

INFLUENCE OF SUBSTITUTING AI BY Mg-Co AND Mn-Co ON THE PROPERTIES OF AlPO₄-5*

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Two kinds of crystalline microporous metal aluminophosphate molecular sieves, magnesium cobalt aluminophosphate (MgCoAPO-5) and manganese cobalt aluminophosphate (MnCoAPO-5), were synthesized by hydrothermal crystallization method in order to improve the surface acidity and catalytic activity of AlPO₄-5. The results of X-ray diffraction, infrared spectra and chemical compositions of MgCoAPO-5 and MnCoAPO-5 indicate that Mg-Co or Mn-Co enter the framework of AlPO₄-5 molecular sieve without disrupting the microporous framework. However, the results of catalytic studies show that MgCoAPO-5 and MnCoAPO-5 possess much higher surface acidity and catalytic activity than the unmodified AlPO₄-5.

Recent advances in the synthesis of novel molecular sieves based on aluminophosphate structures have opened new routes for product-selective catalysis of fuels and chemical feedstocks¹⁻³. However, sieve materials composed only of interconnected aluminate and phosphate units (AlPO₄) have neutral frameworks (i.e., Al/P = 1·0) with no exchangeable cations and, hence, do not possess strong acidity so useful in catalytic application of the aluminosilicate molecular sieves. The negative framework character required to support Brønsted-type acid sites can be generated by (i) substituting divalent cations into framework positions occupied by trivalent aluminum cations or (ii) tetravalent cations into sites occupied by pentavalent phosphorus. One, two or more kinds of additional cations can be incorporated into AlPO_{4-n} frameworks⁴. Indeed, such substitutions of Co(II), Mn(II) and Mg(II) into Al(III) positions and of Si(IV) into P(V) positions have been made in a number of research centres⁵⁻⁹, and a variety of metal-substituted, acid-form aluminophosphate molecular sieve structures have been produced. However, the substitutions of two kinds of additional cations into Al(III) positions have not yet been investigated sufficiently. The objective of this study is to investigate the substitutions of two kinds of divalent cations such as Mg(II)-Co(II) and Mn(II)-Co(II)

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into Al(III) positions and to characterize some of the structural and catalytic consequences of successful substitution.

EXPERIMENTAL

Synthesis

MgCoAPO-5 and MnCoAPO-5 were synthesized using orthophosphoric acid, aluminum isopropoxide, Mg, Co and Mn, Co acetate with triethanolamine as a template. The reactant mixture was stirred thoroughly until homogeneous, sealed in a stainless steel bomb with PTFE lining and heated to 150–200°C for 24–168 h. The range of reactant mixture composition was 0.8 to 1.5 (HOC₂H₅)₃N : 0.1–0.3 MeO : 0.1–0.3 MeO : 0.1–0.3 CoO : 0.75–0.80 Al₂O₃ : 1.0 P₂O₅ : 45–60 H₂O (Me = Mg, Mn). The crystalline product was filtered, washed with distilled water and dried at ambient temperature.

Analysis

The chemical compositions of the products were obtained by EDTA titrimetry and spectrophotometry. The powder XRD spectra and unit cell parameters of the product were measured by $D_{\max} - r$ type diffractometer with the Ni-filtered CuK radiation source. The scanning electron microscopy was carried out using a JSM-840 microscope. The infrared spectrum was recorded with an Alpha Centaur infrared spectrometer.

Reactor System

Catalytic runs were carried out in a fixed-bed continuous flow microcatalytic reactor. Twenty mg of samples were employed and activated at 500°C for 1 h in a H₂ flow at the rate 20 ml/min. The surface acidity of products was measured by the catalyst poisoning with pyridine as a probe and was compared with that of HSZM-5.

RESULTS AND DISCUSSION

Chemical Composition

The chemical compositions of MgCoAPO-5 and MnCoAPO-5 (Table I) show that the P/Al ratio of AlPO₄-5 rised to 1.23 and 1.22 after being substituted by Mg-Co and Mn-Co, respectively. It is evident that some parts of Al in the AlPO₄-5 framework were substituted by Mg-Co and Mn-Co selectively.

The powder XRD spectra of MgCoAPO-5 and MnCoAPO-5 were very similar to that of AlPO₄-5 without extra peaks, only 2θ shifted to low angle and d -spacings increased a little successively, which indicates that Mg-Co and Mn-Co enter the AlPO₄-5 framework without changing its structure (Tables II and III). The unit cell dimensions of MgCoAPO-5 and MnCoAPO-5 are larger than that of AlPO₄-5 slightly (Table IV). This is due to substituting Al(III) by the larger Co(II), Mg(II) and Mn(II) ($r_{Co^{2+}} = 65$ pm, $r_{Mg^{2+}} = 57$ pm, $r_{Mn^{2+}} = 66$ pm vs $r_{Al^{3+}} = 39$ pm for 4-coordinations).

The primary products of MgCoAPO-5 and MnCoAPO-5 are both intense blue-colored, indicating that cobalt is in a tetrahedral environment¹⁰. The scanning

TABLE I
Chemical compositions in wt. % of MgCoAPO-5 and MnCoAPO-5

Sample	MgO; MnO	CoO	Al ₂ O	P ₂ O ₅	C	N	Molar composition
MgCoAPO-5	2.70 (MgO)	5.02	28.49	48.49	4.97	1.12	0.20 (HOC ₂ H ₅) ₃ N : 0.21 MgO : : 0.19 CoO : 0.81 Al ₂ O ₃ : : P ₂ O ₅ : 0.92 H ₂ O
MnCoAPO-5	4.05 (MnO)	5.90	28.50	48.44	4.83	0.99	0.20 (HOC ₂ H ₅) ₃ N : 0.17 MnO : : 0.23 CoO : 0.82 Al ₂ O ₃ : : P ₂ O ₅ : 1.02 H ₂ O

TABLE II
XRD data for the MgCoAPO-5 (1 Å = 0.1 nm)

<i>d</i> /Å	<i>I</i> / <i>I</i> ₀						
12.143	46	3.999	100	2.995	22	2.393	12
6.954	10	3.614	9	2.676	5	2.147	4
6.014	24	3.462	36	2.612	17	2.114	3
4.534	49	3.091	19	2.442	5	1.915	5
4.244	62						

TABLE III
XRD data for the MnCoAPO-5 (1 Å = 0.1 nm)

<i>d</i> /Å	<i>I</i> / <i>I</i> ₀						
12.193	85	4.006	100	3.003	42	2.395	10
6.981	14	3.620	7	2.682	7	1.919	9
6.030	53	3.470	64	2.618	35	1.662	6
4.554	89	3.101	22	2.448	5	1.585	6
4.244	37						

TABLE IV
Unit cell dimensions of $\text{AlPO}_4\text{-5}$, MgCoAPO-5 and MnCoAPO-5 ($1 \text{ \AA} = 0.1 \text{ nm}$)

Sample	$a, \text{\AA}$	$c, \text{\AA}$	Volume, \AA^3	c/a
$\text{AlPO}_4\text{-5}$	13.713	8.427	1 372.4	0.615
MgCoAPO-5	13.799	8.425	1 385.3	0.611
MnCoAPO-5	13.753	8.420	1 379.3	0.612

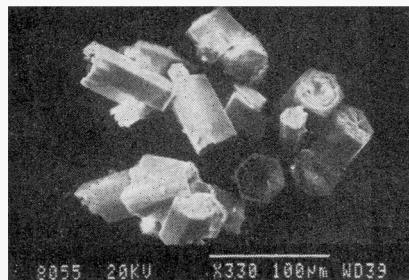


FIG. 1
SEM of MgCoAPO-5

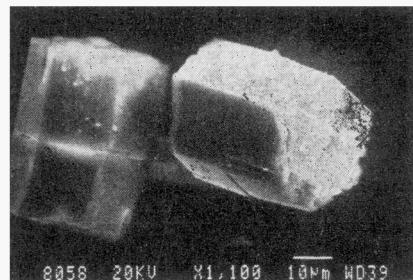


FIG. 2
SEM of MnCoAPO-5

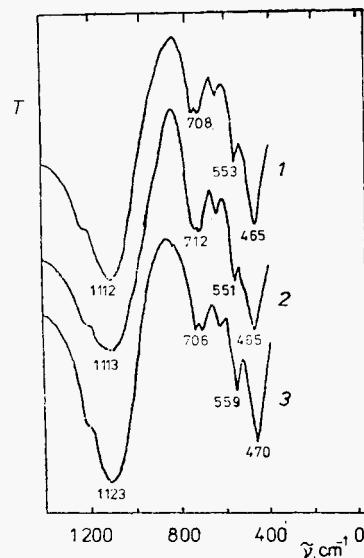


FIG. 3
Infrared spectra: 1 MgCoAPO-5 ,
2 MnCoAPO-5 , 3 $\text{AlPO}_4\text{-5}$

electron micrographs of MgCoAPO-5 and MnCoAPO-5 showed fine single crystal hexagonal prisms, approximately 20–40 μm in diameter and 40–100 μm long (Figs 1 and 2).

Infrared Spectroscopy

The infrared spectra of MgCoAPO-5, MnCoAPO-5 and AlPO₄-5 are shown in Fig. 3, it can be noted that the wavenumbers of MgCoAPO-5 and MnCoAPO-5 shift toward low wavenumbers slightly as compared with those of AlPO₄-5 because the cation dimensions of Mg(II), Mn(II) and Co(II) are larger than that of Al(III) for 4-coordinations. IR evidence further illustrates that the chemical modification during hydrothermal synthesis does induce isomorphous substitutions of Mg-Co and Mn-Co for Al in the AlPO₄-5 framework.

TABLE V

Activity of MgCoAPO-5, MnCoAPO-5 and HZSM-5 expressed as conversion (%)

Sample	Temperature, °C					
	200	250	300	350	400	450
MgCoAPO-5	41.5	89.7	96.0	96.7	98.5	100
MnCoAPO-5	—	18.3	63.4	98.2	100	—
HZSM-5	57.7	90.8	94.8	97.7	98.3	100

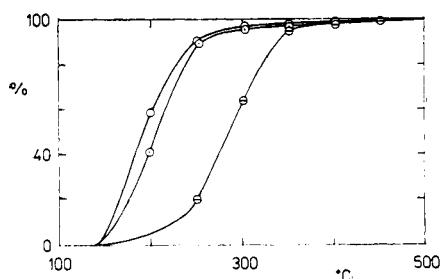


FIG. 4

The dependence of activity, expressed as conversion (%), on reaction temperature for the cracking of cumene: ○ HZSM-5, ● MgCoAPO-5, ◑ MnCoAPO-5

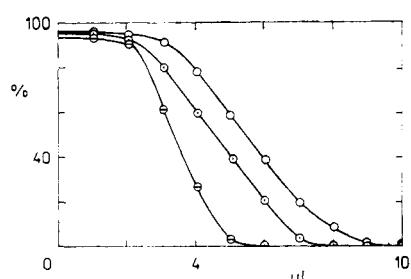


FIG. 5

Effect of poisoning of samples with pyridine (in μl) on the activity of cumene cracking, expressed as conversion (%), at 300°C: ○ HZSM-5, ● MgCoAPO-5, ◑ MnCoAPO-5

Catalytic Activity and Surface Acidity

The catalytic activity of AlPO₄-5, MgCoAPO-5 and HZSM-5 in cumene cracking was measured at various temperatures (Table V and Fig. 4). The results show that AlPO₄-5 is catalytically inactive in cumene cracking, however, MgCoAPO-5 and MnCoAPO-5 remarkably enhance cumene cracking after Mg-Co and Mn-Co introduction into the AlPO₄-5 framework. Especially, the activity of MgCoAPO-5 approaches that of HZSM-5, the activity of MnCoAPO-5 in the lower temperature region is lower than that of HZSM-5, but in the higher temperature region it gradually approaches the same level.

The catalyst poisoning with pyridine under the reaction conditions proportionally lowered the catalytic activity for cumene cracking at 300°C over the MgCoAPO-5, MnCoAPO-5 and HZSM-5, as shown in Fig. 5. From the poisonine experiments it was deduced that the numbers of active acid sites were $3.6 \cdot 10^{20}$, $3.0 \cdot 10^{20}$ and $1.9 \cdot 10^{20}$ per gram on HZSM-5, MgCoAPO-5 and MnCoAPO-5, respectively for cumene cracking. The acidic strength of three kinds of molecular sieves mentioned above decreased in the same order, which is consistent with their catalytic activity.

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