Isopropylation of ethylbenzene with 2-propanol over MnAPO-5 and ZAPO-5

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Received 19 February 2004; accepted 8 April 2004

Pure phases of ZAPO-5 and MnAPO-5 were synthesised hydrothermally using triethylamine as a structure directing agent. The estimation of acid sites (Brönsted and Lewis) in ZAPO-5 and MnAPO-5 was done by TPD measurements of n-butylamine. The alkylation of ethylbenzene (EB) with 2-propanol over the catalysts was studied in a fixed-bed reactor at atmospheric pressure and 250–400 °C. *p*-Isopropyl ethylbenzene (*p*-IPEB) and *m*-isopropyl ethylbenzene (*m*-IPEB) were the products formed. MnAPO-5 was found to be more active than ZAPO-5. MnAPO-5 registered 11% yield of *p*-IPEB and 5.8% yield of *m*-IPEB at 350 °C.

KEY WORDS: MnAPO-5; ZAPO-5; molecular sieves; isopropylation; ethylbenzene.

1. Introduction

Alkylation of aromatic hydrocarbons is a reaction of high commercial significance. Ethylbenzene, isopropylbenzene, isopropyltoluene are a few of the many industrially important chemical intermediates obtained by acid catalysed alkylation of the appropriate aromatics. Aluminophosphate ($AlPO_4$-*n*) molecular sieves have been the subject of extensive studies over the past two decades mostly due to their interesting catalytic properties, ion-exchanging role and molecular sieve effect. $AlPO_4$-*n* possesses an overall framework neutrality owing to the regular alternation of Al^{3+} and P^{5+} tetrahedra in the structure and consequently little acidity. Brönsted acidity can be generated in these materials by replacing Al^{3+} by divalent cations such as Mn^{2+} and Zn^{2+} (MeAPOs) [1–6]. $AlCl_3$ and phosphoric acid show good catalytic performance; however they cause environmental problems such as corrosion and waste disposal etc. Such problems are overcome by the use of microporous ($AlPO_4$-*n*) materials. The present study involves the synthesis of large pore $AlPO_4$-5 molecular sieves substituted with Mn and Zn and the study of their catalytic activity towards vapour phase isopropylation of ethylbenzene with 2-propanol.

2. Experimental

2.1. Synthesis and catalytic studies

MnAPO-5 and ZAPO-5 catalysts were synthesised by hydrothermal methods. More details about synthesis and catalytic studies are described elsewhere [7,8]. The products were identified using Shimadzu GCMS-QP5000. The products were analysed using Shimadzu GC using CP-Sil 19 column.

2.2 Characterisation

ZAPO-5 and MnAPO-5 were characterised by X-ray diffraction (XRD), MAS-NMR, BET, ICP-MS, TGA and *n*-butylamine-TPD measurements, in order to study the structure, surface area, chemical composition, thermal properties and acidity. XRD, MAS-NMR, BET and ICP-MS characterisation details are given elsewhere [8,9]. TGA was carried out for as-synthesised samples using Seiko SSC 5200H thermal analysis system. Acidity measurements were done by *n*-butylamine-TPD [10] method using Seiko SSC 5200H thermal analysis system attached to a TG/DTA 220 module. About 50 mg of calcined catalyst in each run was activated at 500 °C for 1 h in a flow of air and then the system was kept in vacuum ($\sim 10^{-4}$ Torr) at the same temperature. The catalysts were cooled down to room temperature. The given amount of *n*-butylamine (n-BA) was adsorbed on the catalyst in vapour phase. The catalysts adsorbed with *n*-BA were pretreated in vacuum to remove the excess amine from the catalyst surface at room temperature and then the thermal desorption measurements were made and from the weight loss, acidity is determined.

3. Results and discussion

3.1. Structure

The *n*–BA–TPD curves are illustrated in figure 1. From the diagram, it is found that there are three peaks in each run; one exists in the temperature range 50–90 °C due to desorption of physisorbed *n*-BA. The second peak in the range of 110–200 °C should be due to

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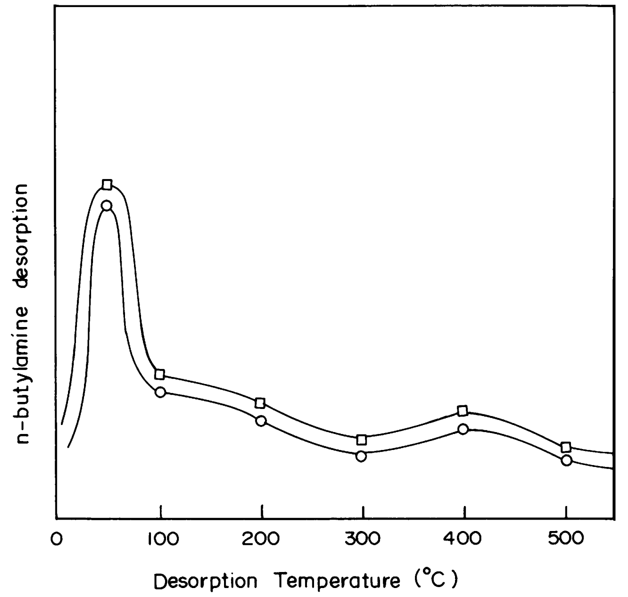

Figure 1. Thermal desorption curves of n-butylamine on ZAPO-5 and MnAPO-5.

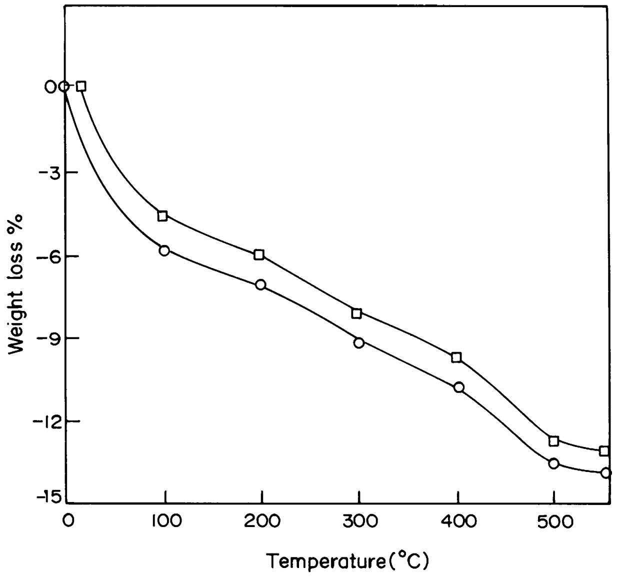

Figure 2. Thermograms of the as-synthesised samples of ZAPO-5 and MnAPO-5.

desorption of *n*-BA from strong acid sites. The third peak in the range of 360-450 °C should be due to the decomposition of *n*-BA into butene etc. The acidity values obtained by this method show good agreement with the calculated values obtained from the chemical composition. The acidity values presented in table 1 show that MnAPO-5 is more acidic than ZAPO-5, indicating higher substitution of Mn in MnAPO-5 than by Zn in ZAPO-5. The thermograms of the as-synthesised catalysts are presented in figure 2. The samples show a weight loss around 90 °C due to the desorption of the physically adsorbed water. The desorption of the organic template takes place in multi-steps in ZAPO-5 and MnAPO-5. The weight loss in the temperature range 250–550 °C is due to the desorption and decomposition of triethylamine occluded inside the channels. The total weight loss is around 12.5 wt.%. The gel composition, chemical composition, surface area and acidity of these catalysts are presented in table 1.

3.2. Isopropylation of ethylbenzene

Isopropylation of ethylbenzene with 2-propanol over ZAPO-5 and MnAPO-5 was studied at 250, 300, 350 and 400 °C, with the feed ratio 1 : 3 for ethylbenzene : 2-propanol, and WHSV 2 h^{-1}. The products of the reaction were found to be *p*-isopropyl ethyl benzene (*p*-IPEB) and *m* isopropyl ethyl benzene (*m*-IPEB).

3.3. Effect of temperature

Isopropylation of ethylbenzene with 2-propanol was carried out in the temperature range 250–400 °C over MnAPO-5 and ZAPO-5. The feed ratio of ethyl benzene EB to 2-propanol was set at 1 : 3 and WHSV 2 h^{-1}. The results obtained are presented in Table 2. show a linear response of conversion with increase in

Table 2
Effect of temperature on the conversion and product yield

Catalysts	Temperature (°C)	Conversion (wt%)	Product yield (wt%)	
			p-IPEB	*m*-IPEB
MnAPO-5	250	2.8	1.6	1.2
	300	4.6	2.3	2.3
	350	16.7	10.9	5.8
	400	13.0	7.0	5.8
ZAPO-5	250	0.4	0.2	0.2
	300	1.3	0.7	0.6
	350	6.8	3.6	3.2
	400	5.2	2.7	2.5

WHSV = 2 h^{-1}; feed ratio = 1 : 3 (ethylbenzene : 2-propanol).

Table 1
Gel composition, molar composition, surface area and acidity of aluminophosphate-based molecular sieves

Catalyst	Gel composition	Molar composition	BET surface area (m^2/g)	Acidity (mmol/g)
ZAPO-5	0.1ZnO : Al_2O_3 : P_2O_5 : TEA : 40H_2O	0.074ZnO : 0.926Al_2O_3 : P_2O_5	252	0.28
MnAPO-5	0.1MnO : Al_2O_3 : P_2O_5 : TEA : 40H_2O	0.087MnO : 0.913Al_2O_3 : P_2O_5	260	0.34

Table 3
Effect of feed ratio (ethylbenzene : 2-propanol) on the conversion and product yield

Catalysts	Feed ratio (mol)	Conversion (wt%)	Product yield (wt%)	
			p-IPEB	*m*-IPEB
MnAPO-5	1 : 1	6.3	3.3	3.1
	1 : 2	8.9	4.6	4.3
	1 : 3	16.7	10.9	5.8
	1 : 4	9.9	5.5	4.4
	1 : 5	9.5	5.2	4.3
ZAPO-5	1 : 1	2.1	1.1	1.0
	1 : 2	2.2	1.2	1.0
	1 : 3	6.8	3.6	3.2
	1 : 4	3.2	1.8	1.4
	1 : 5	3.9	2.0	1.9

Temperature = 350 °C; WHSV = 2 h^{-1}.

temperature over the catalysts. Brönsted acid sites are produced by isomorphous substitution of Mn^{2+} and Zn^{2+} ions in the framework of the catalyst and the reaction was studied over ZAPO-5 and MnAPO-5. These catalysts show a good conversion of EB. Ethylbenzene conversion is low at 250 °C indicating lower isopropyl cation formation. Formation of hydrogen bonded alcohol clusters could be the reason for the suppression of ionisation of 2-propanol over Brönsted acid sites of the catalyst at this temperature. The increase in conversion over ZAPO-5 and MnAPO-5 at 300 °C suggest sufficient dispersal of alcohols in the pores. MnAPO-5 gives higher conversion than ZAPO-5, consistent the order of acidity.

The effect of temperature on product yield was also examined over MnAPO-5 and ZAPO-5 and the results are shown in table 2. The selectivity to *p*-IPEB and *m*-IPEB over the catalysts increases with temperature upto 350 °C, and at 400 °C a decrease is observed. Formation of *p*-IPEB with high selectivity at 350 °C might be due to its free diffusion without steric hindrance through the pores. The lower selectivity towards *m*-IPEB might be due to steric hindrance to diffusion. Other products like benzene, toluene and diethylbenzenes are also formed but only to the extent of <1%. Formation of nearly 11% *p*-IPEB and 5.8% *m*-IPEB yield at 350 °C over MnAPO-5 is an observation to note in this study. The extent of conversion and yield obtained with ZAPO-5 is less than with MnAPO-5 at all temperatures. However, the selectivity to *p*-IPEB and *m*-IPEB is similar for both catalysts.

3.4. *Effect of feed ratio*

Table 3 summarises the results of isopropylation of EB over ZAPO-5 and MnAPO-5 using different ethylbenzene : 2-propanol mole ratios ranging from 1 : 1 to 1 : 5. The reaction was carried out at 350 °C for a period of 1 h with WHSV 2 h^{-1}. EB conversion increases upto 1 : 3 and thereafter a decrease is observed. *p*-IPEB selectivity is maximum at a feed ratio of 1 : 3 over MnAPO-5. The selectivity to *m*-IPEB is nearly the same as *p*-IPEB at all the feed ratios except at 1 : 3.

3.5. *Effect of time-on-stream*

Table 4 illustrates the effect of time-on-stream on the yield of products. There is a decrease in conversion with increase in stream due to blocking of active sites by coke. The rapid decrease in activity of the catalysts with stream might be due to the microporous nature. The coke contents of the catalysts were measured after 1 h and 3 h runs (table 4). The decrease in yield is due to the increase in coke content with time-on stream.

4. Conclusion

The vapour phase isopropylation of ethylbenzene with 2-propanol over ZAPO-5 and MnAPO-5 showed good conversion. The products were *p*-IPEB and *m*-IPEB. The good conversion over ZAPO-5 and MnAPO-5 is due to the Brönsted acidity generated by isomorphous substitution of metal in the framework of the catalyst. MnAPO-5 gives higher conversion of EB and higher yield of *p*-IPEB than ZAPO-5. Although the isomorphic substitution is nearly the same, this obser-

Table 4
Effect of time-on-stream on the conversion and product yield

Catalysts	Time (h)	Conversion (wt%)	product yield (wt%)		Coke (wt%)
			p-IPEB	*m*-IPEB	
MnAPO-5	1	16.7	10.9	5.8	3.8
	2	6.1	3.3	2.8	–
	3	1.4	0.8	0.6	11.1
ZAPO-5	1	6.8	3.6	3.2	3.4
	2	2.0	1.1	0.9	–
	3	0.5	0.3	0.2	10.5

Temperature = 350 °C; WHSV = 2 h^{-1}; feed ratio = 1 : 3(ethylbenzene : 2-propanol).

vation appears to reflect a role for the unpaired electrons in the d-subshell of Mn.

Acknowledgments

We thank Dr. M. Palanichamy of Anna University for helpful discussions during the preparation of this manuscript and Dr. T. Balakrishnan, University of Madras for encouragement.

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