Activity of amorphous V-AlPO$_4$ and Co-AlPO$_4$ in the selective synthesis of *N*-monoalkylated aniline *via* alkylation of aniline with methanol or dimethyl carbonate

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The vapour phase catalytic alkylation of aniline with methanol or dimethyl carbonate (DMC) on amorphous AlPO$_4$ and M-AlPO$_4$ (M = Cu, Ni, Fe, Co and V) has been studied. V-AlPO$_4$ and Co-AlPO$_4$ showed high selectivity towards *N*-monomethylation of aniline. Further studies on the alkylation reactions have been carried out using AlPO$_4$ and M-AlPO$_4$ (M = V and Co) as catalysts at different temperatures and molar ratio of aniline to methanol or DMC. V-AlPO$_4$ is found to show 100% selectivity for *N*-monomethylation of aniline, irrespective of the temperature or the molar ratio of the reactants. On the other hand, Co-AlPO$_4$ shows 100% selectivity for *N*-monomethylated product only when the aniline-to-methanol (or DMC) molar ratio is 2:1. Aniline conversion towards *N*-methylaniline(NMA) was found to be 39%. DMC has been found to be a better methylating agent than methanol with respect to the percentage conversion of aniline to *N*-methylaniline.

Introduction

In the fine chemical, pharmaceutical, drug and dye industries the synthesis of organic intermediates is a high activity research area. Friedel–Crafts (FC) alkylation is one of the well-established reactions in ganic synthesis. It is a well-known fact that Lewis and Brønsted acids catalyse FC reactions. Lewis acids such as AlCl$_3$, TiCl$_4$ and BF$_3$ have been extensively used as catalysts in alkylation reactions. A survey of the literature on heterogeneous catalysis research in the area of alkylation reactions clearly indicated that several attempts have been made to discover the utility of solid acids such as oxides, mixed oxides, clays and zeolites as catalysts in alkylation reactions.[1–9] Such studies have established that solid acids can successfully replace the traditional and hazardous Lewis acid catalysts in acid-catalysed organic synthesis reactions and at the same time these catalysts can be suitably modified to increase the selectivity towards a particular product.

Alkylation of aniline is an important reaction in organic synthesis. This reaction form products such as *N*-alkylated and/or *C*-alkylated anilines that are used as intermediates or additives in dyes, synthetic rubber, herbicides and pharmaceuticals. *N*-Alkylated anilines are synthesised *via* alkylation of anilines. Different alcohols and dimethyl cabonate are used as alkylating agents under different reaction conditions.[10,11]

Several reports have appeared on the alkylation of aniline using methanol or DMC as alkylating agents over various solid acid-base catalysts. It is established that formation of *N*- and/or *C*-alkylated anilines depends not only on the reaction conditions but also on the catalysts used. Woo *et al.*,[12] using metallosilicates of the pentasil family, suggested that weak to moderate and strong acid sites are responsible for *N*-alkylated and *C*-alkylated products, respectively. As for as aniline alkylation with DMC is concerned Sue and Barthomeuf[13] reported 100% selectivity towards *N*-mono- and dialkylation (NMA/NNDMA) in the vapour phase reaction of aniline over KX and KY zeolites as basic catalysts. However, only 10–15% aniline conversion was observed. Silica-supported vanadia catalysts also were found to exhibit good selectivity towards NMA formation but the conversion of aniline still remained low.[11] Campelo *et al.*[14,15] reported 100% selectivity for *N*-alkylation (NMA + NNDMA) in this reaction over AlPO$_4$-based catalysts.

In contrast, we recently observed that in liquid phase alkylation of aniline with DMC over amorphous AlPO$_4$ catalysts incorporating cobalt or vanadium ions, biphenyl urea was obtained as one of the major products.[16] This finding indicates that amorphous M-AlPO$_4$ as catalyst has a much broader scope than the crystalline counterparts. This observation prompted us to make a systematic investigation of the effect of the transition metal ion in vapour phase alkylation of aniline under different reaction conditions.

The main aims of this paper are: (i) preparation of transition metal ion containing amorphous aluminophosphates; (ii) determine the catalytic activity of the aluminophosphates in the reaction between aniline and MeOH or DMC in the vapour phase; (iii) study the effect of reaction parameters such as catalyst bed temperature, molar ratio of the reactants and the nature of the alkylating agent on the nature of the product.

Experimental

Catalyst preparation and characterisation

Amorphous aluminophosphates and M-aluminophosphates (M = V, Fe, Co, Ni and Cu) were prepared by the precipitation method.[17] In a typical preparation aluminium nitrate, metal acetate and phosphoric acid were dissolved in 500 cm^3 of water in a 0.95:0.05:1 molar ratio of aluminium, metal and phosphorous. The solution was heated to 80 °C. To this hot solution 28% aqueous ammonia was added dropwise until the pH of the solution was 6–7.5. The precipitate, after washing with deionised water, was initially dried overnight at 120 °C and finally calcined at 550 °C.

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All the catalysts were analysed for their chemical composition following standard wet analytical and spectroscopic methods.[18] X-Ray diffraction (XRD) patterns of the calcined powders were recorded on a Philips PW 1349/30 diffractometer. BET surface area of the samples were measured using a NOVA-1000 (ver: 3.7). Total surface acidity was estimated by the *n*-butylamine back-titration method using dry benzene as the solvent[19,20] as well as by TPD of ammonia. Thermal stability of a few catalysts was investigated by recording their TGA and DTA patterns.

Catalytic activity studies

The catalytic activity of all the samples in alkylation of aniline with methanol or DMC was investigated in the vapour phase. Vapour phase reactions were conducted in a continuous downflow fixed-bed glass reactor under ambient pressure. For each reaction 500 mg of freshly calcined catalyst was used. The effect of change in the reaction parameters such as the catalyst bed temperature, molar ratio of the reactants or duration of the reaction on the product distribution was investigated.

The reaction products were analysed on a gas chromatograph with FID detector using a 2 m SS column packed with 10% Apeozonal and 10% KOH on chromosorb. The products were identified using authentic samples of the expected products. The conversions and selectivity were calculated with respect to aniline using the following expressions:[21]

$$X_{\mathrm{A}}(\text{mol }\%) = [1 - (\text{mole of aniline in the product per mole of aniline in the feed})] \times 100$$

$$S(\text{mol }\%) = [\text{weight of the aromatic product per mole of aniline reacted}] \times 100$$

Results and discussion

Catalyst properties

The catalysts used and their physico-chemical properties such as total surface acidity, determined by *n*-butylamine titration and TPD of NH_3 methods, BET surface area, percentage of metal and the colour of the as-synthesised samples are listed in Table 1. The total surface acidity and BET surface area are quite in agreement with what is reported in the literature for similar solid acids.[17] Both the *n*-butylamine back-titration method and TPD of NH_3 give the total surface acidity of solids. The acidity values obtained by these methods are not exactly the same due to the difference in the nature of the interaction of these basic molecules and the surface acid sites. Moreover, the variation in the acidity of $AlPO_4$ by the incorporation of transition metal ions cannot be clearly explained with respect to the values obtained by the *n*-butylamine method. However, the acidity values determined by TPD indicate an increase in the surface acidity of M-$AlPO_4$ with respect to plain $AlPO_4$. It is found from the TPD studies that all the adsorbed ammonia was desorbed when the catalysts were heated in the temperature range of 250–300 °C. This indicates that transition metal ion incorporation through co-precipitation with $AlPO_4$ enhances the density of moderate to weak acid sites. Strong acid sites of the catalysts are known to retain adsorbed ammonia up to 550 °C and above. Analysis of catalysts for metal ion content showed that the later was present at about 5%. The absence of any peaks in the XRD pattern of the catalyst samples indicates that they are all amorphous. Thermal analysis (TGA) results indicate that there is continuous loss in weight up to 250 °C, mainly due to the removal of water from the samples. Between 250 and 1000 °C there is no weight loss and no peaks in the DTA curves. This indicates that the materials are thermally stable.

Table 1 The catalysts used in aniline alkylation and their physico-chemical properties

No.	Catalyst	Total surface acidity[a] / mmol g^{-1}	BET surface area/ m^2 g^{-1}	% Metal	Catalyst colour
1	$AlPO_4$	0.41 (0.22)	172	–	White
2	V-$AlPO_4$	0.39 (0.72)	160	4.9	Pale yellow
3	Fe-$AlPO_4$	0.38 (0.87)	161	4.7	Light brown
4	Co-$AlPO_4$	0.46 (1.10)	159	4.75	Violet blue
5	Ni-$AlPO_4$	0.32 (0.89)	171	4.8	Pale yellow
6	Cu-$AlPO_4$	0.34 (0.91)	168	4.9	Light blue

[a] Ammonia TPD acidity values are given within parenthesis.

Catalytic studies

All the catalytic activity studies were conducted in the vapour phase. GC analysis of the products from these studies revealed that the reaction between aniline and methanol or DMC in the presence of $AlPO_4$ and M-$AlPO_4$ (M = V, Fe, Co, Ni, and Cu) catalysts resulted only in *N*-alkylated anilines such as *N*-methylaniline (NMA) and *N*,N-dimethylaniline (NNDMA). The reaction product analysis did not indicate the presence of any *C*-alkylated compounds of aniline, such as toludines. Formation of only *N*-alkylated anilines further confirms the TPD results that the catalysts used are associated with only weak acid sites. Alkylation of aniline is a sequential reaction and follows the order aniline → NMA → NNDMA → toludines. Weak acidity and low reaction temperature favours NMA and NNDMA formation while for the formation of toludines strong acid sites are required.[11]

The quantitative results of the vapour phase alkylation of aniline with methanol (1:1 molar ratio) in the presence of $AlPO_4$ and M-$AlPO_4$ as catalysts is presented in Table 2 An analysis of the data given in this table indicates that the aniline conversion activity of the catalysts is in the following order:

$$\text{Fe-AlPO}_4 > \text{Ni-AlPO}_4 > \text{Cu-AlPO}_4 > \text{Co-AlPO}_4 > \text{V-AlPO}_4 > \text{AlPO}_4$$

A comparison of the catalytic activity of the various catalysts as concerns aniline conversion and their surface acidity (Table 1) indicates that there is no simple correlation between these two quantities. However, it is interesting to note that the products from the alkylation reactions carried out in the presence of Co- or V-containing $AlPO_4$ catalysts showed the formation of only NMA and NNDMA. On the other hand, Fe-, Ni- and Cu-containing samples also resulted in other

Table 2 Percentage conversion in the vapour phase alkylation of aniline with methanol in the presence of M-$AlPO_4$ catalysts[a]

		Selectivity		
Catalysts	% Conversion	% NMA	% NNDMA	% Other products
$AlPO_4$	14	35.7	42.8	21.4
V-$AlPO_4$	20	100	–	–
Fe-$AlPO_4$	51	45.0	29.0	25.4
Co-$AlPO_4$	41	43.0	46.3	–
Ni-$AlPO_4$	48	41.6	33.0	25.0
Cu-$AlPO_4$	43	48.8	27.9	23.2

[a] Conditions: 1:1 molar ratio of the reactants; reaction temperature 250 °C; flow rate 5 ml h^{-1}.

Table 3 Catalytic activity of Co-AlPO$_4$ in the vapour phase alkylation of anline under different reaction conditions

			Selectivity				Selectivity	
T/°C	Aniline: CH$_3$OH	% Conversion	% NMA	% NNDMA	Aniline: DMC	% Conversion	% NMA	% NNDMA
200	1:5	29	34.5	65.5	1:5	60	41.6	58.3
	1:1	22	59.0	40.9	1:1	62	51.6	48.3
	2:1	14	100	–	2:1	30	100	–
250	1:5	53	47.1	52.8	1:5	43	34.8	65.1
	1:1	54	55.5	44.4	1:1	44	54.5	45.4
	2:1	30	100	–	2:1	32	100	–
300	1:5	32	43.75	56.25	1:5	30	46.6	53.3
	1:1	36	58.3	41.6	1:1	36	63.8	36.1
	2:1	19	100	–	2:1	23	100	–

Table 4 Catalytic activity of V-AlPO$_4$ in the vapour phase alkylation of aniline under different reaction conditions

			Selectivity				Selectivity	
T/°C	Aniline: CH$_3$OH	% Conversion	% NMA	% NNDMA	Aniline: DMC	% Conversion	% NMA	% NNDMA
200	1:5	8	100	–	1:5	14	100	–
	1:1	30	100	–	1:1	36	100	–
	2:1	18	100	–	2:1	20	100	–
250	1:5	14	100	–	1:5	17	100	–
	1:1	32	100	–	1:1	39	100	–
	2:1	20	100	–	2:1	25	100	–
300	1:5	12	100	–	1:5	16	100	–
	1:1	17	100	–	1:1	18	100	–
	2:1	16	100	–	2:1	16	100	–

products (not identified) besides NMA and NNDMA. This observation indicates that the former sets of catalysts are associated with only weak acid sites that are active in *N*-alkylation of aniline.

Furthermore, it is noticed that Co-AlPO$_4$, with the higher TPD acidity, exhibited a lower selectivity for NMA because NNDMA was also formed. On the other hand, V-AlPO$_4$, with a lower acidity, exhibited 100% selectivity towards NMA. This is in accordance with the expected trend that catalysts with low acidity exhibit higher selectivity towards NMA formation. With respect to other catalysts containing Fe, Ni and Cu with acid sites whose concentration is lower than in cobalt-containing AlPO$_4$, the latter, however, showed poor selectivity to NMA. These observations clearly indicate that it is not the total surface acidity that is responsible for the catalytic activity of the solid acids but the presence of acid sites with a suitable acid strength and their concentration which is important. Probably among all the metal aluminophosphates only Co- and V-AlPO$_4$ possess acid sites of medium strength that would bring about selective *N*-methylation of aniline because it is known that the solid acids with higher surface acid strength show greater activity towards the formation of *C*-alkylated anilines.[17]

Variation of catalytic parameters

Further experiments were conducted only on V-AlPO$_4$ and Co-AlPO$_4$ to determine the effect of reaction temperature, molar ratio of the reactants and the nature of the methylating agent on the percentage conversion and selectivity towards *N*-methylated products of aniline. The results of the experiments are presented in Table 3 and 4. In Table 3 is given the catalytic activity of Co-AlPO$_4$ in the alkylation of aniline with methanol or DMC, carried out at three different reaction temperatures and using three different molar ratios of aniline and alkylating agents. In Table 4 the results of similar studies carried out using V-AlPO$_4$ are presented.

Effect of catalyst bed temperature. Aniline methylation using methanol or DMC was carried out at three different temperatures, 200, 250 and 300 °C. At 250 °C both Co-AlPO$_4$ and V-AlPO$_4$ showed the highest catalytic activity for the formation of NMA. A change in the ratio of aniline to methanol or DMC did not show any change in the temperature at which these catalysts exhibited their maximum activity. These observations indicate that 250 °C is the optimum reaction temperature for the reaction between aniline and methanol or DMC to yield NMA in the presence of Co-AlPO$_4$ and V-AlPO$_4$ as catalysts. At higher temperatures aniline would probably undergo oxidation and also decompose, resulting in coke formation. This may be the reason for the decrease in the catalytic activity for the formation of NMA at higher temperatures.

Effect of the molar ratio of the reactants and the methylating agent. Aniline alkylation reactions were conducted using three

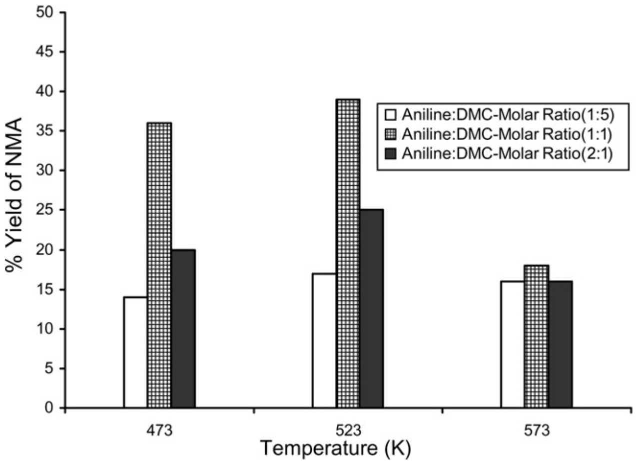

Fig. 1 The effect of temperature and molar ratio of reactants on the vapour phase alkylation of aniline with DMC over V-AlPO$_4$.

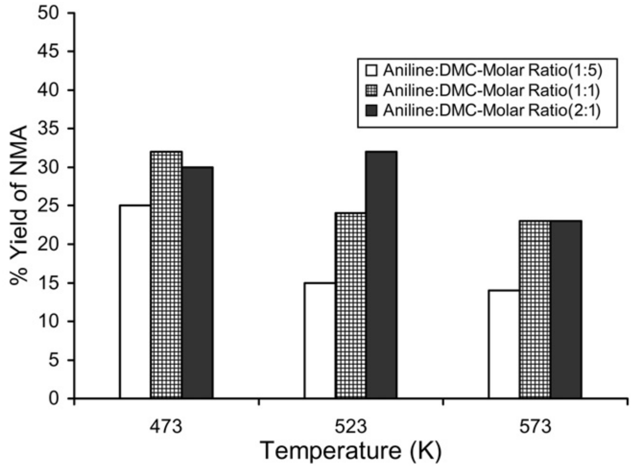

Fig. 2 The effect of temperature and molar ratio of reactants on the vapour phase alkylation of aniline with DMC over Co-AlPO$_4$.

different molar ratios (1:5, 1:1, 2:1) of reactants, using aniline and MeOH or DMC as the methylating agent, at three different catalyst bed temperatures. Five hundred milligrams of either Co-AlPO$_4$ or V-AlPO$_4$ catalyst was used in each reaction. It is observed from the results given in Table 4 that V-AlPO$_4$ showed 100% selectivity for the formation of NMA, irrespective of the molar ratio of the reactants, alkylating agents and the reaction temperature. On the other hand, Co-AlPO$_4$ (Table 3) showed a similar selectivity only when the molar ratio was 2:1, that is in the presence of a lower concentration of methylating agent in the reaction mixture. In the case of Co-AlPO$_4$, due to the higher acid site concentration, when an excess of methylating agent is present further alkylation of the NMA formed would probably take place, resulting in a poor selectivity for NMA. On the other hand, V-AlPO$_4$, with acid sites probably with suitable strength, brings about 100% selectivity for NMA. The results of the experiments with respect to the % of NMA formed at different molar ratios of the reactants and the reaction temperature are represented in the form of bar diagrams in Fig. 1 and 2.

Finally, a comparison of the alkylating activity of methanol with DMC showed that in general DMC resulted in more NMA and NNDMA than MeOH This is probably due to the fact that in the presence of methanol as the alkylating agent water is formed as one of the products. This may poison the active sites on the catalysts that are responsible for the *N*-alkylation activity. Thus, DMC is a better alkylating agent than methanol.

Time-on-stream experiments. The time-on-stream studies were performed at 250 °C with 500 mg of the catalyst (Co-AlPO$_4$ or V-AlPO$_4$) at a feed rate of 5 ml h^{-1}. The feed solution consisted of a 1:1 molar ratio of aniline and MeOH or DMC. The product fractions were collected at 15 min intervals and analysed by GC. A plot of % of NMA formed *versus* time shows that there is no change in the aniline conversion activity of the catalyst with time and in addition, the selectivity towards NMA and NNDMA also remained almost unchanged during 5 h on stream. This indicates that there no apparent deactivation of the catalysts at the selected reaction temperature.

Conclusion

Amorphous aluminophosphates modified by transition metal ions have been found to be good catalysts for the vapour phase synthesis of *N*-alkylated anilines, using MeOH or DMC as the alkylation agents. V-AlPO$_4$has been found to show 100% selectivity for the formation of NMA. No simple correlation between the selectivity and the total surface acidity has been observed. However, none of the catalysts showed any activity for *C*-alkylation of aniline, indicating that they possess only acid sites with moderate acid strength.

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