

## Isomorphous substitution of Mn(II), Ni(II) and Zn(II) in AIPO-31 molecular sieves and study of their catalytic performance

V UMAMAHESWARI, C KANNAN, BANUMATHI ARABINDOO,  
M PALANICHAMY and V MURUGESAN\*  
Department of Chemistry, Anna University, Chennai 600 025, India  
e-mail: v\_murugu@hotmail.com; annalib@sirnetin.ernet.in

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**Abstract.** Isomorphously substituted molecular sieves, MAPO-31, NAPO-31 and ZAPO-31, were prepared under mild hydrothermal conditions from gels containing sources of aluminium, phosphorus, appropriate metal and dipropylamine (DPA), presumably acting as a structure-directing template. They were characterized by XRD, FTIR, TGA, inductively coupled plasma (ICP), ESR, Brunauer, Emmett, Teller (BET) and diffusion reflectance spectroscopy (DRS) techniques. In the XRD, the peak at  $2\theta = 16.7^\circ$  of the metal substituted AIPO-31 is more intense than that of pure AIPO-31 suggesting preferential occupation of the plane corresponding to it as compared to other planes. The O-H stretch in the IR spectra of the metal-substituted molecular sieves is blue-shifted with respect to the parent AIPO-31 molecular sieves possibly due to metal substitution. The  $g$  values obtained from the ESR spectra of MAPO-31 and NAPO-31 also substantiate framework substitution. Ethylation of toluene was carried out between 300 and 450°C over the above catalysts as a model test reaction. The high toluene conversion over metal-substituted molecular sieves proves the isomorphous substitution of metal ions in the AIPO-31 framework.

**Keywords.** Molecular sieves; MAPO-31; NAPO-31; ZAPO-31; ethylation of toluene.

### 1. Introduction

Aluminophosphate molecular sieves are a class of microporous crystalline inorganic solids contemporary to zeolites. Several types of AIPOs have been reported with a rich diversity of structures<sup>1,2</sup>. They are framework oxides of Al and P in tetrahedral coordination with oxygen. In spite of their structural diversity they appear to obey Loewenstein's rule with an avoidance of Al-O-Al bonds and thus include framework topologies analogous to zeolites. Its framework being electrically neutral, with no exchangeable cations<sup>3</sup>, Bronsted acidity is not intrinsic in AIPO-31. This has restricted the use of AIPOs as solid acid catalysts. Hence metal ions have been known to substitute aluminium in many AIPO- $n$  molecular sieve framework structures<sup>4</sup>. Incorporation of transition metal ions in the framework is of particular interest since various transition metal ions are involved in catalytic processes. In addition, substitution of divalent metal ions in the place of Al<sup>3+</sup> can generate Bronsted acidity. Recently Gerd Finger *et al*<sup>5</sup> have

\*For correspondence

discussed the crystal symmetry of isomorphously substituted AIPO-31 based molecular sieves. However their use as catalyst has not yet been attempted so far. In our earlier studies we have studied the catalytic performance of AIPO-5 and AIPO-11 based molecular sieves for ethylation of toluene with ethanol. It was observed that the yield of *m*-ethyl toluene was less over AIPO-5 and not observed over AIPO-11<sup>6,7</sup>. Hence, in the present investigation we have attempted the substitution of Mn<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> ions in AIPO-31, a novel intermediate pore aluminophosphate molecular sieve in an attempt to use catalysts in the ethylation of toluene in the vapour phase.

## 2. Experimental

### 2.1 Synthesis

AIPO-31 was synthesised using the gel composition DPA:Al<sub>2</sub>O<sub>3</sub>:P<sub>2</sub>O<sub>5</sub>:50H<sub>2</sub>O. Aluminium isopropoxide (24 g) was soaked in 30 ml of water for a day. On the day of synthesis 11.5 g phosphoric acid diluted with 17.5 ml of water was added dropwise with vigorous stirring until the mixture was homogeneous. Then 5.1 g of DPA was added drop by drop and the gel was stirred for another 1 h. The resultant gel pH was 5.6. The gel was then autoclaved at 200°C for 24 h. The product was filtered and dried at 110°C for 12 h. It was then calcined at 550°C to remove the template. Adopting the above procedure, MAPO-31, NAPO-31 and ZAPO-31 were prepared with the gel composition DPA:0.2MO:P<sub>2</sub>O<sub>5</sub>:50H<sub>2</sub>O where M = Mn, Ni and Zn respectively.

### 2.2 Characterization

X-ray diffraction analysis was carried out using Siemens D 500 diffractometer in the scan range of  $2\theta$  between 5 and 50° using Cu K<sub>α</sub> source. The identification of peaks was done with reference to compilation of simulated XRD powder patterns. Unit cell parameters were calculated using standard least square refinement technique. FTIR spectra of the samples were recorded on a Perkin–Elmer spectrophotometer using KBr pellets. Thermogravimetric analyses were carried out using Mettler TA 3000 system at a scanning rate of 20°C/min in a stream of dry air. Inductively coupled plasma (ICP) ARL 3410 with minitorch was used to determine the chemical composition of the samples. BET surface area of the samples was measured on a Micromeritics pulse chemisorb 2700 using nitrogen as adsorbate at –176°C. The samples were degasified initially at 200°C for 2 h with a flow of oxygen. ESR spectra were recorded on a Varian E112 spectrophotometer at room temperature. Acidity of the samples was measured by temperature-programmed desorption of ammonia using TGA (Mettler TA 3000). Prior to the adsorption of ammonia the samples were evacuated to 10<sup>-3</sup> torr at 450°C, after which ammonia was allowed to equilibrate at room temperature in a closed vessel. Thermogravimetric analysis was carried out up to 500°C at a scanning rate of 10°C/min. Acidity and acidic strength in mmol/g were determined from the weight loss at various temperatures.

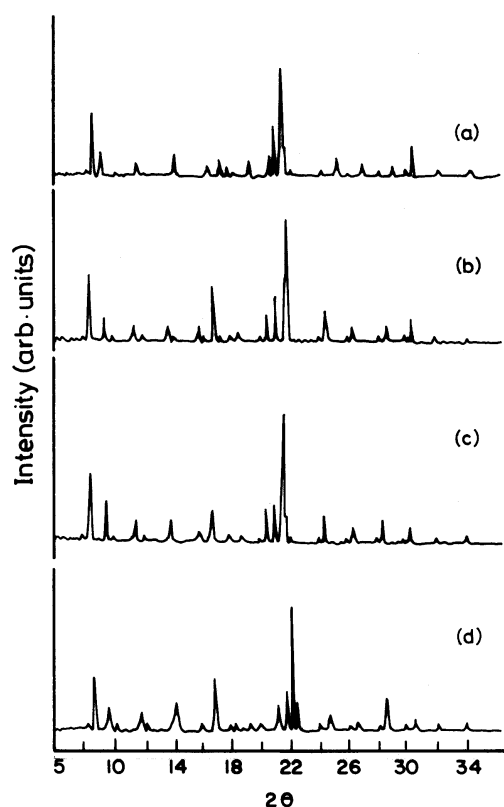
### 2.3 Catalytic studies

The reactor system was a fixed-bed vertical flow type reactor made up of a quartz tube of 40 cm length and 2 cm internal diameter. The quartz reactor was heated to the requisite

temperature with the help of a tubular furnace controlled by a digital temperature controller cum indicator. The bottom of the reactor was provided with a thermowell to keep the chromel–alumel thermocouple for measuring the temperature in the middle of the catalyst bed. About 2 g of the catalyst was placed in the reactor and supported on either side with a thin layer of quartz wool and ceramic beads. The top portion of the reactor was connected to a glass bulb. Reactants were fed into the reactor through the inlet by a syringe infusion pump that can be operated at different flow rates. The bottom of the reactor was connected to a condenser and a receiver to collect the liquid products. After each catalytic run the catalyst was regenerated by passing air free from carbon dioxide through the reactor at 500°C for 6 h. The liquid products were analysed using Hewlett Packard Gas Chromatograph 5890 A with flame ionisation detector. The Bentone column with nitrogen as carrier gas was used.

### 3. Results and discussion

X-ray diffraction patterns of calcined AIPO-31, MAPO-31, NAPO-31 and ZAPO-31 samples are presented in figure 1. The  $2\theta$  values of the patterns have been found to be the same as reported in the literature<sup>8,9</sup>. The XRD peaks observed for AIPO-31 at  $2\theta = 8^\circ$  and  $22^\circ$  are more intense than the peak observed at  $16.7^\circ$ . These are the characteristic peaks of AIPO-31 molecular sieves. Although the line positions of MAPO-31, NAPO-31



**Figure 1.** X-ray diffraction patterns of (a) AIPO-31, (b) MAPO-31, (c) NAPO-31, and (d) ZAPO-31.

and ZAPO-31 are very close to the parent AIPO-31, the intensity patterns have undergone a significant change. The peak at  $16.7^\circ$  in the XRD spectra of substituted AIPO-31 samples is more intense than that of pure AIPO-31. This suggests that the metal ions have preferentially occupied the plane that produces intense peak at  $16.7^\circ$ <sup>10</sup>. In addition, the amount of metal substitution in these catalysts is purposely made less as it would produce structural transformation with entirely different XRD patterns. The unit cell parameters  $a$ ,  $b$ ,  $c$ , unit cell volumes ( $\text{\AA}^3$ ) of AIPO-31 and the corresponding substituted AIPO-31 molecular sieves are presented in table 1. The increased unit cell volume in the case of substituted AIPO-31 molecular sieves is convincing evidence for the isomorphous substitution of metal ions in the  $\text{AlPO}_4$  framework.

FTIR spectra of the catalysts are presented in figure 2. The bands between  $1000$  and  $1200\text{ cm}^{-1}$  are assigned to the asymmetric stretching of  $\text{TO}_4$  tetrahedra and these are characteristic of all zeotype molecular sieves<sup>11</sup>. The absorption in the region  $500$ – $650\text{ cm}^{-1}$  is assigned to vibrations in the double-ring region. Other bands in the spectra at  $700$  and  $470\text{ cm}^{-1}$  are assigned to symmetric stretching of  $\text{TO}_4$  tetrahedra and T-O bends respectively. The spectral features of all AIPO-31 based structures are similar except the O-H vibration in the framework. The O-H vibration in the substituted aluminophosphate molecular sieves is shifted to higher wave numbers in comparison to the corresponding unsubstituted molecular sieve<sup>12</sup>. Hence in the substituted molecular sieves, the O-H bond is strong compared to the same in unsubstituted ones. This may be due to the substitution of more electronegative  $\text{M}^{2+}$  ions in the tetrahedral framework instead of Al sites.

Thermograms of AIPO-31 and their substituted molecular sieves are shown in figure 3. The weight loss between  $70$  and  $100^\circ\text{C}$  is due to the desorption of water. The second weight loss between  $200$  and  $250^\circ\text{C}$  observed for both parent and metal ion substituted molecular sieves is due to the desorption of templates adsorbed onto weak acid sites. There is a third weight loss between  $250$  and  $450^\circ\text{C}$  which is observed only in metal-substituted molecular sieves. It is due to the decomposition and oxidation of template molecules adsorbed on more acidic Bronsted acid sites<sup>13</sup>. The absence of this weight loss in the parent molecular sieve indicates the absence of strong Bronsted acid sites. This is an evidence for the isomorphous substitution of more electronegative metal ions like  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  for aluminium in AIPO-31 molecular sieve.

The ESR spectra of MAPO-31 and NAPO-31 are shown in the figure 4. The  $\text{Mn}^{2+}$  substituted AIPO-31 molecular sieve shows a broad ESR signal with the  $g$  value of  $1.98$ . The broad ESR signal without hyperfine splitting indicates that the  $\text{Mn}^{2+}$  ions strongly interact with their environment in the tetrahedral framework. The  $g$  value of  $\text{Ni}^{2+}$  in NAPO-31 is  $2.0092$ , which is in good agreement with the values reported for NAPO-5

**Table 1.** Unit cell parameters and unit cell volumes of aluminophosphate-based AIPO-31 molecular sieves.

Catalyst	Unit cell parameter ( $\text{\AA}$ )			Unit cell volume $\text{\AA}^3$
	$a$	$b$	$c$	
AIPO-31	20.83	20.83	5.10	2212
MAPO-31	20.86	20.86	5.09	2284
NAPO-31	20.84	20.84	5.12	2293
ZAPO-31	20.87	20.87	5.10	2286

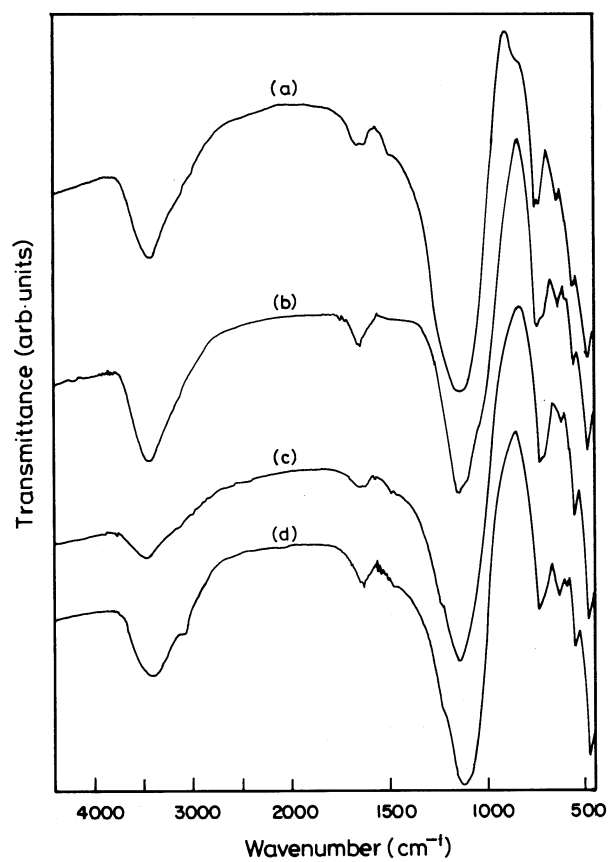


Figure 2. FT-IR spectra of (a) AIPO-31, (b) MAPO-31, (c) NAPO-31, and (d) ZAPO-31.

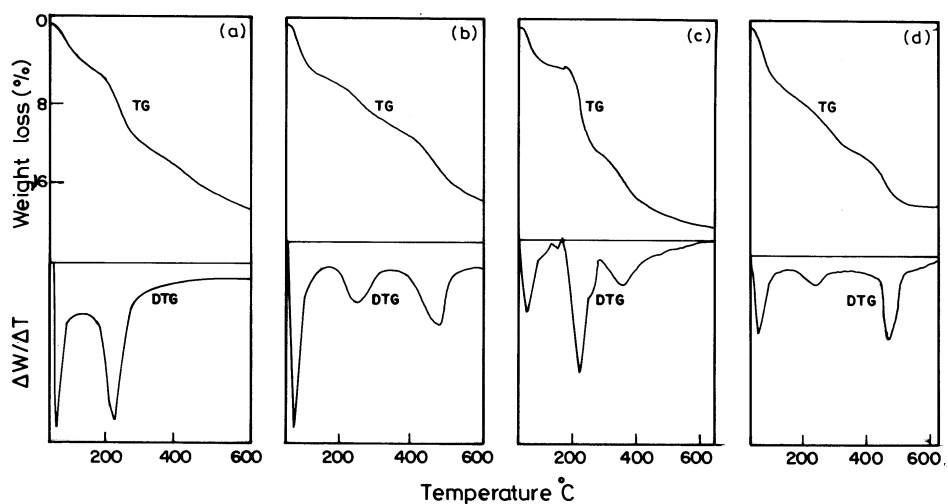


Figure 3. TG and DTG curves for (a) AIPO-31, (b) MAPO-31, (c) NAPO-31, and (d) ZAPO-31.

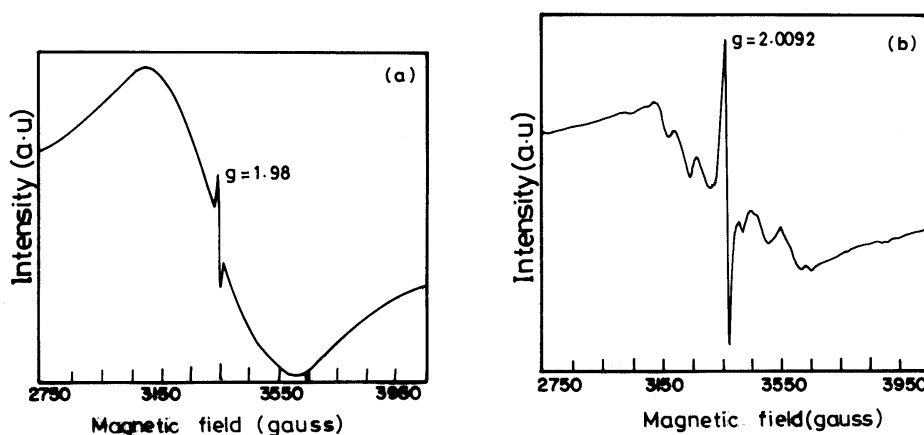


Figure 4. ESR spectra of (a) MAPO-31, and (b) NAPO-31.

and NAPO-11 molecular sieves<sup>14</sup>. Unlike NAPO-5 and NAPO-11, more than two transitions are observed in the ESR spectrum of NAPO-31 molecular sieve. It may be attributed to the incorporation of  $\text{Ni}^{2+}$  in different environments of the tetrahedral framework. The intensities of the ESR signal are weak because of the fewer  $\text{Ni}^{2+}$  ions substituted in the framework. In addition,  $\text{Ni}^{2+}$  is more electronegative than  $\text{Mn}^{2+}$  and hence its unpaired electron is expected to be less interacting with the surroundings than  $\text{Mn}^{2+}$  ions. Hence weak hyperfine splitting of ESR signal is observed in the case of the NAPO-31 molecular sieve. Chemical analysis of the catalysts are reported in table 2. The data clearly indicate the substitution of  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions for Al in the aluminophosphate framework. The extent of metal substitution is in the order  $\text{Mn}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$ .

Values of the total acidity measured using temperature-programmed ammonia desorption of  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  substituted AIPO-31 molecular sieves are given in table 3. The desorption of ammonia between 160 and 300°C is due to weak acid sites of the catalysts<sup>15</sup>. The weight losses between 300 and 500°C are assigned to the strong acid sites of the catalysts. In AIPO-31, the desorption of ammonia between 160 and 300°C is due to the strict alteration of Al-O and P-O tetrahedral coordination which gives rise to a neutral framework by the neutralisation of positive and negative charges present on  $\text{P}^{5+}$  and  $\text{Al}^{3+}$ . The source of weak acidity in AIPO-31 is probably the imperfections in the lattice<sup>16</sup>. However, the incorporation of  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  in the framework of AIPO-31 causes net negative charge on the framework which is balanced by protons. These protons are the strong acid sites in substituted aluminophosphate molecular sieves. Among the substituted molecular sieves, the  $\text{Mn}^{2+}$ -incorporated catalyst exhibits higher acidity than  $\text{Ni}^{2+}$ - and  $\text{Zn}^{2+}$ -substituted ones because of the increased  $\text{Mn}^{2+}$  substitution which has been further confirmed by chemical analysis.

The BET surface area for all the catalysts (table 3) is between 200 and 237  $\text{m}^2/\text{g}$ . Surface areas of the substituted aluminophosphate molecular sieves are nearly the same as that of the corresponding unsubstituted aluminophosphate molecular sieves. Hence, in metal-substituted catalysts, the metal ions are in the framework<sup>17</sup>.

**Table 2.** Chemical analysis of aluminophosphate-based molecular sieves.

Catalyst	Molar composition
AIPO-31	Al <sub>2</sub> O <sub>3</sub> :P <sub>2</sub> O <sub>5</sub>
MAPO-31	0.1 MnO:0.90 Al <sub>2</sub> O <sub>3</sub> :P <sub>2</sub> O <sub>5</sub>
NAPO-31	0.04 NiO:0.96 Al <sub>2</sub> O <sub>3</sub> :P <sub>2</sub> O <sub>5</sub>
ZAPO-31	0.08 ZnO:0.92 Al <sub>2</sub> O <sub>3</sub> :P <sub>2</sub> O <sub>5</sub>

**Table 3.** Acidity and BET surface area of aluminophosphate-based molecular sieves.

Catalysts	Total acidity (weak and strong) (mmol g <sup>-1</sup> )	BET surface area (m <sup>2</sup> g <sup>-1</sup> )
AIPO-31	0.135	200
MAPO-31	0.698	237
NAPO-31	0.481	209
ZAPO-31	0.558	230

**Table 4.** Effect of temperature on the conversion and product yield.

Catalysts	Temp. (°C)	Toluene conversion (wt%)	Product yield (wt%)			
			Benzene	Styrene	<i>m</i> -Ethyl toluene	Diethyl ether
AIPO-31	300	–	–	–	–	2
	350	2.2	1.2	–	1.0	8.8
	400	4.9	2	1.0	1.9	1.1
	450	4	2	1.0	1.0	–
MAPO-31	300	–	–	–	–	21
	350	27.2	2.9	1.1	23.2	12.8
	400	22.4	2.2	2.2	18.0	11.0
	450	19	4.5	4.5	10	1.5
NAPO-31	300	–	–	–	–	11
	350	10.7	1.6	–	9.1	9.3
	400	13	4.8	1.3	6.9	2.0
	450	8	6.0	1.0	1.0	–
ZAPO-31	300	2.5	–	–	2.5	12.5
	350	21.7	5	2.5	18.7	9.8
	400	26	8.5	4.2	13.3	5.0
	450	21.9	10.6	4.9	6.4	2.0

The ethylation of toluene was carried out over AIPO-31, MAPO-31, NAPO-31 and ZAPO-31 molecular sieves in the temperature range 300–450°C. The products formed are styrene, benzene, *m*-ethyl toluene and diethylether. The effect of temperature, reactant ratio and time on stream on toluene conversion and product distributions are discussed below.

Results of the effect of temperature, at reactant feed ratio 1:2 and (WHSV)<sup>-1</sup> 5 h on toluene conversion and product distribution with AIPO-31, MAPO-31, NAPO-31 and ZAPO-31 molecular sieves are given in table 4. The maximum conversion is observed at 350 and 400°C. The yield of ether is high at 300°C but decreases with increase in

temperature. *m*-Ethyl toluene is not formed at 300°C over any of the catalysts except ZAPO-31. As the temperature increases the yield of *m*-ethyl toluene decreases. This observation illustrates that adsorption of toluene on the Bronsted acid sites takes place at 350–400°C. Close adsorption of toluene and ethyl cations on adjacent Bronsted acid sites is considered necessary to account for the formation of *m*-ethyl toluene over these catalysts. Coke deposition occurs at higher temperatures which accounts for the decrease in conversion and product yields<sup>6</sup>.

Enhancement in conversion and product yields over metal-substituted AIPOs compared to the parent sieves convincingly proves isomorphous substitution in AIPO-31 molecular sieves. Among metal-substituted catalysts, high conversion and product yields over MAPO-31 is due to higher incorporation of Mn<sup>2+</sup> in the framework as compared to other cations.

The effect of reactant feed ratio over conversion and product yields is given in table 5. Toluene conversion increases when the feed ratio of toluene to ethanol is changed from 1:1 to 1:2, but further increase to 1:3 decreases conversion though less significantly. Yield of *m*-ethyl toluene follows the same trend as conversion, but the decrease of yield at the ratio 1:3 is more significant. Yield of ether increases as the feed ratio varies from 1:1 to 1:3 for all the metal-substituted catalysts, but at 1:2 it is almost levelled to that for 1:1. *m*-Ethyl toluene and ether are the major products obtained in this reaction but trace quantities of benzene and styrene are also formed. In order to account for the observed data, ethyl cation and toluene are presumed to be adsorbed on the near Bronsted acid sites. Their closeness is felt to be crucial in accounting for the yield of *m*-ethyl toluene. When the feed ratio is 1:1 very closely adsorbed ethyl cations and toluene molecules would be scarce. Hence toluene conversion and yield of *m*-ethyl toluene are less. When the ratio is increased to 1:2, more of ethyl cations and toluene may be in close proximity thereby increasing toluene conversion and yield of *m*-ethyl toluene. But at 1:3, the conversion is almost levelled to that of 1:2, but the yield of *m*-ethyl toluene is less, illustrating decreased adsorption of toluene and its dilution in the ethanol vapour phase. Hence the ethyl carbocations which remain as charge-compensating species on the walls

**Table 5.** Effect of feed ratio on conversion and product yield.

Catalysts	Reactant ratio (moles)	Toluene conversion (wt%)	Product yield (wt%)			
			Benzene	Styrene	<i>m</i> -Ethyl toluene	Diethyl ether
AIPO-31	1:1	1.5	–	–	1.5	3.5
	1:2	3.2	1.2	–	2.0	8.0
	1:3	2	–	–	2.0	7.0
MAPO-31	1:1	4.5	–	–	4.5	9.5
	1:2	27.2	2.9	1.1	23.2	12.8
	1:3	19.1	2.5	1.6	15.0	19.9
NAPO-31	1:1	4.5	–	–	4.5	9.5
	1:2	10.7	1.6	–	9.1	9.3
	1:3	2.2	–	–	2.2	15.8
ZAPO-31	1:1	9.3	2.3	–	7.0	10.7
	1:2	26.2	5	2.5	18.7	9.8
	1:3	5.2	–	–	5.2	35.8



**Table 6.** Effect of time on stream on the conversion and product yield.

Catalysts	Time (h)	Toluene conversion (wt%)	Product yield (wt%)			
			Benzene	Styrene	<i>m</i> -Ethyl toluene	Diethyl ether
AlPO-31	1	3.2	1.2	–	2.0	8.0
	2	1.5	–	–	1.5	3.7
	3	–	–	–	–	2.0
	4	–	–	–	–	1.0
	5	–	–	–	–	1.0
MAPO-31	1	27.2	2.9	1.1	23.2	12.8
	2	20.6	3	2.0	15.6	6.4
	3	15.3	3	1.3	11.0	5.7
	4	2.6	–	–	2.6	5.4
	5	–	–	–	–	3.0
NAPO-31	1	10.7	1.6	–	9.1	15.8
	2	8.7	1.2	–	7.5	6.3
	3	2.6	–	–	2.6	6.0
	4	–	–	–	–	3.0
	5	–	–	–	–	1.0
ZAPO-31	1	26.2	5	2.5	18.7	9.8
	2	9.9	1.2	–	7.5	6.3
	3	2.6	–	–	2.6	6.0
	4	–	–	–	–	3.0
	5	–	–	–	–	1.0

react predominantly with alcohols in the vapour phase to yield ether. In all these cases the conversion and yields of products are greater over metal-substituted molecular sieves as compared to that with the parent, supporting the incorporation of metal ions in the framework.

Time-on stream studies were carried out over  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  substituted AlPO-31 catalysts at  $350^\circ\text{C}$  maintaining the feed ratio at 1:2 and  $(\text{WHSV})^{-1}$  2.5 h. The results are presented in table 6. The metal ion substituted catalysts are more active than the parent AlPO-31 molecular sieves. In the early hours of time on stream, the yield of ether and *m*-ethyl toluene is large but during the latter stages, the yield of ether decreases and *m*-ethyl toluene is not formed. This may be attributed to the blocking of active sites by coke formation.

Among the metal-substituted AlPO-31 molecular sieves MAPO-31 has more Bronsted acidity than others due to the increased substitution of  $\text{Mn}^{2+}$  ions in the framework compared to other metal ions. This accounts for the high toluene conversion.

#### 4. Conclusions

Isomorphous substitution of lower valent metal ions such as  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  in AlPO-31 molecular sieves for  $\text{Al}^{3+}$  has been confirmed through XRD, FTIR, TGA, ESR, BET and TPD studies. These substitutions have been studied in order to impart more Bronsted acidity, as the parent AlPO-31 is electrically neutral without the required acidity. The catalytic activity of these molecular sieves has been examined in ethylation of toluene with ethanol in the vapour phase between  $300$  and  $450^\circ\text{C}$ , to gather supporting evidence

for isomorphous replacement of  $\text{Al}^{3+}$  in the framework. Toluene conversion is greater for metal-substituted molecular sieves than for the parent AIPO-31, proving increased acidity owing to metal substitution. Hence, lower valent metal-substituted aluminophosphate molecular sieves can be conveniently used as catalysts for dehydration of alcohols to ethers and alkylation of aromatics with alcohols in the vapour phase. As expected, isomorphously substituted AIPO-31 molecular sieves exhibit better toluene conversion and better yields of *m*-ethyl toluene in comparison to AIPO-5 and AIPO-11 molecular sieves due to their circular monodimensional channels.

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