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Synthesis, characterization and catalytic activity of ZAPO-5 and ZAPO-11

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Zinc containing aluminophosphates (ZAPO-5 and ZAPO-11) were synthesized hydrothermally using triethylamine and dipropylamine as templates. Structures were confirmed from X-ray powder patterns and unit cell parameters were calculated by a standard least-squares refinement technique. The isomorphous substitution of zinc in the aluminophosphate framework is evidenced by the considerable increase in unit cell volume and from MAS-NMR spectra. Acidity was determined by the TPD-TGA method which shows three different strengths of acid sites. FT-IR, chemical analysis and BET surface area were also reported. The physico-chemical properties of the catalysts were correlated towards the vapour phase transformation of camphene and the results are fully discussed.

Keywords: ZAPO-5; ZAPO-11; molecular sieves; camphene; solid state ^{27}Al and ^{31}P NMR

1. Introduction

Microporous aluminophosphate-based molecular sieves are a new generation of crystalline microporous oxides with one or more additional elements incorporated into the $AlPO_4$ framework. Isomorphous substitution is an important reaction in molecular sieve science. It allows the control of acidity and unit cell volume and has direct bearing on the activity and selectivity of the catalysts. Metal substituted aluminophosphates (MeAPO) mark the first demonstrated incorporation of divalent forms of cobalt, iron, magnesium, manganese and zinc into microporous framework during synthesis [1–3]. Compared to zeolites, aluminophosphate-based molecular sieves seem to have a larger variety of acid sites and a broader acid site distribution [4]. This is especially true for divalent metal substituted aluminophosphate molecular sieves. Among the known aluminophosphate molecular sieves, $AlPO_4$-5 and $AlPO_4$-11 have gained considerable attention on account of their straight channel system. Herein we report the synthesis, characterization and acidity of ZAPO-5 and ZAPO-11 and their catalytic activity towards the transformation of camphene.

2. Experimental

2.1. Materials

Aluminium isopropoxide (Fluka), zinc sulphate (BDH), orthophosphoric acid (85% Qualigens), triethylamine (TEA) (Fluka), dipropylamine (DPA) (Fluka) and camphene (Fluka) were used as purchased.

2.2. Synthesis of ZAPO-5

The gel composition used for ZAPO-5 synthesis was $0.1ZnO : 1TEA : 1Al_2O_3 : 1P_2O_5 : 40H_2O$. Aluminium isopropoxide (28.37 g) was soaked in 30 ml distilled water for 24 h in a stainless steel autoclave (316 type) and vigorously stirred for 1 h. While stirring, 1.99 g zinc sulphate dissolved in 7.8 ml phosphoric acid and 20 ml distilled water was added drop by drop and stirring continued for 1 h. TEA (9.7 ml) was added slowly and allowed for another 1 h stirring. The pH of the gel was 4.4. The autoclave was tightly closed and kept at 175°C under autogenous pressure for 22 h. Then it was cooled to room temperature to get the product whose pH was 9.5. The product was washed several times with distilled water and dried in an air oven at 110°C for 12 h.

2.3. Synthesis of ZAPO-11

ZAPO-11 was synthesized using the following gel composition of $0.1ZnO : 1DPA : 1Al_2O_3 : 1P_2O_5 : 40H_2O$. Aluminium isopropoxide (28.37 g) in 30 ml distilled water was stirred vigorously for 1 h after aging for 24 h. 1.99 g zinc sulphate dissolved in 7.8 ml phosphoric acid and 20 ml distilled water was added drop by drop. This was then stirred for 1 h. DPA (9.5 ml) was added dropwise and stirred for another 1 h. The gel pH was 3.9. A stainless steel autoclave (300 ml, 316 type) with the above contents was kept under autogenous pressure at 200°C for 22 h. The pH after synthesis was 9.7. The solid product formed was washed several times with distilled water and dried in an air oven at 110°C for 12 h.

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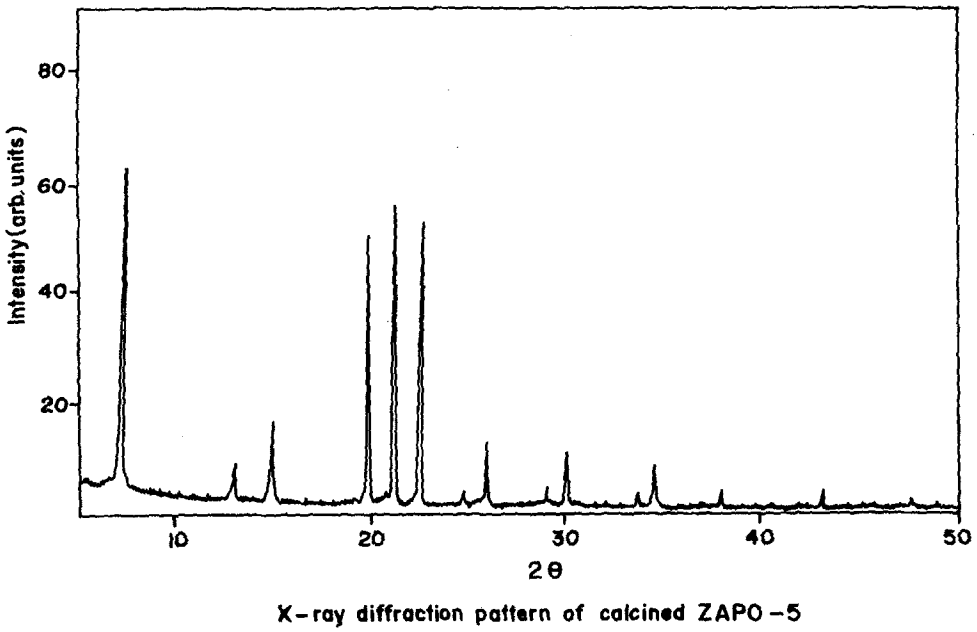

Fig. 1. XRD pattern of ZAPO-5.

Half of each sample was calcined at 550°C for 8 h to remove the template present in the sample.

2.4. Characterization

X-ray diffraction analysis was carried out employing a Siemens D500 diffractometer in the scan range of 2θ between 5 and 50° using Cu Kα as source. The peaks were identified with reference to a compilation of simulated XRD powder patterns [5]. Unit cell parameters were calculated using a standard least-squares refinement technique. ^{27}Al and ^{31}P NMR analysis was carried out using a Bruker MSL 300 spectrometer and IR spectra were recorded in a Bruker IFS 66v FT-IR spectrophotometer using KBr pellets. TG analyses were carried out with a 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 investigate the chemical composition of the samples. BET surface area was measured in a Micromeritics Pulse Chemisorb 2700 using nitrogen as adsorbent at −176°C. Initially samples were degasified at 200°C for 2 h in a flow of oxygen.

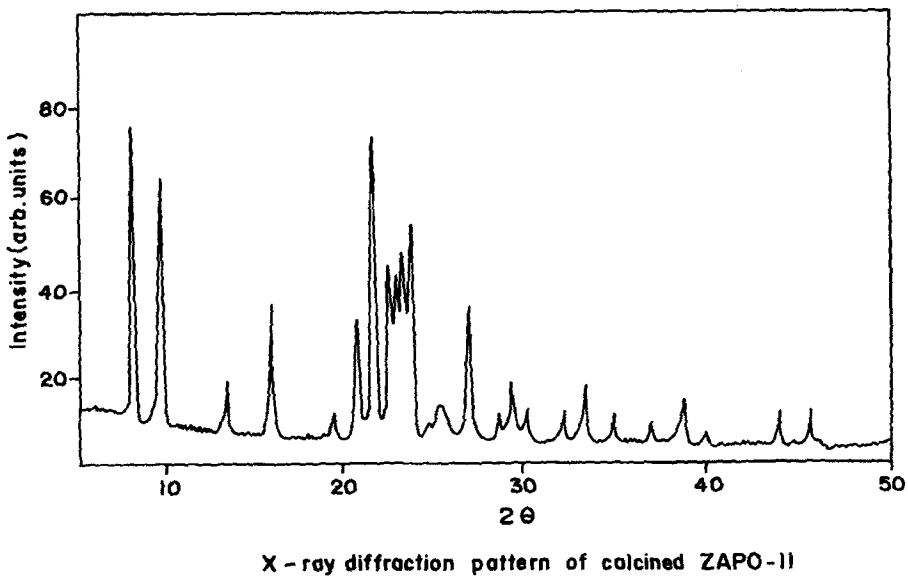

Fig. 2. XRD pattern of ZAPO-11.

Table 1
Unit cell parameters and unit cell volume

Catalyst	a(Å)	b(Å)	c(Å)	v(Å^3)
as-synthesized				
ZAPO-5	13.83	13.83	8.48	1404
ZAPO-11	13.46	18.71	8.40	2115
calcined				
ZAPO-5	13.78	13.78	8.42	1385
ZAPO-11	13.69	18.72	8.23	2109
$AlPO_4$-5	13.64	13.64	8.49	1368 [a]
$AlPO_4$-11	13.48	18.56	8.39	2099 [a]

[a] From ref. [7].

2.5. Acidity

Acidity was measured by temperature programmed desorption (TPD) of pyridine using TGA (Mettler TA 3000). Prior to adsorption, the samples were evacuated to 10^{-3} Torr at 450°C for 2 to 3 h. Then pyridine was allowed to equilibrate at room temperature in a closed vessel. TG analysis was carried out upto 500°C at a scanning rate of 10°C/min. From the weight loss at various temperature ranges, acidity and acidic strength in mmol/g were determined.

2.6. Catalytic studies

Catalytic transformation of camphene was studied in a fixed bed flow type quartz reactor at various temperatures and $(WHSV)^{-1}$. The description of the experimental set up is given elsewhere [6]. The reactant was fed by a syringe infusion pump and the products were analyzed by GC (Hewlett Packard 5890 A).

3. Results and discussion

3.1. Structure

The XRD patterns of as-synthesized ZAPO-5 and ZAPO-11 are shown in figs. 1 and 2 respectively. The patterns are well matched with reported patterns [5]. Unit cell parameters were calculated for both as-synthesized and calcined samples and are listed in table 1 along with unit cell parameters of $AlPO_4$-5 and $AlPO_4$-11 synthesized using the templates TEA and DPA respectively [7]. Substitution of zinc for aluminium consider-

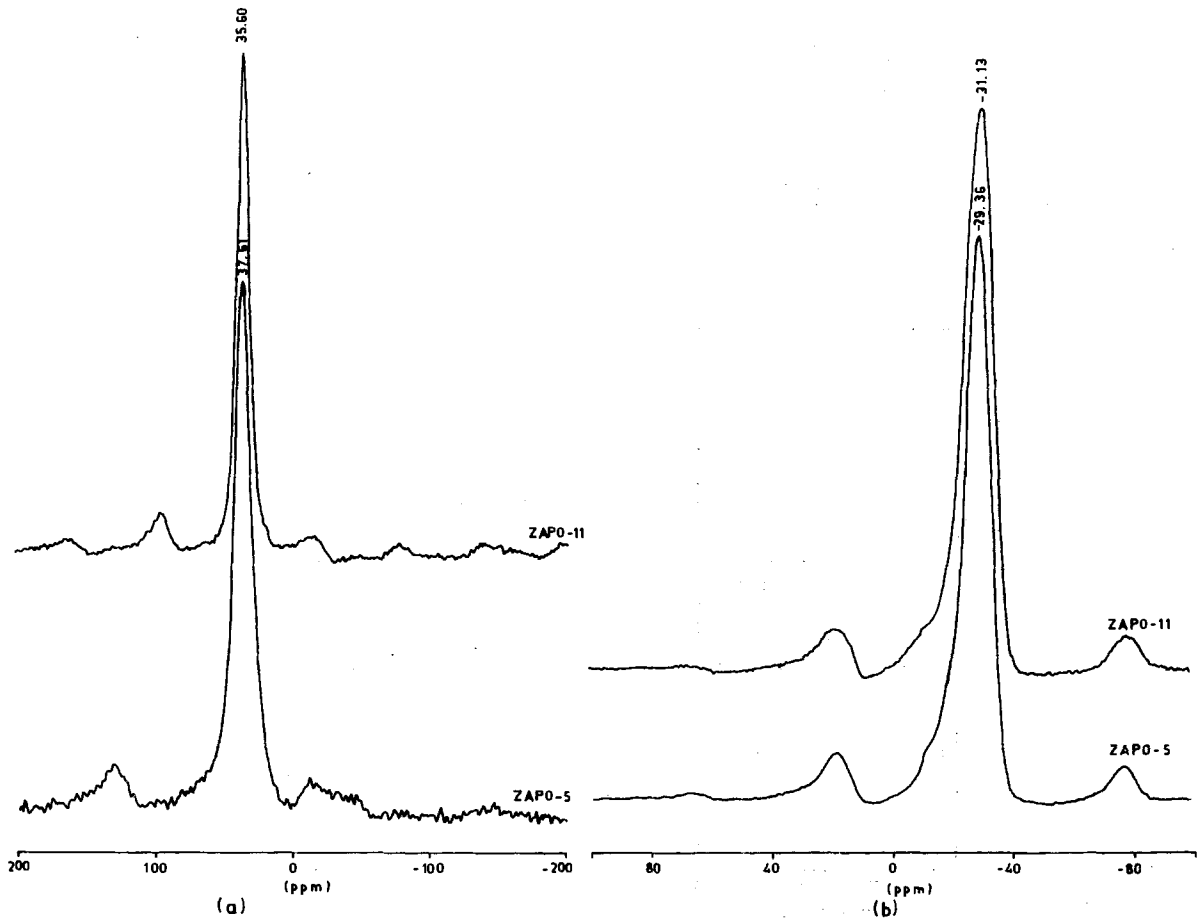

Fig. 3. ^{27}Al NMR (a) and ^{31}P NMR (b) spectra of ZAPO-5 and ZAPO-11.

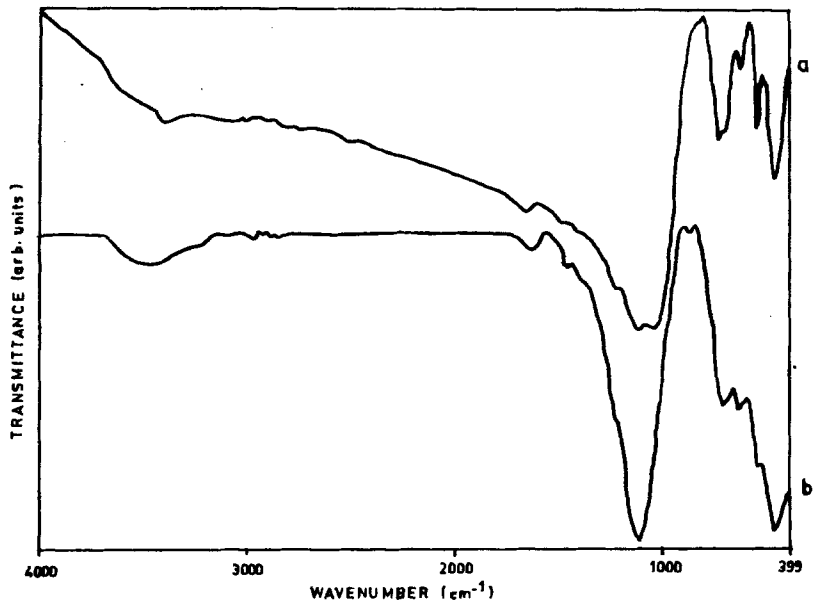

Fig. 4. FT-IR spectra of ZAPO-5 (a) and ZAPO-11 (b).

ably increases the overall unit cell volume which is convincing evidence for the isomorphous substitution of zinc in the aluminophosphate framework. However, the decrease in unit cell volume for the calcined samples may be due to removal of strain after the loss of templates from the voids. Fig. 3 illustrates ^{27}Al NMR and ^{31}P NMR of ZAPO-5 and ZAPO-11. The strong lines at 37.61 ppm (ZAPO-5) and 35.60 ppm (ZAPO-11) for aluminium and at −29.36 ppm (ZAPO-5) and −31.13 ppm (ZAPO-11) for phosphorus are characteristic of the unique tetrahedral environment of aluminium and phosphorus in the lattices of ZAPO-5 and ZAPO-11 [8,9]. The indication of a shoulder in the ^{31}P resonance accounts for zinc incorporated in the lattice. FT-IR spectra in the region encompassing the framework vibrations and –OH vibration of as-synthesized ZAPO-5 and ZAPO-11 are depicted in fig. 4.

TG and their corresponding derivative curves (DTG) of the samples are shown in fig. 5. These samples show a low temperature weight loss around 100°C which is attributed to the loss of water and high temperature weight losses in the range 250–550°C may be ascribed to the desorption of templates present in the intracrystalline pores. Further the desorption of templates proceeds

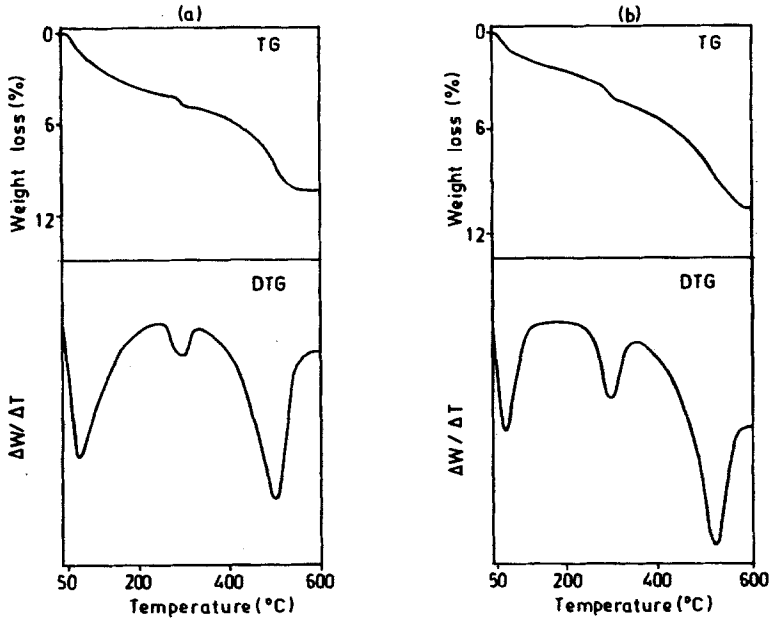

Fig. 5. TG and DTG curves for ZAPO-5 (a) and ZAPO-11 (b).

Table 2
Chemical composition and surface area

Catalyst	Chemical composition	Surface area (m^2/g)
ZAPO-5	$0.07ZnO : 0.96Al_2O_3 : 1P_2O_5$	260
ZAPO-11	$0.06ZnO : 0.95Al_2O_3 : 1P_2O_5$	202

in multiple stages, possibly the release of template first as free amine and then by degradation of proton or metal complexed amine [10]. The total weight loss is about 10.7 and 10.1% for ZAPO-5 and ZAPO-11 respectively. The results of chemical analysis and BET surface area presented in table 2 show a considerable decrease in aluminium content indicating that zinc replaces only aluminium and not phosphorus. ZAPO-5 possesses a higher surface area than ZAPO-11 (table 2) which may be attributed to the large pore size of ZAPO-5. However, the surface areas of ZAPO-5 and ZAPO-11 are almost similar to $AlPO_4$-5 (221 m^2/g) and $AlPO_4$-11 (202 m^2/g) [7] demonstrating that the pores of the structure are not blocked by the incorporation of zinc [11].

3.2. Acidity

Acidity of the catalysts was determined by TPD from pyridine desorption. The values are given in table 3. Peaks at various temperature ranges, 130–190°C, 190–280°C and 280–370°C are assigned as weak, moderate and strong acid sites respectively [12,13]. The weight loss in the temperature range 40–130°C is due to the loss of physisorbed pyridine. The higher acidity value of ZAPO-5 may be due to increased zinc substitution in ZAPO-5 as compared to ZAPO-11 and this has been evidenced from chemical analysis studies.

3.3. Catalytic transformation of camphene

Camphene is well known as a transformation product of α-pinene long before it was found in nature. Its isomerization products are used as fragrant chemicals as well as good solvents [6].

3.4. Effect of $(WHSV)^{-1}$ and temperature

The effect of $(WHSV)^{-1}$ on the conversion of camphene, product yield and product selectivity is given in table 4 while the effect of temperature on the conversion of camphene, product yield and product selectivity is presented in table 5. The data presented in the tables illustrate that increase in both $(WHSV)^{-1}$ and temperature increases the overall conversion of camphene over ZAPO-5 and ZAPO-11. The main product formed from this transformation is tricyclene. Though the yield of tricyclene increases or remains almost constant in some cases, its selectivity decreases with increase in both $(WHSV)^{-1}$ and temperature, whereas both yield and selectivity of bornylene and monocyclic terpenes – which include dipentene, terpinolene, α-terpinene, γ-terpinene, *p*-menthene and *p*-cymene – are found to increase with increase in $(WHSV)^{-1}$ and temperature. These results indicate that lower $(WHSV)^{-1}$ and temperature are favourable for the selective formation of tricyclene.

Table 6 presents the variation in the composition of monocyclics with respect to $(WHSV)^{-1}$ over ZAPO-5. The concentration of dipentene and terpinolene in the product decreases while that of α- and γ-terpinenes increases with increase in $(WHSV)^{-1}$, indicating that the former two are primary while the latter two are secondary menthadienes. On further increase in $(WHSV)^{-1}$, *p*-menthene and *p*-cymene are formed in considerable amounts with simultaneous decrease in the concentration of dipentene, terpinolene, α- and γ-terpinenes. This indicates that the menthadienes formed initially might

Table 3
Acidity and acidic strength of ZAPO-5 and ZAPO-11

Catalyst	Acidity (mmol/g)			
	weak	moderate	strong	total
ZAPO-5	0.18	0.15	0.06	0.39
ZAPO-11	0.17	0.14	0.03	0.34

Table 4
Effect of $(WHSV)^{-1}$ on the camphene conversion and product distribution. Temperature = 300°C, time on stream = 1 h

Sample	$(WHSV)^{-1}$ (h)			
	0.4	0.8	1.2	1.6
$AlPO_4$-5				
camphene conversion (wt%)	12.4	15.7	20.1	24.6
tricyclene yield (wt%)	11.9	14.9	19.1	23.5
bornylene yield (wt%)	0.5	0.7	0.9	1.1
tricyclene selectivity (%)	96.2	94.9	95.3	95.6
bornylene selectivity (%)	3.8	4.2	4.6	4.4
$AlPO_4$-11				
camphene conversion (wt%)	10.6	12.7	14.9	16.8
tricyclene yield (wt%)	10.3	12.4	14.3	16.1
bornylene yield (wt%)	0.3	0.3	0.5	0.6
tricyclene selectivity (%)	97.8	97.5	96.3	96.1
bornylene selectivity (%)	2.0	2.1	3.2	3.7
ZAPO-5				
camphene conversion (wt%)	48.6	53.7	58.9	69.3
tricyclene yield (wt%)	35.1	34.2	34.5	35.1
bornylene yield (wt%)	6.5	9.0	10.1	12.8
monocyclics yield (wt%)	6.9	10.1	14.3	21.3
tricyclene selectivity (%)	72.3	63.6	58.6	50.7
bornylene selectivity (%)	13.4	16.8	17.1	18.5
monocyclics selectivity (%)	14.3	18.9	24.3	30.8
ZAPO-11				
camphene conversion (wt%)	38.4	45.9	51.3	58.8
tricyclene yield (wt%)	31.3	34.8	36.5	40.2
bornylene yield (wt%)	4.9	7.5	9.3	10.8
monocyclics yield (wt%)	1.7	3.6	5.4	7.8
tricyclene selectivity (%)	81.4	75.8	71.2	68.4
bornylene selectivity (%)	12.7	16.3	18.2	18.4
monocyclics selectivity (%)	4.3	7.9	10.6	13.2

Table 5
Effect of temperature on the camphene conversion and product distribution. $(WHSV)^{-1}$ = 1.2 h, time on stream = 1 h

Sample	Temperature (°C)			
	250	300	350	400
$AlPO_4$-5				
camphene conversion (wt%)	16.2	20.1	25.4	30.9
tricyclene yield (wt%)	16.2	19.1	23.4	27.6
bornylene yield (wt%)	–	0.9	2.0	3.3
tricyclene selectivity (%)	100.0	95.3	92.1	89.3
bornylene selectivity (%)	–	4.6	7.9	10.7
$AlPO_4$-11				
camphene conversion (wt%)	10.7	14.9	17.3	192
tricyclene yield (wt%)	10.7	14.3	15.9	17.3
bornylene yield (wt%)	–	0.5	1.4	1.9
tricyclene selectivity (%)	100.0	0.5	1.4	1.9
bornylene selectivity (%)	–	3.2	8.1	8.9
ZAPO-5				
camphene conversion (wt%)	50.7	58.9	69.4	83.7
tricyclene yield (wt%)	31.3	34.5	37.9	42.4
bornylene yield (wt%)	8.2	10.1	12.1	15.8
monocyclics yield (wt%)	11.2	14.3	19.4	25.3
tricyclene selectivity (%)	61.7	58.6	54.7	50.3
bornylene selectivity (%)	16.2	17.1	17.4	18.9
monocyclics selectivity (%)	22.1	24.3	27.9	30.2
ZAPO-11				
camphene conversion (wt%)	45.6	51.3	59.8	70.2
tricyclene yield (wt%)	31.8	36.5	39.9	42.3
bornylene yield (wt%)	7.8	9.3	10.2	12.3
monocyclics yield (wt%)	5.2	5.4	9.7	15.6
tricyclene selectivity (%)	69.7	71.2	66.7	60.2
bornylene selectivity (%)	17.1	18.2	17.1	17.5
monocyclics selectivity (%)	11.4	10.6	16.2	22.2

have undergone further conversion to *p*-menthene and *p*-cymene probably by different reactions, like dehydrogenation and disproportionation [14].

3.5. *Influence of acidity*

Acidity has a direct bearing on camphene conversion.

Table 6
Effect of $(WHSV)^{-1}$ on monocyclics distribution. Temperature = 300°C, time on stream = 1 h

Sample ZAPO-5	$(WHSV)^{-1}$ (h)			
	0.4	0.8	1.2	1.6
monocyclics yield (wt%)	6.9	10.1	14.3	21.3
product distribution (%)				
dipentene	52.3	30.9	–	–
terpinolene	47.7	20.4	–	–
α-terpinene	–	26.2	10.6	–
τ-terpinene	–	22.5	4.8	–
p-menthene	–	–	30.9	31.2
p-cymene	–	–	53.7	68.8

For instance, the conversion of camphene over ZAPO-11 at 300°C and 1.2 h $(WHSV)^{-1}$ is 51.3% whereas under the identical condition 58.9% conversion of camphene over ZAPO-5 is due to the difference in acidity value (table 3). Increase in acidity decreases the selectivity of tricyclene whereas monocyclics are formed in considerable amounts over ZAPO-5 compared to ZAPO-11. This indicates that the weak acid sites are sufficient for the formation of tricyclene whereas strong acid sites are a necessary condition for the formation of monocyclics.

The effects of $(WHSV)^{-1}$ and temperature on the conversion of camphene and product yield over $AlPO_4$-5 and $AlPO_4$-11 are also presented in table 4 and table 5 respectively. Though $AlPO_4$-5 and $AlPO_4$-11 possess neutral frameworks, the low conversion over these catalysts may be attributed to the presence of weak acid sites created from lattice imperfections. The comparison of experimental data on the conversion and product distribution over ZAPO-5 and ZAPO-11 with that of $AlPO_4$-5 and $AlPO_4$-11 clearly indicates that increase in acidity by the incorporation of zinc in the framework is the cause for increase in conversion and product distribution. For instance, the conversion of camphene over $AlPO_4$-5 at 300°C and 1.2 h $(WHSV)^{-1}$ is only 20.1% whereas it is increased to 58.9% over ZAPO-5 under the same conditions. Similarly for $AlPO_4$-11 and ZAPO-11 the values are 14.9 and 51.3% respectively.

4. Conclusion

Strict alternation of Al and P tetrahedra made aluminophosphate molecular sieves become neutral frameworks. Isomorphous substitution of divalent zinc over $AlPO_4$-5 and $AlPO_4$-11 changes their physico-chemical and catalytic properties. Further, the weak acid sites are sufficient for the formation of tricyclene whereas strong acid sites lead to the formation of monocyclics in considerable amounts.

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