

## Synthesis of CoVPI-5 with Bifunctional Catalytic Activity

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A novel cobalt-substituted aluminophosphate VPI-5 with bifunctional catalytic centres is synthesized; the stability, adsorptive and catalytic properties are examined.

The synthesis of VPI-5,<sup>1,2</sup> a member of the ALPO family, has attracted considerable attention for the potential capability of processing large organic molecules. The framework of VPI-5 is permeated by one-dimensional channels circumscribed by 18-membered rings, having a uniform pore diameter of 12 Å. Since the overall framework charge in this material is neutral, VPI-5 does not possess acidic centres responsible for catalytic reactions. A variety of substituted ALPOs have been synthesized to generate active catalysts.<sup>3</sup> Substitution of cobalt into the framework of ALPO-5<sup>4-7</sup> and ALPO-11<sup>8-9</sup> has been reported. Many workers have found Co<sup>2+</sup> preferentially occupies Al<sup>3+</sup> sites and the existence of redox centres in these catalysts has been demonstrated.<sup>6,7,10</sup> Here, we report the synthesis of cobalt-substituted VPI-5 and demonstrate the acidic as well as oxidation-reduction centres of this material.

A gel composition of 0.01 CoO:1.0 Al<sub>2</sub>O<sub>3</sub>:1.0 P<sub>2</sub>O<sub>5</sub>:1.0 NHBu<sub>2</sub>:40 H<sub>2</sub>O was employed during the synthesis. A typical synthesis was as follows: a solution of phosphoric acid (85%, S.D. Fine Chemicals) in water was added to a homogenised mixture of aluminium isopropoxide (Aldrich) and water. Cobalt acetate (S.D. Fine Chemicals) was added before the addition of NHBu<sub>2</sub>. The gel was transferred into stainless-steel autoclaves and the crystallization was carried out at 140 °C for 12 h under static conditions. The crystalline products were collected, washed with water and ethanol and dried at room temperature.

A blue product was obtained after the synthesis. The sample was characterized and identified as crystalline material having VPI-5 structure by X-ray powder diffraction. The SEM photographs of the as-synthesized sample shows that the sample is of homogeneous distribution and is purely one phase. This solid exhibits long cylindrical particles with diameter *ca.* 0.15–0.25 μm. Chemical analysis of the sample gave the composition of Co<sub>0.02</sub>Al<sub>0.41</sub>P<sub>0.50</sub>O<sub>2</sub>. UV-VIS diffuse reflectance spectrum of the as-synthesized sample shows the presence of three prominent absorbance peaks at 539, 582 and 629 nm (Fig. 1). This is attributed to tetrahedral coordination of Co<sup>2+</sup>. Upon calcination of CoVPI-5 in flowing air at 773 K, the sample turns pale green and a new broad adsorption band at ≈ 300–400 nm appears and the adsorption intensities in the

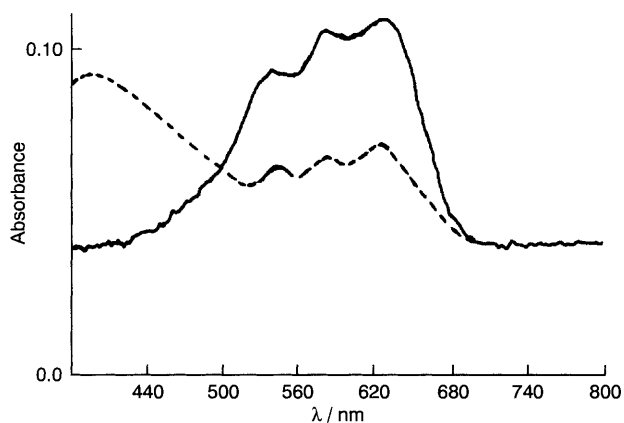


Fig. 1 UV-VIS spectra of CoVPI-5: (—) as-synthesized, (---) calcined

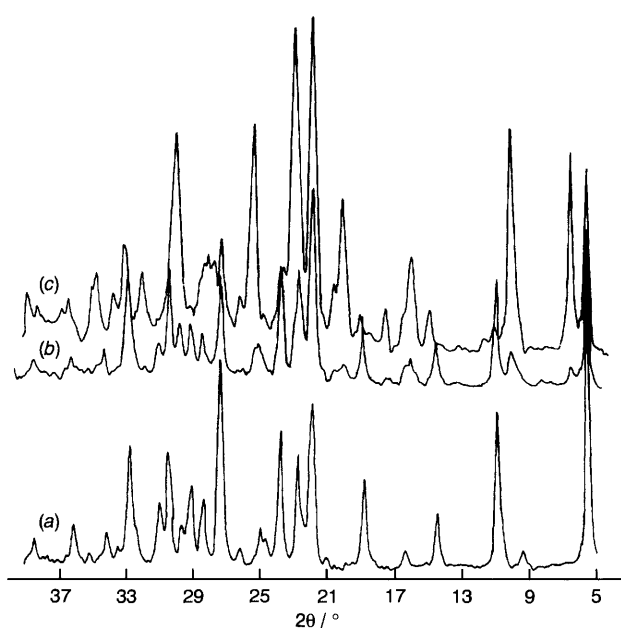


Fig. 2 X-Ray diffractograms of CoVPI-5: (a) as-synthesized, (b) degassed slowly first at 323 K and then at 623 K, (c) degassed directly at 773 K

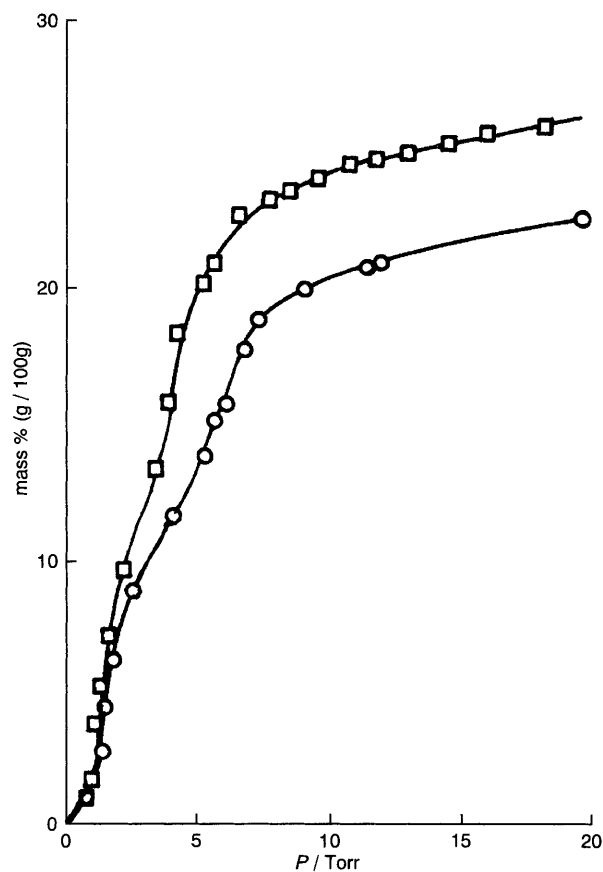


Fig. 3 Water-vapour adsorption isotherm of CoVPI-5 determined at 298 K: (□) degassed slowly at 323 K then at 623 K, (○) degassed directly at 773 K

500–600 nm region decrease. The appearance of a new adsorption band in the 300–400 nm region is assigned to tetrahedral  $\text{Co}^{3+}$ . The sample returns to blue when contacted with flowing  $\text{H}_2$  at 773 K or with room-temperature vapours of methanol; thus  $\text{Co}^{2+}$  can be oxidized to  $\text{Co}^{3+}$  and then reduced back to  $\text{Co}^{2+}$ .

The adsorptive properties and stability of CoVPI-5 were investigated. Water-vapour isotherms were determined on all-glass gravimetric units<sup>11</sup> using a McBain–Baker type silica spring (sensitivity  $\approx 68 \text{ cm g}^{-1}$ ). The adsorption isotherms were measured up to 20 Torr at 298 K and the temperature accuracy throughout the sorption experiments was within  $\pm 1\text{K}$ . The as-synthesized sample (CoVPI-5) was degassed at 323 K for 24 h. The temperature was then slowly increased to 623 K and held for 24 h. The temperature was then lowered to the isotherm temperature (298 K) at which it was allowed to stabilize and maintained for at least 2 h before commencement of the measurement. X-Ray diffractograms were recorded for this sample before and after the sorption experiments [Fig. 2(a) and (b)] to check the structure stability. Some differences in the XRD patterns were observed and are thought to be due to progressive structural transformation. Three distinct steps were observed at low water-vapour pressure ( $< 5$  Torr, Fig. 3). Similar water-vapour adsorption isotherms for VPI-5 were observed by Kenny *et al.*<sup>12</sup> and suggested that the first step is associated with adsorption on a small number of strong specific surface or defect sites. The hysteresis loop between the second and third steps is associated with a phase transformation of the adsorbed water. With the adsorption of water molecules, some of the framework tetrahedral Al atoms undergo a reversible transformation to a octahedral coordination. The third step is consistent with the least strongly adsorbed molecules. Degassing the as-synthesized samples at  $> 773$  K resulted in significant phase transformation to CoAPO-8, shown by XRD patterns [Fig. 2(c)] and the total uptake is considerably lower. It is assumed<sup>12</sup> that ill defined regions are introduced into the framework during the phase transformation creating constrict-

tions in the unidimensional channels which cause the molecular sieving and also some pore blockage.

The main consequence of this modification by the introduction of cobalt into VPI-5 framework should be a bifunctional catalytic activity. Table 1 compares the product distribution for isopropyl alcohol dehydration over ALPO-11, CoAPO-11 and CoVPI-5. The major reaction over ALPO-11 and VPI-5 is dehydration whereas CoAPO-11 and CoVPI-5 produces  $\text{C}_5$  hydrocarbons. Oxidation of alkenes over cobalt catalysts involves formation of an ion radical as an intermediate, as proposed by Bawn and Sharp.<sup>13</sup> This mechanism is extended to the propene oxidation over CoAPO-11 by Prasad and Balakrishnan<sup>14</sup> and  $\text{C}_5$  hydrocarbons selectivity could be enhanced markedly. The formation of  $\text{C}_5$  hydrocarbons due to the oxidation of propene takes place over metallic sites. The calcined CoVPI-5 shows much higher activity than CoAPO-11 in the oxidation of propene, which is formed during the dehydration of isopropyl alcohol and the  $\text{C}_5$  hydrocarbon formation per cobalt atom is also much higher. The oxidation activity of CoVPI-5 is twice as high as that observed for CoAPO-11.

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## References

- 1 M. E. Davis, C. Saldarriaga, C. Montes, J. Garces and C. Crowder, *Nature*, 1988, **331**, 698.
- 2 M. E. Davis, C. Montes and J. M. Garces, *ACS Symp. Ser.*, 1989, **398**, 291; *J. Am. Chem. Soc.*, 1989, **111**, 3919.
- 3 B. M. Lok, C. A. Messenia, R. L. Patton, R. T. Gajik, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1984, **106**, 6092.
- 4 R. A. Schoonheydt, R. De Vos, J. Pilgrims and H. Leeman, *Stud. Surf. Sci. Catal.*, 1989, **49A**, 559.
- 5 V. P. Shiralkar, C. H. Saldarriaga, J. O. Perot, A. Clearfield, M. Chen, R. G. Antony and J. A. Donhoue, *Zeolites*, 1989, **9**, 474.
- 6 L. E. Iton, I. Choi, J. A. Desjardins and V. A. Moroni, *Zeolites*, 1989, **9**, 535.
- 7 C. Montes, M. E. Davis, B. Murray and M. Narayana, *J. Phys. Chem.*, 1990, **94**, 6425.
- 8 N. J. Tapp, N. B. Milestone and J. M. Wright, *J. Chem. Soc., Chem. Commun.*, 1985, 1801.
- 9 S. Ernst, L. Puppe and J. Weitkamp, *Stud. Surf. Sci. Catal.*, 1989, **49A**, 447.
- 10 P. S. Singh, R. Bandyopadhyay, R. A. Shaikh and B. S. Rao, *International Zeolite Symposium*, Quebec, Canada, Oct. 1995.
- 11 V. P. Shiralkar and S. B. Kukarni, *Z. Phys. Chem. (Leipzig)*, 1984, **265**, 313.
- 12 M. B. Kenny, K. S. W. Sing and C. R. Theocharis, *J. Chem. Soc., Chem. Commun.*, 1991, 974.
- 13 C. E. H. Bawn and J. A. Sharp, *J. Chem. Soc.*, 1957, 1854.
- 14 S. Prasad and I. Balakrishnan, *Catal. Lett.*, 1991, **11**, 105.

**Table 1** Catalytic activity in isopropyl alcohol dehydration ( $T = 280^\circ\text{C}$ ;  $\text{WHSV}^a = 3.5$ ; time on stream = 1 h)

Sample	Co (%, m/m)	Selectivity of $\text{C}_5$ hydrocarbons	TON <sup>b</sup> /h
ALPO-11	—	—	—
VPI-5	—	—	—
CoAPO-11(1)	0.65	3.21	4.94
CoAPO-11(2)	3.78	15.14	4.00
CoVPI-5	0.19	1.98	10.42

<sup>a</sup> WHSV = weight hourly space velocity. <sup>b</sup> Turnover number = no. of moles of  $\text{C}_5$  hydrocarbons per cobalt atom.