4-DMDPM alone is formed at longer duration of run. The adsorption and desorption of reactants and products occur fast over the clay catalyst and hence the easy completion of reaction.
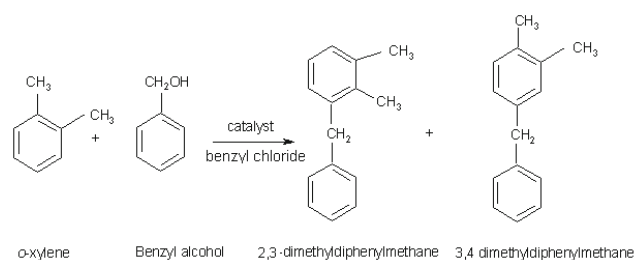

Figure 1. Effect of moisture on activity and product selectivity for single pot benzylation of *o*-xylene

Figure 2. Sceme of the reaction

Table 3. Effect of reaction variables on single pot benzylation of *o*-xylene with benzyl alcohol and benzyl chloride

Reaction variable		Conversion [%]	Selectivity [%][a]	
			2,3-DMDPM	3,4-DMDPM
Temperature [°C]	110	10.2	34.5	65.5
	120	30.2	56.8	43.2
	130	62.5	72.9	27.1
	gentle reflux	100	85.6	14.4
Time [minutes]	15	19.6	87.2	12.8
	30	62.5	72.9	27.1
	45	99.2	9.9	90.1
	60	100	8.6	91.4
Benzyl chloride/ benzyl alcohol	1/6	12.1	82.5	17.5
	2/6	38.2	77.4	22.6
	3/6	62.5	72.9	27.1
	4/6	77.5	60.5	39.5
	5/6	100	54.5	45.5
o-xylene/benzyl alcohol	5	39.8	84.1	15.9
	7.5	60.4	70.1	29.9
	10	62.5	72.9	27.1
	12.5	45.6	79.5	20.5
	15	12.5	90.4	9.6

Presence of benzyl chloride proves crucial in benzylation of aromatic species with benzyl alcohol. Hence, influence of the ratio of the two reagents was checked at standard conditions. From the Table 3, it can be summarised that catalytic activity increases with benzyl chloride concentration. Presence of the co reactant favours 3,4-DMDPM formation. Monoalkylated product selectivity is not altered even at high concentrations of benzyl chloride. Presence of benzyl chloride and benzyl alcohol imposes competition among the two reagents and benzyl alcohol gets preferentially adsorbed on the catalyst surface. Increase in the amount of benzyl chloride thus increases competition and hence improved activities. Presence of the co reactant favours 3,4-DMDPM formation since 3,4-DMDPM is formed by the attack of benzyl carbocation on unadsorbed *o*-xylene where as 2,3-DMDPM is obtained by the reaction of adsorbed *o*-xylene on the catalyst active site[17]. At higher concentrations of benzyl chloride the adsorption of substrate to catalyst active site is not easy owing to steric reasons. This fact gives proof to the preferential adsorption mechanism of benzyl alcohol. Monoalkylated product selectivity is not altered even at high concentrations of benzyl chloride.

The effect of substrate to benzylating agent ratio is also given in Table 3. Catalytic activity first increases and after an optimum ratio of 10, it decreases. However, selectivity pattern does not show much variations with change in concentration of *o*-xylene. Since *o*-xylene is taken in excess, the reaction is supposed to follow pseudo unimolecular mechanism and hence the equivalent relation with benzyl alcohol concentration. Thus, the catalyst is very efficient for the creation of benzyl carbocations even at high concentrations of reagent. Higher reactant molar ratios result in insufficient interaction with catalyst surface for the formation of carbocations, consequently reducing catalytic activity.

Mechanism of the reaction

Yadav et.al formulated a mechanism to account for the inversion phenomenon observed in single pot alkylation of toluene with benzyl chloride and benzyl alcohol[19]. It was proposed that benzyl alcohol gets preferentially adsorbed on the acid site of catalyst and forms a benzyloxonium species. The interaction of the lone pair of electrons associated with chlorine in benzyl chloride then forms a polar complex with the species leading to the formation of a super electrophile. This species then affects the alkylation of toluene at a much faster rate than when benzyl alcohol is present alone. A similar mechanism can explain the observed facts in the present study also. In the single pot alkylation of *o*-xylene with benzyl alcohol and benzyl chloride, competition occurs between the two reagents. Benzyl alcohol gets the upper hand and gets adsorbed in the catalyst active sites. Benzyl carbocations are then formed according to the usual Friedel-Crafts mechanism. The substrate, due to the presence of two electron releasing methyl groups also gets attached to the catalyst surface. Alkylation occurs preferentially on *o*- position considering steric factors and hence increased 3,4-DMDPM concentrations at initial stages.

CONCLUSION

The various points that can be summarised from the foregoing discussion are

– Single pot benzylation of *o*-xylene with benzyl chloride and benzyl alcohol occurs efficiently over pillared clay catalysts with cent percent monoalkylated product selectivity. This can be attributed to the shape selective nature of the pillared clay.

– Metal leaching and moisture adsorption studies confirm the preferential adsorption of benzyl alcohol to catalyst active sites. The prepared catalysts are not moisture sensitive. The reaction occurs by a truly heterogeneous mechanism.

– Reaction variables like time, temperature, substrate to benzyl alcohol ratio, catalyst concentration and ratio of the two benzylating agents had profound influence on catalytic activity. The observed activities and product selectivity pattern can be well explained in terms of preferential adsorption mechanism of benzyl alcohol.

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