Synthesis of a CrCoAPO-5(AFI) molecular sieve and its activity in cyclohexane oxidation in the liquid phase

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A new CrCoAPO-5 was synthesized under hydrothermal conditions, characterised by X-ray diffraction, scanning electron microscopy, infrared spectroscopy, energy dispersive X-ray analysis, thermogravimetric analysis, electron paramagnetic resonance and nitrogen physisorption. The CrCoAPO-5 showed catalytic activity in the liquid phase oxidation of cyclohexane at 115 °C and 1 MPa of oxygen.

KEY WORDS: redox molecular sieves; aluminophosphates; oxidation; cyclohexane

1. Introduction

Since 1982 when $AlPO_4$-5 was reported [1] as a material with very good hydrothermal stability (thermally stable to 1000 °C and stable in 16% steam at 600 °C without loss of the structure), numerous metals such as Fe, Cr, Co, Ti, Mn and Zn, have been introduced into its framework in order to introduce redox properties [2–4]. CoAPO-5 and CrAPO-5 have been widely studied for their possible utility as heterogeneous catalysts in oxidation reactions. Although the heterogeneity of MeAPO-5 materials as catalysts is a very controversial issue [5–8], it is generally recognised that in the absence of polar solvents such as acetic acid these solids work as truly heterogeneous catalysts [7–10].

The substitution of single metals into the $AlPO_4$-5 framework is well established [11,12]. In contrast, double metal substitutions in $AlPO_4$-5 are less common; examples include VTiAPO-5 [13], MnFeAPO-5 [14], GeFeAPO-5 [15] and CoVAPO-5 [16]. Due to the potential application of MeAPO-5s as catalysts, it is of interest to establish if a double metal substitution has any effect on the catalytic performance of these materials. Accordingly, we report here the preparation, characterization and catalytic performance in cyclohexane oxidation of a new CrCoAPO-5 molecular sieve, which incorporates two metals in the $AlPO_4$-5 framework.

2. Experimental

2.1. Synthesis

The CrCoAPO-5 was synthesized from a gel of molar composition $5\times10^{-2}CoO : 2.5\times10^{-2}Cr_2O_3 : Al_2O_3 : P_2O_5 : Pr_3NH : 33H_2O$ under hydrothermal conditions in an autoclave heated at 190 °C for 24 h. The product was washed with water and dried at room temperature. The materials were calcined at 550 °C for 12 h in order to remove the amine template. Samples of CoAPO-5 and CrAPO-5 were synthesised and characterised for comparative purposes according to the procedures described in the patent literature [17].

The materials obtained were characterized by X-ray diffrecation (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), electron paramagnetic resonance (EPR), infrared spectroscopy (IR), thermogravimetric analysis (TG), elemental analysis and nitrogen adsorption. XRD was performed on a Siemens D5000 diffractometer employing Cu Kα radiation ($\alpha = 0.1542$ nm). The crystallinity of each sample was examined by comparing the intensity of the 100 and 210 reflections with those of the uncalcined $AlPO_4$-5.

Infrared spectra were collected between 4000 and 500 cm^{-1} using a Bio-Rad FTS-40 spectrometer with 2–5% of the catalyst dispersed in a KBr pellet. Thermogravimetric analysis was conducted using a TGA 2950 Thermal Analyst 2100 at temperatures from 20 to 800 °C with a heating rate of 20 °C/min in an air atmosphere. Microphotographs and EDAX analyses were performed on a Philips SEM 505 instrument equipped with an EDAX detecting unit. The chemical composition was determined using EDAX and the result was compared with those obtained for Al, Si and P by gravimetry and for cobalt and chromium by AAS analyses of solutions prepared by thermal acid digestion of the samples. The surface area and pore volume were determined by nitrogen adsorption using an ASAP 2000 Micromeritics instrument. EPR measurements were carried out on a Bruker EPR 300 spectrometer at room temperature and at 4–10 K.

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2.2. Catalytic experiments

The oxidation of cyclohexane was carried out in a 300 ml autoclave Parr reactor at 115 °C with neat cyclohexane and with cyclohexane and various potential promoters such as methyl ethyl ketone (MEK), cyclohexanol (CyOH) or acetic acid. The reactor was initially passivated with a solution of sodium pyrophosphate in order to avoid any catalytic activity of its walls. A further description of the reactor has been given by Jacobs and coworkers [18]. The reaction was performed at 115 °C for 6 h using 0.5 g of CrCoAPO-5 (3.54% Co and 3.12% Cr) catalyst with 75 ml of cyclohexane and the headspace was filled with oxygen under a total pressure of 1 MPa. In the cases when promoters were used the ratio promoter : cyclohexane was 1 : 10.

A separate reaction using aqueous H_2O_2 (30%) as oxidant and acetone as solvent (1 : 5 v/v) was performed at 70 °C under an argon atmosphere for 12 h. The temperature was then increased to 90 °C in order to determine if the catalyst was active; however, no conversion was observed.

The heterogeneity of the reaction was examined by further testing of the filtrate for catalytic activity according to the methodology suggested by Sheldon *et al.* [8]. In this procedure, the products from the reaction were filtered hot and the supernatant left reacting without any solid catalyst under the same initial conditions, 115 °C and an oxygen pressure of 1 MPa, for another 12 h. The products of the reaction were analysed each hour.

The catalyst was washed with acetone and dried at 80 °C for 2 h, then reused after each reaction. Catalysts were reused twice under each set of conditions.

The reaction samples were analysed by gas chromatography using a capillary column (30 m × 0.53 mm ID) BP 2.0 coupled to FID and TCD detectors. Identification of the products was carried out using GC-MS.

3. Results and discussion

3.1. Characterisation

The XRD data for all the solids show them to be MeAPO-5 materials with AFI topology [19]. Figure 1 illustrates the XRD of the CrCoAPO-5.

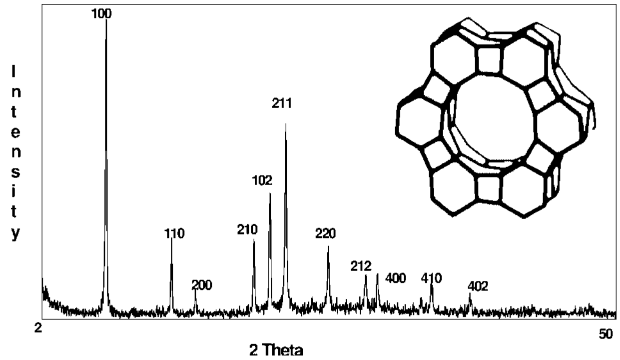

Figure 1. XRD for CrCoAPO-5 over the range 2° ⩽ 2θ ⩽ 50°. The Miller indices of the reflections are shown in the figure.

The CrCoAPO-5 shows a type I nitrogen adsorption isotherm (figure 2), characteristic of MeAPO-5 materials [20], with a BET surface area of 353 m^2 and a BJH pore volume of 0.058 cm^3/g. The CrCoAPO-5 exhibited a type H4 hysteresis loop, behaviour typical of a solid with narrow slit-like pores [21].

The microphotographs (figure 3) show the typical hexagonal shape of $AlPO_4$-5 and the presence of some needles of $AlPO_4H_1$ [22] which was not detected by XRD (presumably because of the low concentration of this species). The catalyst compositions determined by EDAX and gravimet-

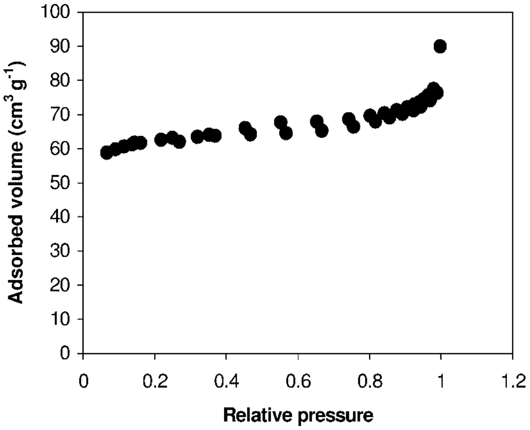

Figure 2. Nitrogen adsorption isotherm for CrCoAPO-5.

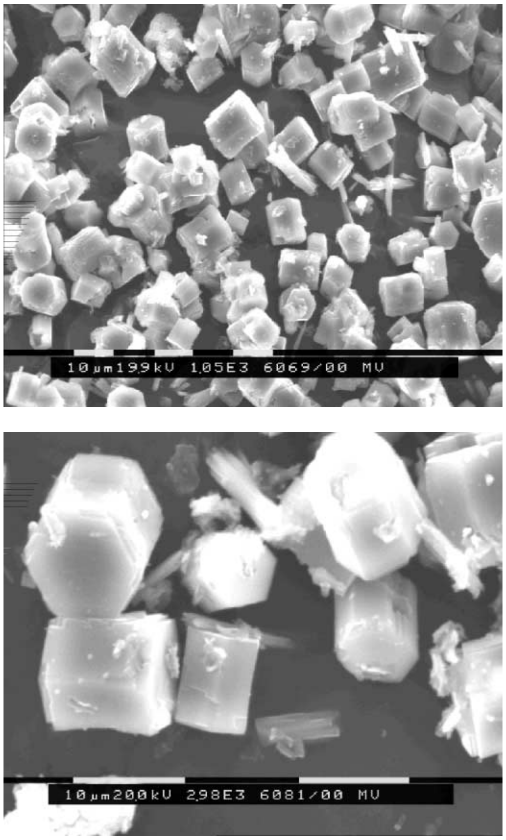

Figure 3. Scanning electron micrographs of CrCoAPO-5; each scale marking corresponds to 10 μm.

ric analyses are $0.06CoO : 0.03Cr_2O_3 : Al_2O_3 : 0.91P_2O_5$ for CrCoAPO-5; $0.06CoO : Al_2O_3 : 0.94P_2O_5$ for CoAPO-5 and $0.03Cr_2O_3 : Al_2O_3 : 0.97P_2O_5$ for CrAPO-5. The chemical composition determined by EDAX is in good agreement with those obtained by elemental analysis indicating uniform distributions of the chromium and cobalt in the CrCoAPO-5. Mapping of a 30 μm crystal of the sample at twelve different points showed a practically constant composition, indicating a homogeneous distribution of chromium and cobalt through the crystal.

Both the IR spectrum and the TG analysis indicate that the template was completely removed by the calcination step. IR absorption bands at 3679 and 3768 cm^{-1} are assigned to OH vibrations in P–OH and Al–OH groups, respectively; however, the low intensities of these absorptions suggest that the OH groups were present in only trace amounts.

The EPR spectrum (figure 4) of CrCoAPO-5, as synthesised, showed a signal at $g = 2.00$ that corresponds to Co^{II} [23]. This signal disappeared at low temperature (4 K). The room temperature EPR spectrum of calcined CrCoAPO-5 showed signals at $g = 2.00$ and $g = 1.98$ corresponding to Co^{II} [23] and Cr^{V} [24], respectively. Again the signal for cobalt disappeared at low temperature. An analogous temperature dependence of the cobalt signal in a CoAPO-5 sample was reported by Gorte and coworkers [25], but was not observed in material of the same composition by Howe and coworkers [26].

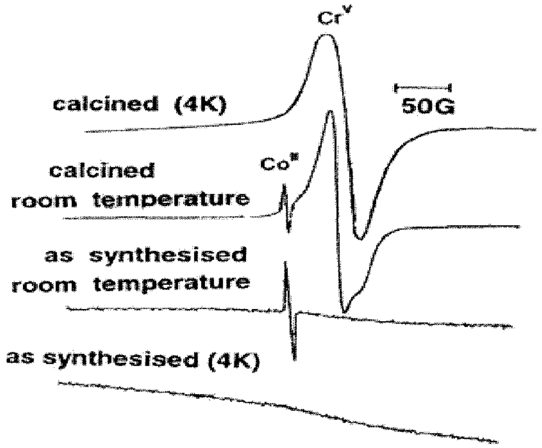

Figure 4. EPR spectra of CoCrAPO-5; all scans are from 2500 to 4000 G.

3.2. Catalytic testing

CrCoAPO-5 catalysed the oxidation of cyclohexane and the results are shown in table 1. Leaching of the metal into the solution occurred, as established by AAS analyses of the supernatant solution (see table 1). However, the catalytic activity of CrCoAPO-5 was greater than that expected for these dissolved metal concentrations [27]. For example, Jacobs and Vanoppen [10] reported a conversion less than 0.005% using 50 ppb of cobalt naphthenate and neat cyclohexane at 130 °C after 5 h. With CrCoAPO-5 at 115 °C in 6 h a conversion of 5.9% was achieved while 45 ppb of cobalt were leached. Comparison with the results of Jacobs suggests that at this concentration of dissolved cobalt under the conditions of the reaction a conversion of almost zero is expected. And with the 89 ppb of chromium leached a conversion less than 0.5% is expected [29].

The leaching tests showed that although the reaction continues after the removal of the solid catalysts (table 1) the conversion from the leached metals, *i.e.*, the homogeneous catalysis, is considerably less than that obtained with the heterogeneous systems. For example, the reaction with neat cyclohexane and the supernatant after removing the solid CrCoAPO-5 catalyst showed a conversion of only an additional 0.5% during the 12 h of testing of the leachate. This is considerably less than the conversion using the solid CrCoAPO-5 catalyst for 6 h (5.9%). Thus, although the CrCoAPO-5 apparently has both heterogeneous and homogeneous catalytic activity, its effect as an homogeneous catalyst is small.

In a separate, longer experiment using CrCoAPO-5 as catalyst with acetic acid as promoter the reaction ceased after 8 h. Jacobs and coworkers [28] noted that CoAPO-5 in acetic acid showed initial activity, but only a relatively short lifetime and then appears to act as an inhibitor. The present study shows that CrCoAPO-5 in the presence of acetic acid exhibits similar behaviour. Thus, the use of acetic acid leads to improved conversions, but decreased lifetimes. The data of table 1 indicate that the use of the most polar solvent, acetic acid, resulted in the greatest levels of leaching.

Table 1

Activity of CrCoAPO-5 in cyclohexane oxidation with O_2 at 115 °C for 6 h; promoters were used in a ratio of 1 : 10 (V/V). The final column gives the total conversion after 18 h, the first 6 h with catalyst and the remaining 12 h in the leaching test. Other products include valeric, succinic and butyric acids.

Catalyst (promoter)	Conversion (%)	Selectivity (%)				Dissolved [Cr] (ppb)	Dissolved [Co] (ppb)	Test of leaching conversion (%)
		Cyclohexanol	Cyclohexanone	Adipic acid	Others			
CrCoAPO-5 (none)	5.9	69	3	15	13	45	89	6.4
CrCoAPO-5 (MEK)	17.8	80	–	12	8	70	105	19.1
CrCoAPO-5 (CH_3COOH)	50	55	8	15	22	120	270	Reaction ceased after 8 h
CrCoAPO-5 (CyOH)	4.2	85	9	2	4	81	136	4.8
CoAPO-5 (none)	4.2	69	11	13	8	80	–	4.6
CrAPO-5 (none)	3.3	8	69	12	11	–	91	3.8

The catalyst was recycled three times without loss of its activity, but a very small amount of metal leaching was detected during each recycle. The amount of leaching was only 0.02–0.06% (for chromium) and 0.04–0.11% (for cobalt) of the initial metal loadings of the CrCoAPO-5 and consequently did not affect the activity of the heterogeneous catalyst. The leaching of chromium was greater than the leaching of cobalt for all the cases studied here.

In a further test, using H_2O_2 as oxidant and acetone as solvent, the CrCoAPO-5 did not show any activity

4. Conclusion

A new material, CrCoAPO-5, has been prepared and characterised and its catalytic activity examined. The catalytic activity of CrCoAPO-5 is similar to those of either CoAPO-5 or CrAPO-5 under the same conditions and with similar loadings of cobalt and chromium. The selectivity of the mixed metal CrCoAPO-5 is similar to that of CoAPO-5, but differs markedly from that of CrAPO-5 and is clearly not a composite of the average selectivities of a combination of CoAPA-5 and CrAPO-5. The selectivity towards cyclohexanol can be increased by the addition of MEK or cyclohexanol; MEK serves also to significantly increase the activity. Some activity due to leaching of cobalt and chromium into the solution was observed. Thus, although CrCoAPO-5 generates both homogeneous and heterogeneous catalysis, the predominant contribution is as an heterogeneous catalyst.

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