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Bifunctional catalytic centres in cobalt substituted aluminophosphate molecular sieve, CoAPO-11

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A cobalt substituted aluminophosphate molecular sieve, CoAPO-11 has been synthesized by using n-dibutylamine as template. It was characterized by XRD, MASNMR, TPD, thermal analysis and catalytic test reactions. The study reveals bifunctional catalytic centres in CoAPO-11.

Keywords: Characterization of CoAPO-11; bifunctional centres in CoAPO-11

1. Introduction

Microporous inorganic solids are useful materials for catalysis, adsorption, and, ion exchange. Among these, aluminophosphate molecular sieves ($AlPO_4$) contain Al and P as framework atoms [1]. Since the overall framework charge in these materials is neutral, an $AlPO_4$ does not possess ion-exchange capacity or strong acidity responsible for catalytic properties of aluminosilicates. A variety of substituted $AlPO_4$'s have been synthesized to generate active catalysts [2]. By varying the type and concentration of the substituent ions, catalytic properties of $AlPO_4$'s can be modified to suite particular reactions [3]. The mildly acidic pH of the synthesis medium coupled with the peculiar gel chemistry of the system aids successful incorporation of divalent, trivalent and tetravalent elements into an $AlPO_4$ framework [2,4].

Many workers have recently reported substitution of cobalt into the framework of $AlPO_4$-5 [5–8]. The existence of redox centres in these catalysts has been demonstrated [7,8]. TPD measurements have shown presence of acid sites in CoAPO-11 implying substitution of Co^{2+} for Al^{3+} [9,10].

The work presented in this paper describes synthesis, characterization and some catalytic properties of CoAPO-11. We have used n-dibutylamine (DBA) as organic additive in the synthesis of CoAPO-11, to demonstrate once again the suitability of higher secondary amines in synthesis of $AlPO_4$-11 materials [11].

2. Experimental

CoAPO-11 was synthesized by using a gel composition of 0.085CoO. 1.0DBA. $1.0Al_2O_3$. $1.0P_2O_5$. $40H_2O$. Cobalt acetate dopant was added after addition of DBA. Synthesis procedure reported in an earlier communication was followed [11].

The sample was characterized by XRD (Philips PW 1730, CuK_α radiation). MASNMR (Bruker MSL 300) spectra for Al and P nuclei were obtained at a spinning speed of 3–5 kHz and 7–9 kHz, respectively. TPD of ammonia was measured by conventional gas chromatographic technique, and thermal analysis carried out using a Netz'ch STA 409 thermal analyzer. Sorption of n-hexane was carried out in a Cahn balance with P/P_0 of 0.5 at room temperature. Catalytic studies were carried out in conventional down-flow silica reactor. Gaseous products were analyzed by GC (Shimadzu R 16A) on Porapak N and n-Octane-Porasil C columns and liquid products on Bentone 34 (5%) + DIDP (5%).

3. Results and discussion

An intense blue coloured product was obtained after the synthesis. Tapp et al. [9] have attributed the blue colour to tetrahedral coordination of cobalt. But we find that blue colour of the product is not always an indication of a crystalline product.

X-ray diffraction pattern of the sample was similar to that of unsubstituted $AlPO_4$-11. No additional peaks indicative of other phases were observed. Chemical analysis of the sample gave the composition $(CO_{0.04}Al_{0.46}P_{0.48})O_2$ which indicates a net charge of -0.06. Nearly 17% of the cobalt was exchangeable with Na^+ ions by treatment with NaCl solution. Sorption experiments showed an uptake of 4% n-hexane against 8% observed for $AlPO_4$-11 [1]. These results show presence of cobalt in extra-framework positions and as occluded oxides.

Single resonance peaks at 33 and -30 ppm were observed for both ^{27}Al and ^{31}P MASNMR spectra respectively (fig. 1a–d). Some broadening of the peaks in contrast to the peaks for unsubstituted $AlPO_4$-11 may be attributed to interaction of the transition metal in the framework with ^{27}Al and ^{31}P nuclei [8]. Some differences between the MASNMR spectra of the as-synthesized and calcined samples were noted. A small resonance near zero ppm, probably due to trace of unreacted starting material, was present in the ^{27}Al spectrum of the as-synthesized sample. This signal was absent in the calcined sample. The side bands which became more prominent upon calcination were not as intense as reported in the case of CoAPO-5 [8]. In the ^{31}P spectrum, no P-OH defect groups could be detected under CP conditions. A shoulder peak at -22 ppm whose intensity increased under CP conditions was observed in the case of the calcined sample. This may be due to interaction of framework P with OH^-/H_2O [12].

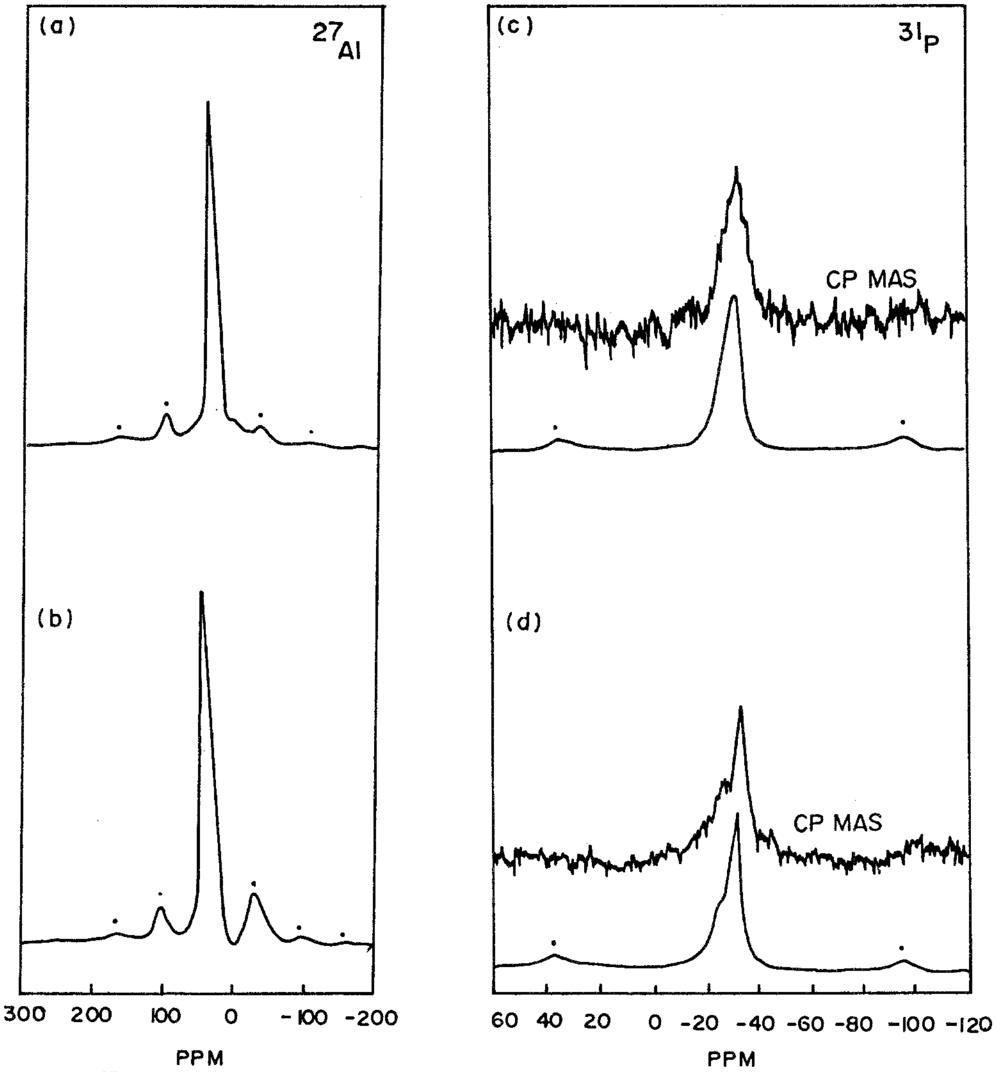

Fig. 1 (a) ^{27}Al MASNMR spectrum of as-synthesized CoAPO-11; (b) ^{27}Al MASNMR spectrum of calcined CoAPO-11; (c) ^{31}P MASNMR and CP MASNMR spectra of as-synthesized CoAPO-11; (d) ^{31}P MASNMR and CP MASNMR spectra of calcined CoAPO-11.

An exothermic peak was observed in the temperature range of 280–350 ° C in the DTA curve in thermal analysis (fig. 2). This may be caused by the removal of occluded template. The associated change in colour from blue to yellow green indicates +3 oxidation state of cobalt in the calcined sample. The blue colour was restored on reduction with hydrogen or on exposure to methanol vapour even at room temperature. In the latter case, methanol was oxidized to formaldehyde by framework Co^{3+}. A similar observation has been reported in the case of CoAPO-5 by other workers [7,8]. This can be explained on the basis

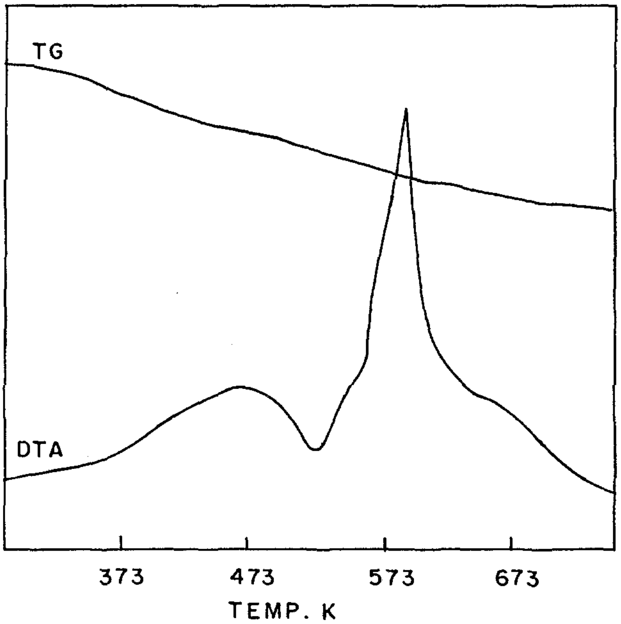

Fig. 2. Thermoanalytical traces for CoAPO-11.

of the mechanism suggested by Iton [7]:

$$CH_3OH + Co^{3+} \rightarrow CH_3O. + Co^{2+} + H^+$$

$$CH_3O. + Co^{3+} \rightarrow CH_2O + Co^{2+} + H^+.$$

Temperature programmed desorption chromatogram of ammonia from CoAPO-11 sample in the temperature range of 72 ° C to 420 ° C exhibited peaks due to desorbed ammonia (fig. 3). This indicates presence of acidity in the sample as extraneous oxides and hydroxides do not enhance acidity [13].

Thus, formation of formaldehyde from methanol, the resultant change in colour of the cobalt species and the presence of desorption peaks of NH_3 in the TPD study may be taken as evidence for substitution of cobalt for aluminium in the aluminophosphate.

In agreement with the availability of acid sites in the sample, CoAPO-11 converts methanol to hydrocarbons under certain conditions (temperature 400 ° C, WHSV = 3.5). The liquid fraction consists mainly of methylated aromatics similar to those observed for conversion over ZSM-5 zeolites [14].

Table 1 compares the product distribution for isopropanol dehydration for $AlPO_4$-11 and CoAPO-11. While the major reaction over $AlPO_4$-11 is only dehydration, reaction over CoAPO-11 is more complex leading to higher hydrocarbons.

Alkene oxidation over cobalt catalyst involves formation of an ion radical as an intermediate in a mechanism proposed by Bawn [15]. The mechanism may be

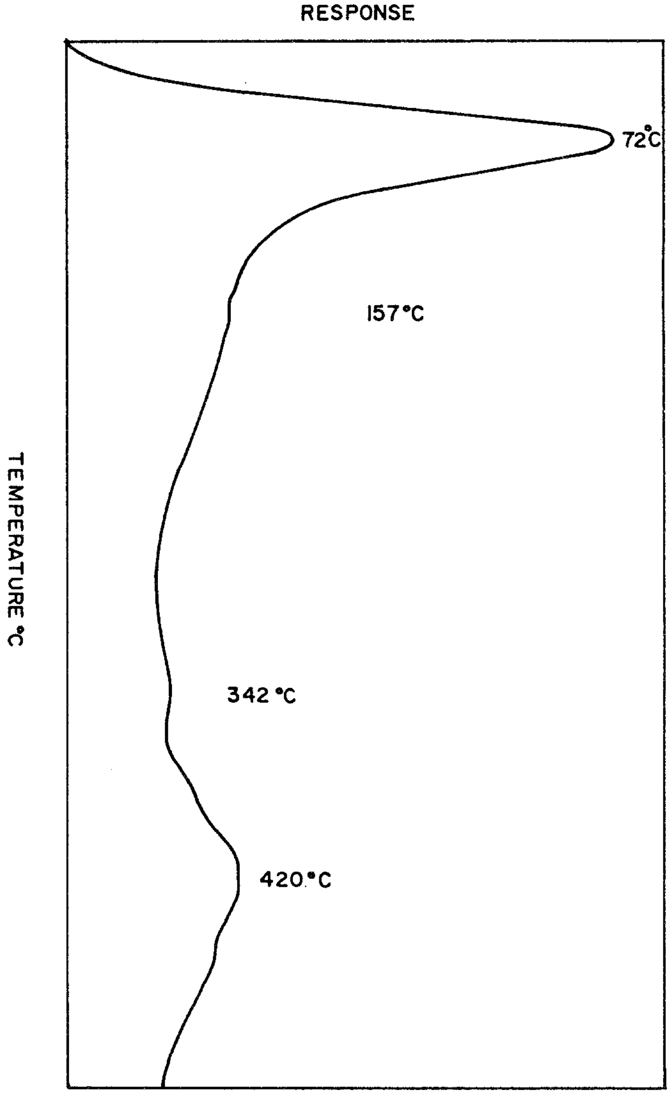

Fig. 3. TPD chromatogram of CoAPO-11.

extended to the reaction over CoAPO-11 as shown below:

$$CH_3\text{-}CH{=}CH_2 + Co^{3+} \rightarrow CH_3\text{-}\overset{+}{C}H\text{-}\dot{C}H_2 \leftrightarrow CH_3\text{-}\dot{C}H\text{-}\overset{+}{C}H_2 + Co^{2+}$$

$$2CH_3\text{-}\overset{+}{C}H\text{-}\dot{C}H_2 \rightarrow C_{5+} \text{ hydrocarbons} + H^+.$$

$$Co^{2+} + H^+ \rightarrow Co^{3+} + \tfrac{1}{2}H_2.$$

The C_{5+} selectivity could be enhanced markedly by using propene as feed.

In conclusion, it is shown that substituted $AlPO_4$-11 materials, CoAPO-11 in the present work can be synthesized in the presence of n-dibutylamine although

Table 1
Comparison of $AlPO_4$-11 and CoAPO-11 in isopropanol dehydration. Conditions: Temp. = 300 ° C; WHSV = 3.5; TOS = 3 hours

	$AlPO_4$-11	CoAPO-11
Isopropanol conversion	97.5	100
Product distribution (wt%)		
Ethane and ethylene	0.01	0.1
Propylene	98.21	84.21
Butane and butenes	0.08	0.57
C_{5+} hydrocarbons	1.71	15.11

previous workers mention the use of lower amines for the purpose as organic additive. Characterization experiments and catalytic data on methanol and isopropanol conversion reveal bifunctional catalytic properties of CoAPO-11.

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