Comparison of Thermal Stability, Acidity, Catalytic Properties and Deactivation Behaviour of Novel Aluminophosphate-based Molecular Sieves of Type 36

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MnAPO-36, ZAPO-36, CoAPO-36, MAPO-36 and MAPSO-36 with similar molar chemical composition have been prepared and characterized. Magnesium-incorporated aluminophosphate of type 36 showed higher thermal stability than the manganese- zinc- or cobalt-incorporated aluminophosphates. In situ IR acidity measurements of the type 36 aluminophasphates show the presence of Brønsted and Lewis acid sites. In the mono-substituted aluminophosphates, the concentration of Brønsted acid sites and the ratio of Brønsted to Lewis acid sites is higher on MAPO-36 than on MnAPO-36, ZAPO-36 and CoAPO-36. Brønsted acid site density is higher on MAPSO-36 (di-substituted aluminophosphate) than on MAPO-36. The results of stepwise thermal desorption and temperature-programmed desorption of pyridine indicate that the number of strong acid sites and acid strength distribution are strongly affected by the nature of the element substituted in the AIPO₄-36 framework. The MnAPO-36, ZAPO-36, CoAPO-36, MAPO-36 and MAPSO-36 possess significant catalytic activity in the cracking of aliphatic hydrocarbons, conversion of o-xylene and also in the reaction of ethanol to form aromatics at 673 K. In the ethanol, pentane, 3-methylpentane, cyclohexane, o-xylene and ethylbenzene conversion reactions, MAPSO-36 exhibited higher catalytic activity than MnAPO-36, ZAPO-36, CoAPO-36 and MAPO-36. The deactivation behaviour of these aluminophosphate molecular sieves in the ethylbenzene conversion reaction was also investigated. Results show that the type of element incorporated also strongly affects the acidic and catalytic properties of the aluminophosphates.

Investigations on microporous crystalline aluminophosphates with different heteroatoms is of broad interest because of the development of new catalysts. Recently, a series of newgeneration metal aluminophosphate (MeAPO-*n*), silico aluminophosphate (SAPO-*n*) and silico-metal aluminophosphate (MeAPSO-*n*) molecular sieves was reported.¹⁻⁴ Type 36 aluminophosphate, a novel crystalline microporous molecular sieve,²⁻⁴ has a unique three-dimensional structure with monoclinic symmetry (cell parameters: a = 13.148 Å, b = 21.577 Å, c = 5.164 Å and $\beta = 91.84^{\circ}$) and contains a unidimensional 12-ring elliptical channel system having a free aperture between 6.5 and 7.4 Å.^{5,6}

MAPO-36 (magnesium-substituted aluminophosphate) shows significant catalytic activity in the aliphatic and aromatic hydrocarbon and alcohol conversion reactions^{3,7} and higher acidity than MAPO-5, SAPO-5 and AlPO₄-5.8 Since type 36 aluminophosphates are more catalytically active than large-pore aluminophosphates of type 5 and 46,^{3,7,9} it is important to understand the changes in the physical and chemical properties of this material produced by the incorporation of different elements into the AlPO₄-36 framework. The acidic and catalytic properties of the aluminophosphate are dependent on the type of framework-substituted elements. So far, very little information is available on the acidity and catalytic behaviour of type 36 aluminophosphates with differ-ent elements incorporated.^{3,7,8} Therefore, the present study deals with the thermal stability, surface properties, acidity, acid strength distribution, catalystic properties and deactivation of MnAPO-36, ZAPO-36, CoAPO-36, MAPO-36 and MAPSO-36 molecular sieves.

Experimental

The type 36 aluminophosphate material was synthesized by hydrothemal crystallization from a reactive aluminophosphate gel containing additional cation(s) [Mn, Zn, Co, Mg, (Mg + Si)] and tripropylamine as organic template. The typical gel compositions used to obtain pure aluminophos-

phate of type 36 were as follows: Pr₃N-MnAPO-36, 1.95 $Al_2O_3 \cdot 1.01 \ \tilde{P}_2O_5 \cdot 40.0 \ H_2O \cdot 0.33 \ HOAc; \ Pr_3N-CoAPO-36,$ 2.0 Pr₃N · 0.17 CoO · 0.92 Al₂O₃ · 1.0 P₂O₅ · 40.0 H₂O; Pr₃N-1.80 $Pr_{1}N \cdot 0.17$ MgO · 0.92 $Al_2O_3 \cdot 1.0$ MAPO-36 P2O5 40.0 H2O 0.33 HOAc and Pr3N-MAPSO-36, 1.86 $Pr_3N \cdot 0.17 MgO \cdot 0.92 Al_2O_3 \cdot 0.085 SiO_2 \cdot 0.962 P_2O_5 \cdot 40.0$ $H_2O \cdot 0.33HOAc$. The reactive aluminophosphate-based gel was crystallized initially at 378 K for 50 h and finally at 423 K for 24 h. The sources of Al₂O₃, P₂O₅, MnO, ZnO, CoO, SiO₂ and MgO were aluminium isopropoxide (Fluka), orthophosphoric acid [(85%) Merck, FRG], manganese acetate (Merck, FRG), zinc acetate (Merck, FRG), cobalt nitrate hexahydrate (Merck, FRG), Kieselgel 500 (Merck, FRG) and magnesium acetate (Merck, FRG), respectively. The tripropylamine used was synthetic grade (Merck). The procedures for gel preparation and catalyst processing are already reported.¹⁰ The as-synthesized MnAPO-36, ZAPO-36, CoAPO-36, MAPO-36 and MAPSO-36 were calcined at 773, 753, 763, 813 and 763 K, respectively, for 16 h. Details of the characterization techniques, acidity and catalytic activity measurements are mentioned elsewhere.¹⁰⁻¹³ The reaction conditions are given in the respective tables and figures.

Results

The characteristics of MnAPO-36, ZAPO-36, CoAPO-36, MAPO-36 and MAPSO-36 are presented in Table 1. Characterization of these materials by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetry/differential thermogravimetry/differential thermal analysis (TG/DTG/DTA), and N₂- and H₂O-sorption capacity measurements indicated their highly crystalline nature. The elemental composition of these materials obtained by atomic absorption spectroscopy (AAS) and chemical analysis shows that they do not possess excess of Al, P or the substituted element. Morphological investigations revealed that the

 Table 1
 Type 36 aluminophosphate-based molecular sieves and their properties

		N sorption	H O sorption	c	rystal	framework charge
sieve	molar chemical composition	capacity/mmol g ⁻¹	capacity/mmol g ⁻¹	shape	length/µm	(electron/T atom)
MnAPO-36	0.16 MnO $\cdot 0.92$ Al ₂ O ₂ $\cdot 1.0$ P ₂ O ₅	5.44	17.1	Т	10	-0.04
ZAPO-36	0.16 ZnO $\cdot 0.92$ Al $\cdot O_3 \cdot 1.0$ P $\cdot O_5$	5.43	17.0	Т	8	-0.04
CoAPO-36	$0.16C_{0}O \cdot 0.92Al_{2}O_{3} \cdot 1.0P_{2}O_{5}$	5.46	17.1	Т	14	-0.04
MAPO-36	$0.16MgO \cdot 0.92Al_{2}O_{3} \cdot 1.0P_{2}O_{5}$	5.48	17.2	Т	12	-0.04
MAPSO-36	$0.158 \widetilde{MgO} \cdot 0.082 \widetilde{SiO}_2 \cdot 0.92 \widetilde{Al}_2 O_3 \cdot 0.959 P_2 O_5$	5.45	17.1	Т	11-15	-0.06

T: Thin, rod-like.

crystals are thin and rod-like, 8–15 μ m in length. Type 36 aluminophosphates possess higher N₂- and H₂O-sorption capacities than type 5 aluminophosphates.^{3,8} The results of the thermal analysis indicated that is an oxidizing atmosphere, the total weight loss of the as-synthesized MnAPO-36, ZAPO-36, CoAPO-36, MAPO-36 and MAPSO-36 amounts to 14.6, 15.3, 14.4, 14.0 and 14.1 wt.%, respectively.

The surface composition of the type 36 aluminophosphates determined by X-ray photoelectron spectroscopy (XPS) measurements are listed in Table 2. In the calcined MnAPO-36, CoAPO-36, MAPO-36 and MAPSO-36 samples but not ZAPO-36, the Al: P ratio on the surface is higher than that in the bulk, which indicates that the concentration of aluminium is higher on the surface of these materials. Comparison of bulk and surface E : P ratios [framework substituted atom : phosphorus, i.e. Mn : P in MnAPO-36, Zn : P in ZAPO-36, Co: P in CoAPO-36, Mg: P in MAPO-36 and (Mg + Si): P in MAPSO-36] indicated that the bulk concentration of the framework-substituted atom is lower than the surface concentration for ZAPO-36, MAPO-36 and MAPSO-36. The XPS binding energy data for the aluminophosphates are given in Table 3. The binding energies were referenced to Au $4f_{7/2}$ at 84.0 eV (precision $\pm 0.10-0.15$ eV). The binding energy measured for Al 2p (74.1-75.4 eV) in the type 36 aluminophosphates and Si 2p (102.7 eV) in MAPSO-36 are similar to that of the tetrahedrally coordinated Al 2p and Si 2p in the low-silica zeolites.¹⁴ The binding energy for P 2p and O 1s are in the ranges 134.0-135.8 and 532.0-532.8

eV, respectively. The observed binding energy for $Mn 2p_{3/2}$ in MnAPO-36 is 644.8 eV, which is close to that of tetrahedrally coordinated Mn in KMnO₄.¹⁵ The binding energy for Zn $2p_{3/2}$ in ZAPO-36 is 1022.6 eV and for Co $2p_{3/2}$ in CoAPO-36 is 782.5 eV. In the case of the MAPO-36 and MAPSO-36 samples, the Mg 2p binding energy values (50.4 50.3 eV) are close to the binding energy of tetrahedrally coordinated Mg in the spinel structure.^{16,17}

Fig. 1 shows the variation in thermal stability of the aluminophosphate-based materials with the frameworkincorporated atom. The crystallinity of MnAPO-36, ZAPO-36, CoAPO-36 and MAPSO-36 remains 100% at their respective calcination temperature. The crystallinity of ZAPO-36, CoAPO-36 MnAPO-36. and MAPSO-36 decreases above their respective calcination temperature. Compared with MnAPO-36, ZAPO-36, CoAPO-36, and MAPSO-36, MAPO-36 possesses higher thermal stability. The order of thermal stability (expressed in terms of crystallinity at 825 K) is as follows: MAPO-36 > MnAPO-36 > MAPSO-36 > CoAPO-36 > ZAPO-36. The results of the thermal stability of the aluminophosphate materials indicate the dependence of the thermal stability of the material on the nature of the framework-substituted element.

In situ infrared investigations of chemisorbed pyridine on the aluminophosphates of type 36 revealed the presence of Brønsted and Lewis acid sites. For these materials, Brønsted and Lewis acid sites were observed in the ranges 1543-1545cm⁻¹ and 1447-1451 cm⁻¹, respectively. The ratio of

Table 2 Surface and bulk composition of type 36 aluminophosphate-based molecular sieves

						atomi	c ratio	
		surface	composition	(atom %)	A	l : P ^a	E	: P ^a
molecular sieve	Al 2p	P 2p	O 1s	E	bulk	surface	bulk	surface
MnAPO-36	16.73	18.06	64.80	Mn 2p _{3/2} 0.38	0.92	0.93	0.08	0.02
ZAPO-36	15.44	17.51	65.12	Zn 2p _{3/2} 1.93	0.92	0.88	0.08	0.11
CoAPO-36	16.80	17.0	65.10	Co $2p_{3/2}$ 1.10	0.91	0.99	0.08	0.06
MAPO-36	16.77	18.14	61.22	Mg 2p 3.86	0.92	0.93	0.08	0.21
MAPSO-36	15.96	13.28	63.56	Mg 2p 1.50 Si 2p 5.69	0.96	1.2	0.13	0.54

^a All ratios quoted relative to unity. E, Framework substituted atom(s) [*i.e.* Mn in MnAPO-36, Zn in ZAPO-36, Co in CoAPO-36, Mg in MAPO-36 and (Mg + Si) in MAPSO-36].

 Table 3
 XPS data for type 36 aluminophosphate-based molecular sieves

		bind	ing energy/eV ^a		
molecular sieve	Al 2p	Р 2р	O 1s	E	
MnAPO-36	75.4	135.8	532.8	Mn 2p _{3/2} 644.8	
ZAPO-36	75.3	134.9	532.6	$Zn 2p_{3/2}$ 1022.6	
CoAPO-36	75.0	134.7	532.0	$Co 2p_{3/2} 782.5$	
MAPO-36	74.1	134.0	532.1	Mg 2p 50.4	
MAPSO-36	74.7	134.5	532.4	Mg 2p 50.3	Si 2p 102.7

^{*a*} Referenced to Au $4f_{7/2} = 84.0 \text{ eV}.$



Fig. 1 Dependence of the thermal stability on the type of framework-incorporated atom in $AIPO_4$ -36 (calcination temperature 825 K, period 16 h)

Brønsted to Lewis acid sites at 473 K is lower on MnAPO-36 than on the other aluminophosphates (Fig. 2). The order of the Brønsted to Lewis acid sites ratio at 473 K is as follows: MnAPO-36 < ZAPO-36 < CoAPO-36 < MAPO-36 < MAPSO-36. In the case of the mono-substituted aluminophosphates, the Brønsted to Lewis acid sites ratio indicated that the incorporation of Mg into the AlPO₄-30 framework produces a greater number of Brønsted acid sites then the substitution of Mn, Zn or Co into the framework. In the case of MAPSO-36, a disubstituted aluminophosphate, the presence of a higher concentration of Brønsted acid sites than that on MAPO-36 is attributed to the additional framework negative charge developed by the incorporation of Si into the MAPO-36 framework. In the MAPO-36 and MAPSO-36 samples, the concentrations of magnesium in the aluminophosphate are the same. The ratio of Brønsted to Lewis acid sites revealed that the density of Brønsted acid sites and acidity of the aluminophosphates of type 36 are strongly dependent on the type of element incorporated into the AlPO₄-36 framework.

The site energy distribution obtained from stepwise thermal desorption (STD) of pyridine on the type 36 aluminophosphates is shown in Fig. 3. The strength of the site involved in the pyridine chemisorption is expressed in terms of the desorption temperature (T_d) , which lies in the range of temperatures in which the chemisorbed pyridine is desorbed. Here, T_d^* is a measure of the maximum strength possessed by the site and corresponds to the temperature at which the pyridine chemisorbed on the strongest sites is desorbed. The columns in the figure show the strength distribution of the sites [equivalent to 0.21 (MnAPO-36), 0.23 (ZAPO-36), 0.10(CoAPO-36), 0.10 (MAPO-36) and 0.20 mmol g⁻¹



Fig. 2 Dependence of the Brønsted to Lewis acid sites ratio $(n_{Brønsted}/n_{Lewis})$ on the type of framework-incorporated atom in AlPO₄-36



Fig. 3 Acid strength distribution on (□) MnAPO-36, (■) ZAPO-36, (∞) CoAPO-36, (∞) MAPO-36 and (∞) MAPSO-36, $T_d = 1$, 323-373; 2, 373-423; 3, 423-473; 4, 473-523; 5, 523-573; 6, 573-673 and 7, 673- T_d^* K.

(MAPSO-36)] involved in the chemisorption at the lowest temperature of the STD (*i.e.* 323 K). Sites of strength 673 < $T_{\rm d}/{\rm K} \leq T_{\rm d}^*$ were obtained from the amount of pyridine chemisorbed at 673 K. On the other hand, the sites of strength $T_1 < T_d \leq T_2$ were obtained from the amount of pyridine which was initially chemisorbed at T_1 , but desorbed by increasing the temperature to T_2 . Fig. 4 shows the temperature dependence of the chemisorption of pyridine on the aluminophosphates. The chemisorption data were obtained from the STD data by the procedure described earlier.^{10–13} The chemisorption of pyridine at higher temperatures points to the involvement of the stronger sites. The q_i vs. T curve, therefore, presents a type of site energy distribution in which the number of sites is expressed in terms of the amount of pyridine chemisorbed as a function of the sorption temperature. The STD and temperature-programmed desorption (TPD) of pyridine investigations have revealed the presence of a broad acid strength distribution on the type 36 aluminophosphates. Comparison of the acid strength distribution and the chemisorption vs. temperature curves for the aluminophosphates of type 36 shows that MnAPO-36, ZAPO-36, CoAPO-36, MAPO-36 and MAPSO-36 differ markedly in their acidity and acidity distribution. The pyridine STD results show that the site energy distribution is less broad and very few weak acid sites are present on MAPO-36 compared with MnAPO-36, ZAPO-36, CoAPO-36 and MAPSO-36. The amount of pyridine chemisorbed above 673 K in the aluminophosphates is as follows: MnAPO-36, 0.012 mmol g^{-1} ; ZAPO-36, 0.030 mmol g^{-1} ; CoAPO-36, 0.034 mmol g^{-1} ; MAPO-36, 0.045 mmol g^{-1} ; MAPSO-36, 0.050 mmol g^{-1} . The order of the strong acid sites over the aluminophos-



Fig. 4 Temperature dependence of the chemisorption of pyridine on (\bigcirc) MnAPO-36, (\bigcirc) ZAPO-36, (\triangle) CoAPO-36, (\blacktriangle) MAPO-36 and (\square) MAPSO-36

phates follows the order of the Brønsted to Lewis acid sites ratio.

In Table 4, the results of ethanol conversion over MnAPO-36, ZAPO-36, CoAPO-36, MAPO-36 and MAPSO-36 are compared. In the ethanol conversion reaction over monosubstituted aluminophosphates, MAPO-36 exhibited a higher conversion and yield of aromatics than MnAPO-36, ZAPO-36 and CoAPO-36. This is attributed to the presence of more strong acid sites on MAPO-36. In the case of MAPSO-36 (a di-substituted aluminophosphate), the conversion of ethanol and formation of aromatics were higher than on MnAPO-36, ZAPO-36, CoAPO-36 and MAPO-36. The observed order of catalytic activity and aromatics selectivity is the same as found for the Brønsted to Lewis acid sites ratio. Current investigations on the acidity and acid strength distribution on these materials indicated that the concentration of Brønsted acid sites is higher on MAPSO-36. Also TPD and STD of pyridine over these materials showed that the amount of pyridine chemisorbed on MAPSO-36 above 673 K was higher, indicating the presence of stronger acidic sites. The aliphatics distribution in the ethanol conversion reaction is quite different for the various aluminophosphates. MAPO-36 showed lower yields of C₂ aliphatics and higher C_3 , C_4 and C_{5+} -yields than MnAPO-36, ZAPO-36, CoAPO-36 and MAPSO-36. The distribution of the aromatics formed on MnAPO-36, ZAPO-36, CoAPO-36, MAPO-36 and MAPSO-36 is also quite different. MAPO-36 gives higher benzene and toluene yields and lower trimethylbenzene vield than the other aluminophosphates. The yield of xylenes in the ethanol conversion reaction is higher on CoAPO-36, while the yield of C_{9+} -aromatics is higher on ZAPO-36. The large differences on the acidity and acid strength distribution on the aluminophosphates due to incorporation of different types of elements in the AlPO₄-36 framework are responsible for the different distributions of aromatics in the ethanol conversion reaction.

The results in Tables 5 and 6 indicate that the catalytic activity of the aluminophosphates varies in the pentane and cyclohexane reactions. In the pentane and cyclohexane conversion reactions, MAPSO-36 showed higher catalytic activity and aromatic formation than MnAPO-36, ZAPO-36, CoAPO-36 and MAPO-36. Note that the distributions of aliphatics and aromatics in the reaction of pentane and cyclohexane over the catalytic activity and formation of aromatics in the pentane and cyclohexane reactions is as follows: MnAPO-36 \leq ZAPO-36 < CoAPO-36 \leq MAPO-36 < MAPO-36 < MAPO-36 < matrix formation of benzene and toluene were greater on ZAPO-36, while xylene forma-

50 0 aromatics concentration (wt.%) MAPSO-36 40 conversion (%), MAP0-36 30 CoAPO-36 Ο 20 MnAPO-36 0 10 MAPSO-36 MnAPO-36 CoAPO 36 MAPO-36 . 0 0.00 0.01 0.02 0.03 0.04 0.05 0.06 strong acid sites concentration/mmol g⁻¹

Fig. 5 Changes in catalytic activity with the type of framework-incorporated atom in $AIPO_4$ -36: (\bigcirc) concentration of aromatics, (\bigcirc) conversion

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Fig. 6 Catalytic activity of (\bigcirc) MnAPO-36, (\spadesuit) ZAPO-36, (\triangle) CoAPO-36, (\triangle) MAPO-36 and (\square) MAPSO-36 in the conversion of ethylbenzene as a function of pulse number. Reaction conditions: amount of catalyst 100 mg, He flow rate 30 cm³ min⁻¹, temperature 673 K, pulse size 1 mm³.

tion was greater over MAPSO-36. In the cyclohexane reaction, the yields of xylenes and trimethylbenzenes were higher over CoAPO-36.

The catalytic activities of the aluminophosphates in the pentane and cyclohexane conversion reactions are also expressed in terms of the catalytic turnover rates, $N_{\rm E}$ and $N_{\rm F}$. $N_{\rm E}$ denotes the catalytic turnover rate per frameworksubstituted atom [i.e. Mn in MnAPO-36, Zn in ZAPO-36, Co in CoAPO-36, Mg in MAPO-36 and (Mg + Si) in MAPSO-36]. $N_{\rm F}$ denotes the catalytic turnover rate per strong acid site (i.e. number of molecules reacted per strong acid site s^{-1}). In the pentane conversion reaction over the catalysts (Table 7), the turnover rate per frameworksubstituted atom $(N_{\rm E})$ is higher for MAPO-36 followed by MAPSO-36 and CoAPO-36, whereas the turnover rate per strong acid site (N_F) is in the order: MAPO-36 > MAPSO-36 > MnAPO-36 > CoAPO-36 > ZAPO-36. While in the cyclohexane conversion reaction, the turnover rate per framework-substituted atom (N_E) is higher for MAPO-36 followed by MAPSO-36 and CoAPO-36, whereas the turnover rate per strong acid site (N_F) is in the order: MAPSO-36 = MAPO-36 > CoAPO-36 > MnAPO-36 > ZAPO-36

Fig. 5 shows the correlation between the catalytic activity of the aluminophosphates in the conversion of 3methylpentane and the strong acid sites. The catalytic activity of the aluminophosphate depends on the number of strong acid sites and the type of framework-incorporated element. The manganese-incorporated aluminophosphate of type 36 shows a lower conversion of 3-methylpentane and lower concentration of aromatics formed.

MAPSO-36 showed higher catalytic activity in the oxylene conversion reaction (Table 8) and formation of more toluene, trimethylbenzenes and other C_{9+} aromatics. The observed xylene losses (which reflects the selectivity for isomerization in the o-xylene conversion) over the aluminophosphates are as follows: CoAPO-36 (9.2 wt.%), MnAPO-36 (9.6 wt.%), ZAPO-36 (10.0 wt.%), MAPO-36 (20.8 wt.%) and MAPSO-36 (25.8 wt.%). The higher xylene losses over MAPO-36 and MAPSO-36 indicate that disproportionation is more pronounced than isomerization in the o-xylene conversion reaction over these materials.

Fig. 6 shows the result of ethylbenzene conversion on the aluminophosphates. The conversion of ethylbenzene (in the first pulse experiment) over MAPO-36 and MAPSO-36 is higher than that over MnAPO-36, ZAPO-36 and CoAPO-36. The conversion of ethylbenzene decreases with pulse number. The influence of pulse number on the fractional ethylbenzene activity (x) [where x = (conversion of ethylbenzene for a par-

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					product	distribution	t (wt.%)					aroma	tics distril	bution		
molecular sieve	conversion (%)	aromatics concentration (wt.%)	CH₄	C ₂ aliphatics	C ₃ aliphatics	C ₄ aliphatics	C ₅₊ aliphatics	aromatics	total	benzene	toluene	ethylbenzene	xylenes	trimethyl benzenes	other C ₉₊ aromatics	total
MnAPO-36	63.1	0.9	0.1	94.5	1.8	1.2	1.0	1.4	<u>10</u>	4.0	18.0	3.5	30.0	24.5	20.0	8
ZAPO-36	70.0	1.7	0.3	90.3	2.0	3.0	2.0	2.4	100	5.9	17.6	2.9	32.3	17.6	29.4	100
CoAPO-36	72.6	3.4	0.3	92.5	0.7	0.8	1.0	4.7	100	2.9	11.8	2.9	50.1	14.7	17.6	100
MAPO-36	76.0	4.4	0.1	61.4	7.0	8.0	17.7	5.8	<u>10</u>	7.6	31.4	Ι	40.1	8.9	12.0	100
MAPSO-36	85.1	5.7	0.1	78.1	5.1	1.8	8.2	6.7	100	3.5	28.0	8.8	35.0	15.9	8.8	100
Reaction cond	litions: amou	int of catalyst 50	mg, He	flow rate 90	$cm^3 min^{-1}$,	pulse size 5	mm ³ , tempe	stature 673 K								

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 Table 4
 Conversion of ethanol on type 36 aluminophosphate-based molecular sieves

				Table 5 C	conversion of	pentane on t	ype 36 alumi	nophosphate	-based m	olecular siev	'es				
					product	distribution	(wt. %)				e	romatics di	stribution (w	t.%)	
molecular sieve	conversion (%)	aromatics concentration (wt.%)	CH4	C ₂ aliphatics	C ₃ aliphatics	C ₄ alphatics	C ₅₊ alphatics	aromatics	total	benzene	toluene	xylenes	trimethyl benzenes	other C ₉₊ aromatics	total
MnAPO-36	5.4	1.2	1.4	34.5	22.5	16.9	2.5	22.2	100	8.3	16.7	29.0	23.0	23.0	8
ZAPO-36	12.3	1.8	2.0	31.5	28.4	20.5	3.0	14.6	100	11.1	38.9	22.2	11.1	16.7	100
CoAPO-36	14.3	2.1	2.2	29.5	29.0	21.4	3.3	14.6	100	5.6	22.2	27.8	5.6	38.8	100
MAPO-36	33.1	2.6	3.0	27.4	32.0	24.5	5.5	7.9	100	4.8	14.3	28.6	14.3	38.0	100
MAPS-36	36.2	3.3	2.5	23.8	28.7	31.8	4.1	9.1	100	0.9	30.3	44.5	15.2	9.1	100
Deaction cond	tione: amount	of catalvet 100 mg	n Hefton	v rate 30 cm ³	min ^{- 1} nulee	ciza 1 mm ³	temperature	X 773 V							

Reaction conditions: amount of catalyst 100 mg, He flow rate 30 cm³ min⁻¹, pulse size 1 mm³, temperature 673 K.

				Table 6	Conversion	of cyclohexa	ine on type	36 aluminoph	osphate-	-based mole	scular sieve	s				
					product (distribution	(wt. %)					aromatio	cs distribut	tion (wt.%)		
molecular sieve	conversion (%)	aromatics concentration (wt.%)	CH₄	C ₂ aliphatics	C ₃ aliphatics	C ₄ alphatics	C _{5 +} alphatics	aromatics	total	benzene	toluene	ethyl benzene	xylenes	trimethyl benzenes	other C _{9f} aromatics	total
MnAPO-36	4.9	0.8	1.4	10.0	13.1	7.5	51.8	16.3	100	1.6	20.6	1.6	36.5	26.0	13.7	100
ZAPO-36	11.6	2.0	3.3	10.4	8.0	7.9	53.2	17.2	100	4.4	14.2	2.3	34.6	24.0	20.5	100
CoAPO-36	20.1	4.3	1.4	10.1	13.1	12.8	41.2	21.4	100	1.7	20.3	6.4	38.2	26.4	7.0	100
MAPO-36	35.6	9.0	1.7	22.4	16.0	12.0	22.6	25.3	100	6.0	19.2	4.3	31.4	19.6	19.5	100
MAPSO-36	44.6	11.1	2.0	14.8	20.1	17.4	20.8	24.9	100	2.5	22.4	5.8	35.8	18.0	15.5	100

31.85

5315

78.5

78.5

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1.77

3.05

5.27

4.35

hexane at 673 K cyclohexane pentane $N_{\rm E}$ /molecules per E s⁻¹ $N_{\rm F}$ /molecules per SA s⁻¹ $N_{\rm E}$ /molecules per E s⁻¹ $N_{\rm F}$ /molecules per SA s⁻¹ molecular sieve MnAPO-36 0.03 1.39 0.74 34.2

1.15

1.18

2.48

2.11

Comparison of the catalytic activity of type 36 aluminophosphate-based molecular sieves in the conversion of pentane and cyclo-

E, Framework substituted atom(s) [i.e. Mn in MnAPO-36, Zn in ZAPO-36, Co in CoAPO-36, Mg in MAPO-36 and (Mg + Si) in MAPSO-36]. SA, Strong acid site.

Table 8 Conversion of o-xylene on type 36 aluminophosphate-based molecular sieves

					produc	t distribution	(wt.%)			
molecular sieve	conversion (%)	aliphatics	benzene	toluene	p-xylene	<i>m</i> -xylene	o-xylene	trimethyl benzenes	other C ₉₊ aromatics	total
MnAPO-36	40.3	0.2	0.5	2.5	13.0	16.7	60.1	6.1	0.3	100
ZAPO-36	55.2	0.3	0.4	3.2	20.2	25.0	44.8	5.7	0.4	100
CoAPO-36	70.1	0.3	0.3	3.3	27.0	33.9	29.9	4.3	1.0	100
MAPO-36	72.2	0.6	0.8	7.5	22.6	28.8	27.8	10.2	1.7	100
MAPSO-36	74.3	0.7	0.7	8.6	21.7	25.8	26.7	13.0	2.8	100

Reaction conditions: amount of catalyst 50 mg, He flow rate 90 cm³ min⁻¹, pulse size 5 mm³, temperature 673 K.

ticular pulse)/(conversion of ethylbenzene for the first pulse)] of the aluminophosphates shown in Fig. 7, represents the deactivation trend. The deactivation of CoAPO-36 and ZAPO-36 is more pronounced than that of MnAPO-36, MAPO-36 and MAPSO-36.

0.06

0.07

0.16

0.11

In the case of the type 36 mono-substituted aluminophosphates, the overall catalytic activity results indicate that the Mg-incorporated aluminophosphate shows higher catalytic activity and a lower deactivation rate than the Mn-Zn- or Co-incorporated aluminophosphates. Comparing the catalytic activities of MAPO-36 and MAPSO-36, it is observed that the catalytic acitivity of MAPO-36 is enhanced by the incorporation of an additional element (Si) in the MAPO-36 framework.

Conclusion

The type 36 aluminophosphates with different elements incorporated differ widely in their thermal stability, the concentration of Brønsted and Lewis acid sites, site energy dis-



Fig. 7 Effect of the pulse number on the fractional catalytic activity of (O) MnAPO-36, (•) ZAPO-36, (Δ) CoAPO-36, (\blacktriangle) MAPO-36 and (D) MAPSO-36 in the conversion of ethylbenzene. Reaction conditions: amount of catalyst 100 mg, He flow rate 30 cm³ min⁻¹, temperature 673 K, pulse size 1 mm³.

tribution, number of strong acid sites, catalytic properties and deactivation behaviour. The results of the present study show that these properties of the aluminophosphates are strongly influenced by the nature of the frameworkincorporated element.

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Table 7

ZAPO-36

CoAPO-36

MAPO-36

MAPSO-36