MAPO-18 (M ≡ Mg, Zn, Co): a New Family of Catalysts for the Conversion of Methanol to Light Olefins

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Incorporation of divalent metals Mg, Zn and Co into the structure of $AlPO_4$-18 yields solid acid catalysts that generate 65 to 70% light olefin (ethene and propene) products with 100% conversion of methanol in the range 350 to 400 °C

The microporous silicoaluminophosphate SAPO-34 and its metal-incorporated analogues (*e.g.* Ni-SAPO-34), are structurally analogous to the naturally occurring zeolite chabazite,[1] and are excellent solid acid catalysts for the conversion of methanol to light olefins.[2–4] But members of the MAPO-34† family, in which the $AlPO_4$-34 (chabazite) structure is devoid of framework silicon, have such poor thermal stability that little is known of their presumed solid acid catalytic properties. $AlPO_4$-18 is structurally very similar to $AlPO_4$-34: the stacking of the double-six-ring layers is ABAB in the (18) and AAAA in the (34) families, so that the size and shape of the cavities are essentially the same in each family.[5]

We have found that samples of MAPO-18 containing small amounts of metal have a thermal stability that greatly exceeds that of the corresponding MAPO-34 family. We have also discovered that MAPO-18 catalysts are very good for the selective production of ethene and propene from methanol.

Hitherto, it has proved difficult to synthesize (from appropriate precursor gels) members of the MAPO-18 family using the template tetraethylammonium hydroxide that favours[6] production of $AlPO_4$-18. We have found that *N,N*-diisopropylethylamine readily directs the formation of $AlPO_4$-18, SAPO-18[7] and MAPO-18 (M = Mg, Zn, Co, Ni, *etc.*) All these substituted materials are thermally stable, and SAPO-18 (to be reported fully elsewhere[7]) along with MgAPO-18,

ZnAPO-18 and CoAPO-18 are very active and selective Brønsted acid catalysts for methanol conversion to light olefins.[8]

The $AlPO_4$-18 and MAPO-18 samples were synthesized hydrothermally by heating an aluminophosphate and a metal alminophosphate gels, respectively, in the presence of *N,N*-diisopropylethylamine ($C_8H_{19}N$) at 150–180 °C for 3–10 days. Full details will be given elsewhere,[8] but briefly, the aluminium and phosphorus sources were aluminium hydroxide hydrate and phosphoric acid, respectively. Either a metal oxide or a metal acetate was used as the divalent metal source. The empirical gel composition was $1.0–2.0C_8H_{19}N : 0.08$ $MO : 0.96Al_2O_3 : P_2O_5 : 50H_2O$ for all the MAPO-18 samples. Template-free samples were obtained by calcining the corresponding as-synthesized ones in gaseous O_2 at 550 °C for 5–10 h. Since the Co^{II} in an aluminophosphate framework is susceptible to oxidation during calcination,[9] the CoAPO-18 sample was heated in H_2 at 400 °C after calcination to reduce the Co^{III} to Co^{II}. Prior to each diffuse reflectance IR (Fig. 1) measurement, the template-free sample was dehydrated at 500 °C in N_2. The temperature programmed desorption (TPD) of NH_3 was carried out in standard fashion. The catalytic performance was tested in a quartz tubular microreactor (weight hourly space velocity, WHSV = 1.5 h⁻¹).

Since $AlPO_4$-18 does not show any IR absorption (Fig. 1) within the lower OH stretching frequency region, it is reasonable to propose that the absorptions for the MAPO-18 samples within this region stem from the hydroxyls bridging a metal and a P atom and that these bridging hydroxyls are the origin of Brønsted acidity. Nevertheless, the position and shape of the absorptions for MAPO-18 samples are different from one another, reflecting considerable variation in the strength of Brønsted acid sites.

All MAPO-18 samples have a TPD peak (Fig. 2) at 150–180 °C, which is believed to be associated with Lewis acid sites and/or P–OH groups. In addition, ZnAPO-18, CoAPO-18 and MgAPO-18 each exhibits a weak desorption at *ca.* 410,
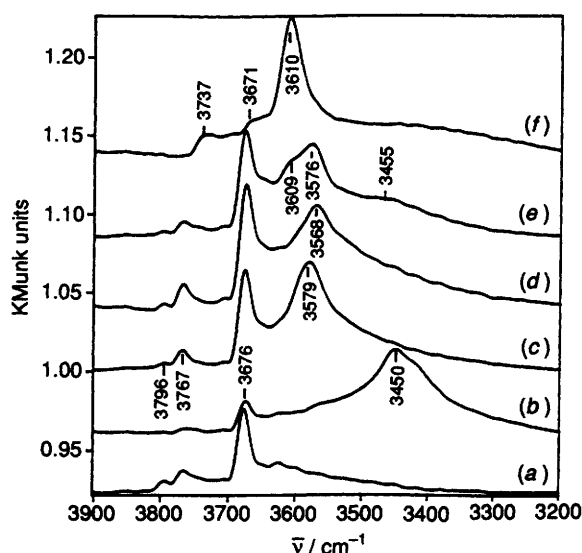
Fig. 1 Diffuse reflectance infrared Fourier transform (DRIFT) spectra within the OH stretching region for (*a*) $AlPO_4$-18, (*b*) NiAPO-18, (*c*) ZnAPO-18, (*d*) CoAPO-18, (*e*) MgAPO-18 and (*f*) HZSM-5 (Si : Al=23) (The amount of the hydroxyls present is not proportional to the absorption intensity since particle size affects the latter.) The species include P–OH (3676 cm⁻¹), Al–OH (3767 and 3796 cm⁻¹) and bridging M–OH–P (within 3300–3640 cm⁻¹). The spectrum for HZSM-5 is consistent with that reported previously,[10] the absorption at 3610 cm⁻¹ being assignable to hydroxyls bridging a Si and an Al atom.
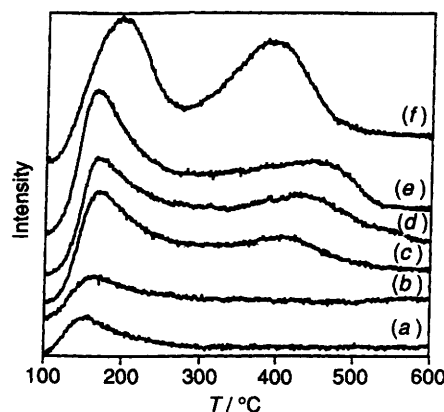
Fig. 2 TPD of ammonia for (*a*) $AlPO_4$-18, (*b*) NiAPO-18, (*c*) ZnAPO-18, (*d*) CoAPO-18, (*e*) MgAPO-18 and (*f*) HZSM-5 (Si : Al = 23). The rate of temperature rise was 5 °C min⁻¹.

Table 1 Catalytic performance of $AlPO_4$-18 and MAPO-18 for methanol conversion (time on stream: *ca.* 10 min; WHSV = 1.5 h^{-1})

Sample	Temp. °C	Methanol conv. (%)	Distribution of products (%, exclusive of water)				
			Me_2O	CH_4	C_2H_4	C_3H_6	C_{4+}
$AlPO_4$-18	250	0	0	0	0	0	0
	300	21	100	0	0	0	0
	350	52	100	0	0	0	0
	400	73	100	0	0	0	0
NiAPO-18	250	5	100	0	0	0	0
	300	29	100	0	0	0	0
	350	63	100	0	0	0	0
	400	75	100	0	0	0	0
ZnAPO-18	250	31	100	0	0	0	0
	300	70	96.4	0.2	0.5	2.1	0
	350	100	0	0.3	17.9	50.7	30.8
	400	100	0	0.3	24.9	46.6	27.5
CoAPO-18	250	39	100	0	0	0	0
	300	87	63.8	1.6	4.6	18.4	11.5
	350	100	0	0.3	14.9	51.8	32.5
	400	100	0	0.3	22.4	51.2	25.6
MgAPO-18	250	31	100	0	0	0	0
	300	88	35.5	1.6	7.2	34.2	21.7
	350	100	0	0.3	13.0	51.0	35.1
	400	100	0	0.3	20.1	49.6	29.7

430 and 450 °C, respectively. All these weak peaks, which are believed to result from the Brønsted acid sites, are at temperatures higher than that for HZSM-5 (*ca.* 400 °C), signifying[10,11] that the strength of the Brønsted acid sites is in the order HZSM-5<ZnAPO-18<CoAPO-18<MgAPO-18. (The absence of high-temperature TPD desorption for NiAPO-18 is probably due to the bridging OH groups being located in double six-rings that are not accessible to the NH_3.)

The Brønsted acidity for $AlPO_4$-18 and MAPO-18 are reflected by their catalytic performance for methanol conversion (Table 1). Because of its minimal Brønsted acidity, $AlPO_4$-18 catalyses methanol conversion to dimethyl ether only even at elevated temperatures (*e.g.* 500 °C). NiAPO-18 is similar to $AlPO_4$-18, but ZnAPO-18, CoAPO-18 and MgAPO-18 are all very active and selective for methanol conversion to ethene and propene. At 350 °C, the conversion reaches 100% over all three samples. However, at 300 °C, the performance of the samples correlates with their observed strength as Brønsted acids. Of the three MAPO-18s with accessible Brønsted acid sites, MgAPO-18 exhibits the highest and ZnAPO-18 the lowest conversion of methanol to hydrocarbons. The activity in terms of methanol conversion to hydrocarbons at 300 °C is in the order $AlPO_4$-18 = NiAPO-18≪ZnAPO-18<CoAPO-18<MgAPO-18. This is in line with the results from IR and TPD studies. At 400 °C, all of the three active MAPO-18 samples last for at least 2 h on stream without significant decrease in conversion, and after regeneration by calcination, the completely deactivated samples recover their original activity. It is an intriguing fact, yet to be fully understood, that whereas Ni-SAPO-34 is one of the best,[4] NiAPO-18, which has essentially the same framework structure, is one of the poorest catalysts for the conversion of methanol to ethene.

Footnote

† M is being used to represent a metal here to avoid confusion with Me for methyl, but in other papers the authors may use Me.

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