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Synthesis of FeCoMnAPO-5 molecular sieve and catalytic activity in cyclohexane oxidation by oxygen

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A new FeCoMnAPO-5 with AFI structure was synthesized under hydrothermal conditions and characterized by XRD, FT-IR, X-ray fluorescence, nitrogen adsorption and SEM. The oxidation of cyclohexane with molecular oxygen was studied over the catalyst at 403 K. It show d higher activity compared to FeAPO-5, CoAPO-5 and MnAPO-5. The FeCoMnAPO-5 catalyst was recycled twice without loss of activity or selectivity.

KEY WORDS: molecular sieves; aluminophosphate; oxidation; cyclohexane.

1. Introduction

Since 1986 when metal incorporated aluminophosphate molecular sieves were first reported, numerous metals, which include Ti, V, Cr, Mn, Co, Ni, Zn, Fe, Mg, etc., have been introduced into their framework in order to enhance their acid and redox properties [1–3]. FeAPO-5, CoAPO-5 and MnAPO-5 molecular sieves have been widely studied in many kinds of reactions and show remarkable catalytic performance. For example, they have been used as catalysts for the catalytic oxidation:of cyclohexane to cyclohexanol and cyclohexanone [4]; of *p*-xylene to terephthalic acid; and of *p*-cresol to *p*-hydroxyl-benzaldehyde in mathanolic sodium hydroxide [5]. Also, the activity of these materials has been found for the ammoximation of cyclohexanone with ammonia and H_2O_2 to ε-caprolactam [6]. To our knowledge, there is no report on simultaneously substituted the three metals (Fe, Co, Mn) into its framework and of the resulting catalytic behavior, although the substitution of a single metal into aluminophosphate molecular sieves is well recognized [1,7].

For the potential wide applications, it is interesting and necessary to study the preparation method of FeCoMnAPO-5 and its catalytic properties. This paper constitutes the first report of the synthesis, characterization and catalytic performance in cyclohexane oxidation of FeCoMnAPO-5, where there is incorporated of three metals into the AIPO-5 framework. It is found to be an active, recyclable heterogeneous catalyst for the partial oxidation of cyclohexane by molecular oxygen under mild conditions.

2. Experimental

2.1. Sample preparation and characterization

Pseudoboehmite (78.6 wt% Al_2O_3), H_3PO_4 (85 wt% sol in water), $Co(CH_3COO)_2 \cdot 4H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were used as the sources of aluminium, phosphorus, cobalt, manganese and iron. FeCoMnAPO-5 was synthesized from the gel with following molar composition:0.02 Fe:0.02 Co:0.02 Mn:0.94 Al:1.0 P:0.75 Et_3N:20 H_2O. In a typical synthesis, the calculated amount of pseudoboehmite was hydrolyzed for 30 min. Then the solution of $Fe(NO_3)_3$, $Co(CH_3COO)_2$ and $Mn(CH_3COO)_2$ added to the alumina slurry at room temperature. After stirring 1 h, H_3PO_4 was added dropwise. Et_3N was slowly added to the homogeneous gel after vigorous stirring for 2 h. Finally, the entire gel was further stirred for another 2 h and the pH of the gel of this stage is about 5.5. The final gel was transferred into a Teflon-lined autoclave and crystallized at 453 K for 48 h. After the autoclave was quenched by cool water, the solid product was obtained by centrifugation. Then the solid was washed by deionized water for several times. After drying at 393 K for 8 h, it was calcined at 823 K for 24 h in flowing air. For comparison, CoAPO-5, MnAPO-5 and FeAPO-5 molecular sieves with the same molar ratio of Me/Al as that of FeCoMnAPO-5 and AlPO-5 were synthesized according to the literature [4].

The X-ray powder diffraction (XRD) patterns were obtained using Rigaku Miniflex with Cu Kα radiation ($\lambda = 0.1542$ nm). The FT-IR spectra were collected between 4000 and 400 cm^{-1} on a Bruker Tensor 27 FT-IR spectrameter after 32 scans for a resolution of 4 cm^{-1} in KBr media. The surface area and pore volume was determined by N_2 adsorption at 77 K on ASAP 2000 micromeritics instrument. The metal content of the

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molecular sieve was determined using a Philips Margix X-ray fluorescence spectrameter. Microphotography was performed with a KYKY-1000 SEM instrument (Beijing Oriental Jicheng Co. Ltd., China).

2.2. Catalytic test

Catalytic reactions were performed in a 100 mL autoclave reactor with a Teflon insert inside. Typically, 15 g cyclohexane, 0.1 g (65 wt%) *tert*-butyl hydroperoxide (TBHP) and 0.2 g catalyst were placed in the reactor. Then, after sealing, the reactor was heated to the reaction temperature, while agitation was ensured by an external magnetic stirrer. Upon heating to the reaction temperature, the reactor was charged with 1.0 MPa of O_2 while O_2 was fed continuously to maintain constant pressure. When the reaction was stopped, the catalyst was separated by filtration after the reaction mixture was diluted with 15 g ethanol to dissolve the by-products. The reaction products were identified by comparison with authentic products and by GC-MS analysis. The products were analyzed by GC and titration. After the decomposition of CHHP to cyclohexanol by adding triphenylphosphine to the reaction mixture, the quantitative analyses of cyclohexanol and cyclohexanone was carried out by Agilent 4890D gas chromatography, which was equipped with OV-1701 column (30 m × 0.25 mm × 0.3 μm), and the internal standard was methylbenzene. The concentration of alkyl hydroperoxide was determined by iodometric titration, and the by-products acid and ester by acid-base titration. Typically, 0.2 g triphenylphosphine was added 7 g reaction mixture, the solution was allowed to stand for 30 min before diluted with 25 mL acetone and 25 mL deionized water and then titrated with 0.1 M NaOH. The solution was refluxed for 1 h after adding 20 mL 0.1 M NaOH and then titrated with 0.1 M HCl.

After the separated catalyst was washed with ethanol three times, dried at 393 K for 2 h and then activated at 823 K for 3 h. The regenerated catalyst was used for the recycling study.

3. Results and discussion

The BET surface area and pore volume were 163 m^2 g^{-1} and 0.139 cm^3 g^{-1}, respectively. Figure 1 shows the XRD pattern of the FeCoMnAPO-5: it is identical with that of AFI structure in the literature [7,8]. Besides peaks due to AlPO-5, no other phase appeared, demonstrating that the sample is phase pure and highly crystallized in the AFI structure. The peak positions of FeCoMnAPO-5 XRD pattern are shifted to the left corresponding to that of pure AlPO-5. This implies that the lattice constants ($a.$ = 13.85 Å, d_{100} = 12.00 Å) increase when Fe (0.63 Å), Co (0.74 Å) and Mn (0.83 Å) substitution of Al (0.52 Å) atom in the aluminophosphate network compared to AlPO-5 (a = 13.77 Å, d_{100} = 11.93 Å) [8]. These proofs indicate that the three metals are incorporated simultaneously into the Framework of the sample. The metal content of FeCoMnAPO-5, determined by X-ray fluorescence, shows that 1.2 wt% of Mn, 1.1 wt% of Fe and 1.2 wt% of Co incorporate the framework. The SEM picture (figure 2) shows that the particle size of as-synthesized products ranges from 50 to 100 μm.

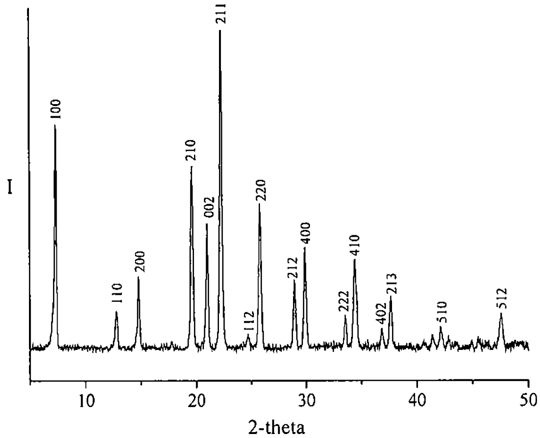

Figure 1. XRD pattern of FeCoMnAPO-5.

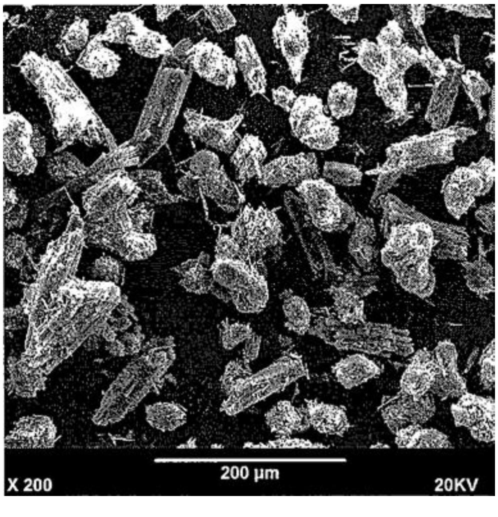

Figure 2. SEM picture of FeCoMnAPO-5.

After calcination at 823 K in air, the template was completely removed as determined by FT-IR spectroscopy (figure 3). The vibration bands of the FeCoMnAPO-5 (trace b) framework, 1109 cm^{-1} and 472 cm^{-1}, are shifted to lower wavenumbers with respect to those of AlPO-5, which are 1113 cm^{-1} and 477 cm^{-1}, respectively (trace a). This is because that the Fe–O, Co–O and Mn–O bonds are longer than the Al–O bond [9]. At the same time, it also confirms that the three metals are substituted into the framework of AlPO-5. The colour

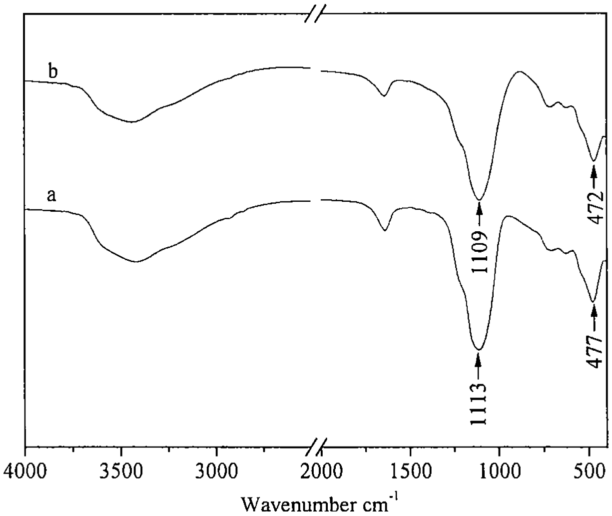

Figure 3. FT-IR spectra of FeCoMnAPO-5 (trace b) and AlPO-5 (trace a).

Table 1

Catalytic oxidation of cyclohexane over MeAPO-5 catalysts

Me	Convsion (mol%)	Product distribution (mol%)[a]				
		A	K	CHHP	Acid	Ester
FeCoMn	6.8	31.1	34.0	4.6	21.2	9.2
Mn	3.7	38.6	25.9	19.9	8.5	7.1
Co	5.6	31.7	28.1	26.5	9.3	4.4
Fe	2.0	4.7	17.6	65.8	6.2	5.7

[a] A, cyclohexanol; K, cyclohexanone; Acid, mainly adipic acid; Ester, dicyclohexyl adipate, hexanolactone and other ester.

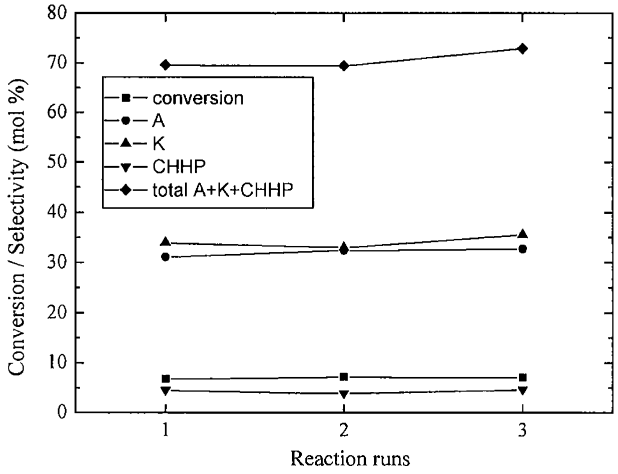

Figure 4. Recycling studies over calcined FeCoMnAPO-5.

of the catalyst changes from darkish colour to green–yellow after calcination. We attribute the change of colour to that Co(II) and Mn(II), which are incorporated into the framework, were raised to their III oxidation states during calcination. On the other hand, the valence changes are of considerable importance for redox reactions [2,10,11]. However, the calcined green–yellow material was found to change to grey after exposure in air for long time. Perhaps, this is related to the changes of coordination environments of the metals in air for long time [12].

The liquid phase oxidation of cyclohexane was carried out at 403 K for 3 h using molecular oxygen as oxidant and the results are shown in table 1. It can be seen that the FeCoMnAPO-5 showed good activity in oxidation cyclohexane to cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide (CHHP) that can decompose to cyclohexanol and cyclohexanone. At the same time, FeCoMnAPO-5 showed higher activity than those of a single metal into AlPO-5. The distribution of CHHP over FeCoMnAPO-5 is lower than those over MnAPO-5, CoAPO-5 or FeAPO-5 and this implies that it has stronger ability to decompose CHHP. The higher activity of FeCoMnAPO-5 may be attributed to the interaction of Fe–Co–Mn. In order to check the reusability of the catalyst, it was recycled twice, and the results are shown in figure 4. It can be observed that the activity and selectivity are similar to those of the fresh catalyst. Thus, the results indicate the FeCoMnAPO-5 is an efficient, recyclable heterogeneous catalyst for the oxidation of cyclohexane by oxygen.

The reaction had an induction time, and it could be remarkably shortened by the addition of a small amount of TBHP that acts as a radical initiator. The reaction was stopped by addition of 5 wt% hydroquinone, which is a free-radical scavenger. These tests show that the oxidation process proceeds by a radical mechanism, in agreement with the views of Thomas *et al.* [2,3,6] and Sheldon [13] on the cyclohexane catalytic oxidation by MeAPO-5.

4. Conclusions

In conclusion, a new material, FeCoMnAPO-5, has been prepared and characterized. It is proved that the three metals are incorporated into the framework of the AlPO-5. The catalytic activity of FeCoMnAPO-5 in cyclohexane oxidation is higher than that of FeAPO-5, MnAPO-5 and CoAPO-5. FeCoMnAPO-5 has stronger ability to decompose CHHP than the single metal into AlPO-5. Evidences indicate a tree radical mechanism for the catalytic oxidation. It is an efficient and recyclable catalyst for the oxidation of cyclohexane by molecular oxygen.

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