

# Synthesis, characterization and catalysis of (Co, V)-, (Co, Cr)- and (Cr, V)APO-5 molecular sieves

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## Abstract

A series of MAPO-5 and (M, N)APO-5 (with M and N = Co<sup>2+</sup>, Cr<sup>3+</sup> and V<sup>4+</sup>) molecular sieves have been hydrothermally synthesized and characterized. The as-synthesized and calcined samples were investigated with XRD, ICP, DRS UV–vis spectroscopy, ESR, <sup>27</sup>Al MAS NMR techniques to explore the valence, coordination and location of the incorporated transition metal ions. It was shown that isomorphous substitution of Co<sup>2+</sup> for Al<sup>3+</sup> convincingly occurred, and V<sup>4+</sup> also anchored to the sample by coordinating to two framework oxygen atoms and most probably occupying P<sup>5+</sup> sites, while no unambiguous spectroscopic evidence was provided for the incorporation of Cr<sup>3+</sup> in the lattice, although chemical analysis suggests this possibility in the case that Co<sup>2+</sup> or V<sup>4+</sup> are added to the synthesis gel. The preferential sequence for the incorporation of these transition metal ions in the AFI framework is: Co<sup>2+</sup> > V<sup>4+</sup> > Cr<sup>3+</sup>. After calcination, almost all V<sup>4+</sup> ions were oxidized to V<sup>5+</sup>, whereas Cr<sup>3+</sup> ions were oxidized to Cr<sup>5+</sup> and Cr<sup>6+</sup>. As catalysts, the (M, N)APO-5 molecular sieves are highly active for the selective oxidation of cyclohexane with a high cyclohexanone/cyclohexanol ratio in the presence of H<sub>2</sub>O<sub>2</sub>. The reaction temperature and solvent significantly influenced the catalytic behavior. Although some leaching of the transition metal ions was observed, the catalytic performance remained stable at least within five repeated runs.

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## 1. Introduction

AlPO<sub>4</sub>-*n* molecular sieves have no ion exchange property and acidity due to its electrically neutral structure originating from the strict alternation of AlO<sub>4</sub><sup>-</sup> and PO<sub>4</sub><sup>+</sup> tetrahedra in the framework. Nevertheless, this type of materials has a much more flexible framework, as compared to zeolites. This allows the isomorphous substitution of Al<sup>3+</sup> and/or P<sup>5+</sup> by transition metal ions. This process is of considerable interest since it gives rise to materials with acid and/or redox sites and consequently leading to interesting catalytic

properties [1–5]. In this respect, Co-, Cr-, Fe-, Mn-, Ti- and V-containing aluminophosphate molecular sieves have been extensively studied [6–38]. However, most attention has been focused on the isomorphous substitution of Al<sup>3+</sup> and/or P<sup>5+</sup> by one type of transition metal ion only.

In fact, detailed studies on the incorporation of two different transition metal ions in the framework of AlPO<sub>4</sub>-5 may provide important and interesting information about their physical and chemical properties. First, it may lead to the creation of new potential catalysts since framework incorporation of two or more metal ions could control the acidic and catalytic properties of the MeAPOs in a subtler manner. As compared with single metal ion-incorporated APOs, MeAPOs containing two or more metal ions have different types of metal specificity, acid sites, redox centers,

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active site strength and number of reactive sites. This is necessary for reactions involving the requirement of various active centers. Furthermore, it is also possible to exert an effect on the reaction intermediates [13]. In addition, studying of MeAPO-*n* molecular sieves with two or more metal ions may reveal which type of transition metal ion is preferentially incorporated in the aluminophosphate framework.

It has already been shown that framework transition metal ions (type and concentration) in MeAPO-*n* strongly affect the acidity and distribution of acid sites, and as a consequence, the activity and selectivity of the generated materials [13]. Kapoor and co-workers reported that VTAPO-5 molecular sieves exhibited an activity similar to that of VAPO-5, but much higher than that of TAPO-5 in the auto-oxidation of methanol [14]. Additionally, the products formed on VTAPO-5 catalyst were also much more complex than those obtained on VAPO-5 molecular sieves, although methyl formate and acetaldehyde were mainly produced. Blasco et al. found that as compared with VAPO-5, (Mg, V)APO-5 showed a higher selectivity to ethylene in the oxidative dehydrogenation of ethane due to the presence of Bronsted acid sites [15].

The goal of this paper is to report on the synthesis, characterization and catalysis of (Co, V)-, (Co, Cr)- and (Cr, V)APO-5 molecular sieves for the oxidation of cyclohexane. A comparison was further made with the corresponding single transition metal ion-substituted materials to assess the effect of a second transition metal ion on the spectroscopic and catalytic properties and reveal the preferential sequence of Co<sup>2+</sup>, V<sup>4+</sup> and Cr<sup>3+</sup> ions for the occupation of framework sites.

## 2. Experimental

### 2.1. Catalyst synthesis

MAPO-5 and (M, N)APO-5 molecular sieves were synthesized with bidistilled water, pseudo-boehmite (70% Al<sub>2</sub>O<sub>3</sub>, Catapal), H<sub>3</sub>PO<sub>4</sub> (85 wt.% in aqueous solution, Acros), trimethylamine (TEA, 99%, Acros), and one or two types of transition metal ion salts (Co(CH<sub>3</sub>-COO)<sub>2</sub>·4H<sub>2</sub>O (97%, Acros), CrCl<sub>3</sub> (UCB) and VO(SO<sub>4</sub>)·5H<sub>2</sub>O (pure)). The gel started from the mixture of 1.0TEA:(0–0.4)MO (or M<sub>2</sub>O<sub>3</sub>):(0–0.08)N<sub>2</sub>O<sub>3</sub> (or NO<sub>2</sub>):(0.75–1)Al<sub>2</sub>O<sub>3</sub>:(0.92–1)P<sub>2</sub>O<sub>5</sub>:40H<sub>2</sub>O. The preparation procedure is as follows: H<sub>3</sub>PO<sub>4</sub> was first dissolved in water, followed by the addition of the transition metal ion salts. Then, pseudo-boehmite was added to the solution at 0 °C under continuous stirring condition after the transition metal ion salts were dissolved. Finally, triethylamine as templating molecule was dropwise introduced to the above mixture after 25 min. This mixture was further stirred for 1 h. The resultant gel was sealed in a Teflon-lined autoclave and crystallized under autogeneous pressure without stirring at 150–190 °C for 16–48 h. The as-synthesized solids were filtered, washed with bidistilled water, and further dried at 60 °C.

### 2.2. Catalyst characterization

The crystalline phase purity of the as-synthesized solids was identified with a Siemens D5000 X-ray diffractometer with Cu K $\alpha$  radiation. The diffuse reflectance (DR) UV–vis spectra were recorded on a Varian Cary 5 spectrometer with an integration sphere against a white Halon reference standard in the region 1000–200 nm. The chemical compositions of the as-synthesized molecular sieves were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Scan 16, TJA Corporation). The accuracy of the ICP-AES measurements was confirmed by measuring several times the same sample and quite similar analysis results were obtained. The numbers reported in the paper represent a mean value calculated from three independent measurements of the same sample. The electron spin resonance (ESR) spectra were measured by a Bruker ESP 300E spectrometer. <sup>27</sup>Al MAS NMR spectra of the as-synthesized solids were carried out on a Bruker DRX400 nuclear magnetic resonance spectrometer (9.4 T). A 0.3  $\mu$ s pulse length with the rf field of  $\approx$ 150 kHz was applied. The repetition time was set to 0.2 s and 3000 scans were accumulated. An aqueous solution of Al(NO<sub>3</sub>)<sub>3</sub> was used as reference compound. The spin rate of the rotor was 20 kHz for all <sup>27</sup>Al NMR measurements.

### 2.3. Catalyst testing

The catalytic performance of MAPO-5 and (M, N)APO-5 molecular sieves calcined at 530 °C for 10 h was tested with cyclohexane ( $\geq$ 99.5%, used as purchased without further purification, Beijing Chem. Corp.) oxidation as model reaction in the presence of H<sub>2</sub>O<sub>2</sub> (30% in aqueous solution, Beijing Chem. Corp.). Except as specified, the reaction was carried out at 60 °C in a 50-mL sealed stainless steel autoclave for 40 h. A typical batch is as follows: 18.5 mmol of C<sub>6</sub>H<sub>12</sub>, 18.5 mmol of H<sub>2</sub>O<sub>2</sub>, 0.1 g of catalyst and 10 mL of solvent (solvent = acetone (CH<sub>3</sub>COCH<sub>3</sub>,  $\geq$ 99.5%, Beijing Chem. Corp.), 1,2-dichloroethane (CH<sub>2</sub>ClCH<sub>2</sub>Cl,  $\geq$ 99%, Beijing Chem. Corp.), methanol (CH<sub>3</sub>OH,  $\geq$ 99.5%, Beijing Chem. Corp.), acetonitrile (CH<sub>3</sub>CN, 95%, Beijing Chem. Corp.) and carbon tetrachloride (CCl<sub>4</sub>,  $\geq$ 99.5%, Beijing Chem. Corp.)). The product was analyzed with a GC-9A gas chromatograph equipped with a packed PEG column (3 m) and a flame ionization detector.

## 3. Results and discussion

### 3.1. Catalyst synthesis and characterization

The chemical compositions and sample notations of MAPO-5-*x* and (M, N)APO-5-*x*-*y* are summarized in Table 1 with *x* and *y* representing the [M]:[P] and [N]:[P] molar ratio in the synthesis gel, respectively. Fig. 1 shows as examples the XRD patterns of the as-synthesized (Co,V)APO-5-0.05–0.03, (Co,Cr)APO-5-0.05–0.03 and

Table 1  
Chemical composition of the as-synthesized MAPO-5 and (M, N)APO-5 molecular sieves

Sample code	Chemical composition of the gel				Chemical composition of the formed products											
	Al/P	Co/P	Cr/P	V/P	Al/P	(Co + Al)/P	(Co + Al + V)/P	(Co + Al)/(P + V)	(Co + Al + V)/(P + V)	(Co + Al + Cr)/P	(Cr + Al + V)/P	(Cr + Al)/(P + V)	(Co + Al + Cr)/(P + V)	(Al + V)/P	(Al + V)/(P + V)	(Cr + Al)/P
VAPO-5-0.01	0.99	—	—	0.01	1.00	—	—	1.00	—	—	—	—	—	1.01	—	—
VAPO-5-0.03	0.97	—	—	0.03	1.02	—	—	1.00	—	—	—	—	—	1.03	—	—
VAPO-5-0.05	0.95	—	—	0.05	1.02	—	—	0.99	—	—	—	—	—	1.04	—	—
CrAPO-5-0.01	0.99	—	0.01	—	1.01	—	—	—	—	—	—	—	—	—	—	1.03
CrAPO-5-0.03	0.97	—	0.03	—	1.01	—	—	—	—	—	—	—	—	—	—	1.02
CrAPO-5-0.05	0.95	—	0.05	—	0.98	—	—	—	—	—	—	—	—	—	—	1.02
(Co, V)APO-5-0.05-0.01	0.94	0.05	—	0.01	0.96	1.02	1.02	0.96	1.02	—	—	—	—	—	—	—
(Co, V)APO-5-0.05-0.03	0.92	0.05	—	0.03	0.96	1.02	1.01	0.95	1.03	—	—	—	—	—	—	—
(Co, V)APO-5-0.05-0.05	0.90	0.05	—	0.05	0.94	1.00	0.98	0.92	1.02	—	—	—	—	—	—	—
(Co, V)APO-5-0.10-0.03	0.87	0.10	—	0.03	0.97	1.03	1.00	0.96	1.03	—	—	—	—	—	—	—
(Co, V)APO-5-0.15-0.03	0.82	0.15	—	0.03	0.89	1.07	0.99	0.88	1.02	—	—	—	—	—	—	—
(Co, Cr)APO-5-0.05-0.01	0.94	0.05	0.01	—	0.95	1.00	—	—	—	—	—	—	1.01	—	—	—
(Co, Cr)APO-5-0.05-0.03	0.92	0.05	0.03	—	0.92	0.97	—	—	—	—	—	—	0.99	—	—	—
(Co, Cr)APO-5-0.05-0.05	0.90	0.05	0.05	—	0.92	0.96	—	—	—	—	—	—	1.00	—	—	—
(Co, Cr)APO-5-0.10-0.03	0.87	0.10	0.03	—	0.93	1.03	—	—	—	—	—	—	1.05	—	—	—
(Co, Cr)APO-5-0.15-0.03	0.82	0.15	0.03	—	0.87	1.01	—	—	—	—	—	—	1.03	—	—	—
(Cr, V)APO-5-0.01-0.01	1	—	0.01	0.01	1.04	—	—	1.02	—	1.05	1.09	1.05	—	1.07	1.07	1.07
(Cr, V)APO-5-0.03-0.01	0.98	—	0.03	0.01	0.98	—	—	0.97	—	1.00	1.01	1.00	—	0.99	1.00	1.00
(Cr, V)APO-5-0.05-0.01	0.96	—	0.05	0.01	0.97	—	—	0.96	—	1.00	1.01	1.00	—	0.97	1.01	1.01
(Cr, V)APO-5-0.05-0.03	1	—	0.03	0.03	1.08	—	—	1.05	—	1.10	1.16	1.10	—	1.11	1.11	1.13

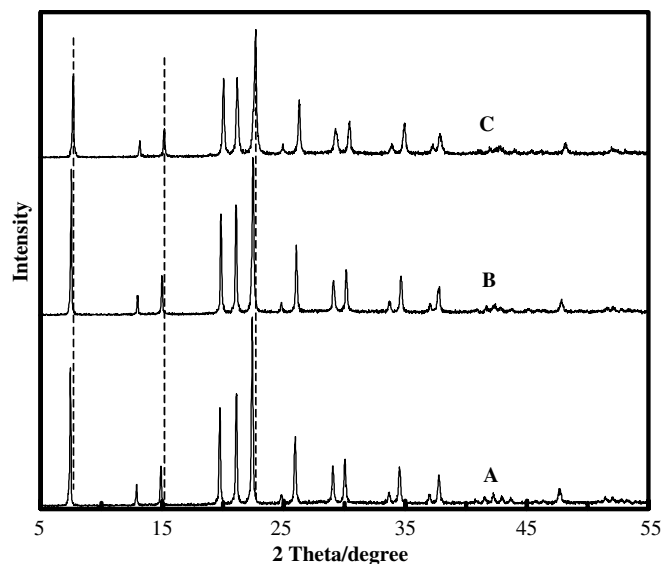


Fig. 1. XRD patterns of the as-synthesized (A) (Co, V)APO-5-0.05-0.03, (B) (Co, Cr)APO-5-0.05-0.03 and (C) (Cr, V)APO-5-0.03-0.03 samples.

(Cr, V)APO-5-0.03-0.03 materials. Clearly, all samples had AFI topology with a high crystallinity, and no impure crystalline phase was detected [10]. Despite of this, it was found that all reflections in the XRD patterns of Co-containing samples shifted to lower positions, as compared to the materials free of this element. This reveals that addition of Co in the synthesis gel led to an enlargement of the unit-cell volume as a result of the unit-cell expansion [8–11], showing that  $\text{Co}^{2+}$  ions were easily incorporated in the framework. This is further confirmed by the data shown in Table 1. It can be concluded from Table 1 that for the Co-containing MeAPO molecular sieves, the [Al]:[P] molar ratio severely deviated from 1, as compared to the [Co + Al]:[P] ratio. Transition metal ion-substituted microporous aluminophosphates, as a general rule, have a good unity in their chemical compositions with respect to framework T contents because Al and P tetrahedra are alternatively linked via oxygen atoms in the microporous aluminophosphates [3,5–11,33,34]. In contrast, for the CrAPO-5 molecular sieves, the [Al]:[P] ratio was more close to 1 than the [Cr + Al]:[P] ratio. This suggests that  $\text{Cr}^{3+}$  cations are with this synthesis method difficult to isomorphously replace framework  $\text{Al}^{3+}$ . In the case of VAPO-5 molecular sieves, the [Al]:[P + V] ratio was almost 1, while the [Al]:[P], particularly [Al + V]:[P] ratios deviated from unity. This indicates that  $\text{V}^{4+}$  ions might also be incorporated in the framework, and probably occupied the P sites [3,22,33,34]. Thus, the [Co + Al]:[P + V] ratio, as expected, were more close to 1 than other possible ratios of chemical compositions for the (Co, V)APO-5 molecular sieves (Table 1). However, for the (Cr, V)APO-5-0.03-0.03 sample, no possible ratio was found to approximate 1. It is worth noting that for the (Co, Cr)APO-5 molecular sieves, the [Co + Al + Cr]:[P] ratio more approached 1 than the [Co + Al]:[P] ratio when the Cr content in the synthesis

gel was low. This also holds true for the (Cr, V)APO-5 molecular sieves. As compared with the [Al]:[P], [Al]:[P + V], [Cr + Al + V]:[P], [Al + V]:[P] and [Cr + Al]:[P] ratios, the [Cr + Al]:[P + V] was nearer to 1. The reason is not clear for the moment since no unambiguous spectral evidence was found for the framework incorporation of  $\text{Cr}^{3+}$ , as shown in the following sections. The isomorphous substitution of  $\text{Cr}^{3+}$  for  $\text{Al}^{3+}$  in the framework might be possible since  $\text{CH}_3\text{COO}^-$  was an effective co-templating molecule for the framework incorporation of Cr when triethylamine and pseudo-boehmite were used as template and Al source respectively [25]. Incorporation of  $\text{Cr}^{3+}$  ions in the framework of  $\text{AlPO}_4\text{-5}$  molecular sieves has recently been confirmed as well by X-ray absorption spectroscopy (EXAFS-XANES) [32], although it required the presence of two extra-framework oxygen atoms to complete its pseudo-octahedral coordination environment. Nevertheless, the general non-unity of the chemical compositions of Cr-containing samples indicates that among the studied transition metal ions,  $\text{Cr}^{3+}$  is the most difficult one to be incorporated in the framework (Table 1). The preferential sequence of these transition metal ions for the occupation of framework sites is therefore of the order:  $\text{Co}^{2+} > \text{V}^{4+} > \text{Cr}^{3+}$ .

This sequence in ease of framework substitution is further confirmed by spectral characterization. Fig. 2 shows the DR UV–vis spectra of the as-synthesized MAPO-5 and (M, N)APO-5 molecular sieves. A strong triplet band between 500 and 650 nm was observed in the DR UV–vis spectra of all Co-containing samples. This is attributed to  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$  of high-spin  $\text{Co}^{2+}$  ( $d^7$ ) in tetrahedral coordination [2–5,8–11], evidencing the isomorphous substitution of  $\text{Al}^{3+}$  ions by  $\text{Co}^{2+}$ . The similar band intensity of (Co, Cr)APO-5-0.05–0.05 and (Co, V)APO-5-0.05–0.03 to that of CoAPO-5-0.05 shows that  $\text{Cr}^{3+}$  and  $\text{V}^{4+}$  ions have no

strong influence on the incorporation of  $\text{Co}^{2+}$  in the framework.

In contrast,  $\text{Cr}^{3+}$ -containing  $\text{AlPO}_4\text{-5}$  samples all had two absorbance bands around 440 and 620 nm with a shoulder at about 680 nm although the last two bands of (Co, Cr)APO-5-0.05–0.05 were overlapped by the above-mentioned strong triplet band. The former two bands can be assigned to  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\text{v})$  and  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$  d–d transitions, respectively, while the last one arises from spin-forbidden transitions [3,24,35]. This is typical for octahedrally coordinated  $\text{Cr}^{3+}$ , whereas no evidence was found for the presence of tetrahedral  $\text{Cr}^{3+}$  ions [3,24,35]. After calcination, two new bands at about 280 and 345 nm appeared (not shown), which are ascribed to the charge-transfer transition of  $\text{O} \rightarrow \text{Cr}^{6+}(\text{d}^0)$ , suggesting that part of  $\text{Cr}^{3+}$  was oxidized to chromate-like species [3,24,35]. As for the as-synthesized V-containing aluminophosphates, two broad bands could be distinguished. One was located at the region of 280–350 nm, and increased in intensity with V content. The other absorption band was between 570 and 640 nm. This is indicative of the presence of vanadyl-like and oligomeric species, and the amount of which increased with increasing vanadium content in the synthesis gel [3,12,22,27].

The ESR spectra of the as-synthesized and calcined (Co, Cr)APO-5-0.05–0.03 are as examples shown in Fig. 3. CrAPO-5 and (Cr, V)APO-5 molecular sieves showed similar spectral characteristics. The ESR spectra of the as-synthesized Cr-containing samples were dominated by an isotropic signal and a broad signal with  $g$  of about 2 and 5.2, respectively. This is characteristic of  $\text{Cr}^{3+}$  in a distorted octahedral coordination [3,24,25,31,35,36]. After calcination, a strong and narrow signal, attributed to isolated  $\text{Cr}^{5+}$ , appeared with a  $g = 1.97$ , whereas the broad signal with the  $g \approx 2$  disappeared. This strong signal could be deconvoluted into four signals at  $g_{\parallel 1} = 1.949$ ,

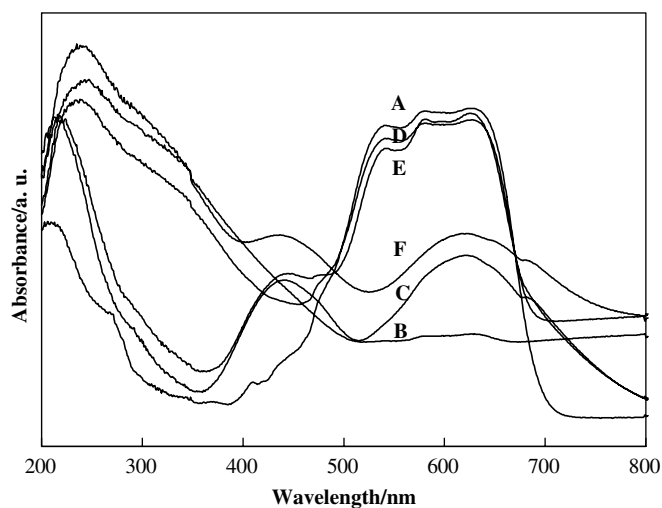


Fig. 2. DR UV–vis spectra of the as-synthesized (A) CoAPO-5-0.05, (B) VAPO-5-0.03, (C) (Co, V)APO-5-0.05–0.03, (D) CrAPO-5-0.05, (E) (Co, Cr)APO-5-0.05–0.05 and (F) (Cr, V)APO-5-0.05–0.03.

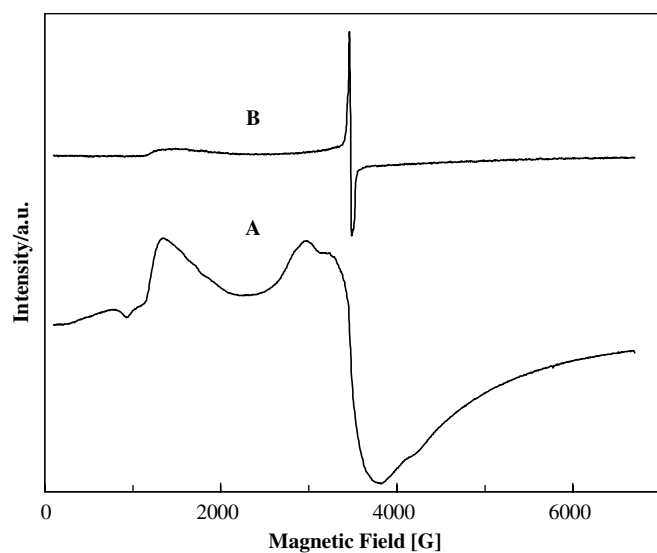


Fig. 3. ESR spectra of the (A) as-synthesized and (B) calcined (Co, Cr)APO-5-0.05–0.03 at room temperature.

$g_{\perp 1} = 1.988$ ,  $g_{\parallel 2} = 1.967$ ,  $g_{\perp 2} = 1.977$  respectively. The former two  $g$  values are attributed to tetrahedral-like  $\text{Cr}^{5+}$  species [31], while the other two  $g$  values are attributed to square-pyramidal  $\text{Cr}^{5+}$  species [3,31,35,36]. Combining with the DR UV–vis characterization, it could be concluded that  $\text{Cr}^{3+}$  ions were oxidized to  $\text{Cr}^{5+}$  and  $\text{Cr}^{6+}$  ions after calcination.

It has been shown that tetravalent vanadium displays a quite complex ESR spectrum of eightfold hyperfine splitting as a result of the interaction of the unpaired electron of  $\text{V}^{4+}$  ( $S = 1/2$ ) with the nuclear spin of  $^{51}\text{V}$  ( $I = 7/2$ ). This is in good agreement with the as-synthesized V-containing samples (Fig. 4). The spectral similarity of (Co, V)APO-5-0.05–0.03 to VAPO-5 indicates that V sites in the (Co, V)APO-5 and VAPO-5 molecular sieves had a similar local geometry [27], *viz.* part of them was present in the state of isolated square-pyramidal and/or distorted octahedral vanadyl-like ( $\text{VO}^{2+}$ ) species [3,12,15,22,33,37]. After calcination, no ESR signal was detected, showing that all  $\text{V}^{4+}$  ions were oxidized to the EPR-inactive  $\text{V}^{5+}$ . In our previous work, it was found by simulating the spectrum that two signals of  $\text{S}_1$  and  $\text{S}_2$  were present in the VAPO-5 molecular sieves besides a broad one characteristic for extra oxide clusters [22]. Since all tetrahedral sites in  $\text{AlPO}_4\text{-5}$  are crystallographically equivalent, it is unlikely that  $\text{S}_1$  and  $\text{S}_2$  are due to the  $\text{VO}^{2+}$  located at different lattice positions in the framework. Thus, it is more reasonable to assume that these two signals result from the different ligands of  $\text{VO}^{2+}$ .  $\text{S}_2$  represents the  $\text{V}^{4+}$  ions coordinated by O and  $\text{H}_2\text{O}$ , while  $\text{S}_1$  is associated with  $\text{VO}^{2+}$  ions interacting with protonated templating molecule since it could not be recovered by  $\text{H}_2$  reduction after calcination [13]. However, the exact location of  $\text{V}^{4+}$  in the framework is still in a debate. Some authors suggested that  $\text{V}^{4+}$  substitutes

for  $\text{Al}^{3+}$  [38], while other research groups believe it replaces  $\text{P}^{5+}$  [22,33,34]. Nagarajan et al. very recently deduced from ESR and hyperfine sublevel correlation (HYSCORE) spectroscopy that  $\text{VO}^{2+}$  species is present in the as-synthesized VAPO-5 by equatorially coordinating to two framework oxygen atoms and presumably three water molecules in a distorted octahedral geometry with phosphorus and aluminum framework atoms in the second coordination shell [37]. Despite of the controversy, the common point in all the well-documented literature reports is that vanadyl-like species is anchored to the framework via coordination to two framework oxygen atoms.

$^{31}\text{P}$  MAS NMR spectrum can provide convincing evidence for the framework incorporation of heteroatoms in microporous aluminophosphate materials, but for Co-, Cr- as well as V-containing AFI materials, the strong dipolar coupling of  $^{31}\text{P}$  with unpaired electrons of  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{V}^{4+}$  makes this very difficult. In contrast, it is possible to determine whether the isomorphous substitution of transition metal ions for  $\text{Al}^{3+}$  occurs by the shift of the line characteristic for tetrahedral  $\text{Al}^{3+}$  [13,14,28]. Akolekar as well as Kapoor and co-workers found a significant shift of tetrahedrally coordinated  $^{27}\text{Al}$  when transition metal ions were incorporated in the framework of  $\text{AlPO}_4\text{-5}$  and other microporous aluminophosphates [13,14]. The  $^{27}\text{Al}$  MAS NMR spectra (Fig. 5) of the as-synthesized  $\text{AlPO}_4\text{-5}$ , MAPO-5 and (M, N)APO-5 molecular sieves show that all samples displayed three lines around 34, 6 and  $-15$  ppm although the last band was present as a shoulder for Co-containing materials. These three lines can be ascribed to tetrahedral, penta-coordinated as well as octahedral Al sites, respectively. This is not uncommon for the as-synthesized aluminophosphate-based molecular sieves. Regardless of the similarity, it was found that the band position was slightly different. As compared with  $\text{AlPO}_4\text{-5}$  (33.3 ppm), the tetrahedral  $^{27}\text{Al}$  lines of the (Co, V)APO-5-0.10–0.03 (34.7 ppm) and (Co, Cr)APO-5-0.05–0.03 (34.3 ppm) samples shifted with more than 1 ppm, while no apparent shift was observed for the CrAPO-5-0.03 (33.6 ppm) and VAPO-5 (33.5 ppm) molecular sieves. This supports the isomorphous substitution of  $\text{Co}^{2+}$  for  $\text{Al}^{3+}$  in Co-containing samples, whereas no clear evidence was found for the incorporation of  $\text{Cr}^{3+}$  and  $\text{V}^{4+}$  ions in the lattice Al sites. This is in agreement with DRS UV–vis and ESR analysis results. As we know,  $\text{Cr}^{3+}$  ions could only occupy lattice  $\text{Al}^{3+}$  sites, while  $\text{V}^{4+}$  might replace both  $\text{Al}^{3+}$  and  $\text{P}^{5+}$  ions. Since no shift of the tetrahedral  $^{27}\text{Al}$  line was observed for the CrAPO-5 and VAPO-5, it is reasonable to deduce that  $\text{Cr}^{3+}$  ions were not incorporated in the framework, or the incorporated amount was too small to significantly affect the  $^{27}\text{Al}$  position, whereas  $\text{V}^{4+}$  ions occupied the P sites, in accordance with the chemical analysis results shown in Table 1. As for the (Cr, V)APO-5-0.03–0.03 sample, the reason for a shift of 0.7 ppm is not so clear. It is known that paramagnetic species such as  $\text{Cr}^{n+}$  with  $n < 6$  could quench  $^{27}\text{Al}$  NMR lines due to relaxation phenomena [39]. Thus, a close vicinity of  $\text{Cr}^{3+}$  ions to

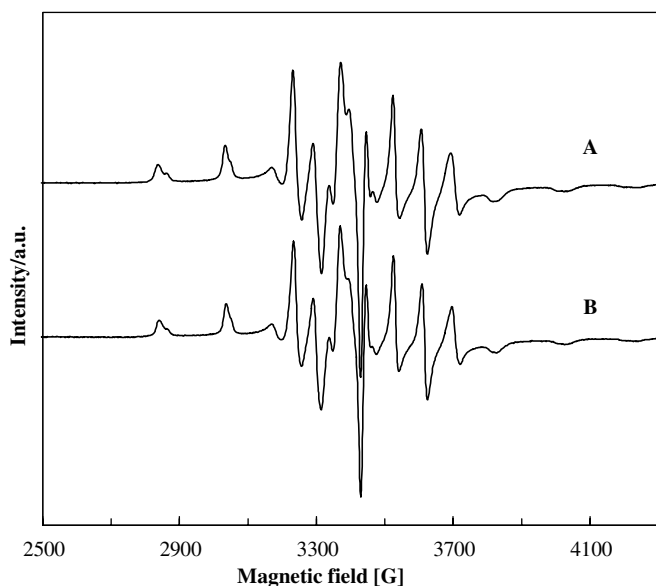


Fig. 4. ESR spectra of the as-synthesized (A) VAPO-5 and (B) (Co, V)APO-5-0.05–0.03 at room temperature.

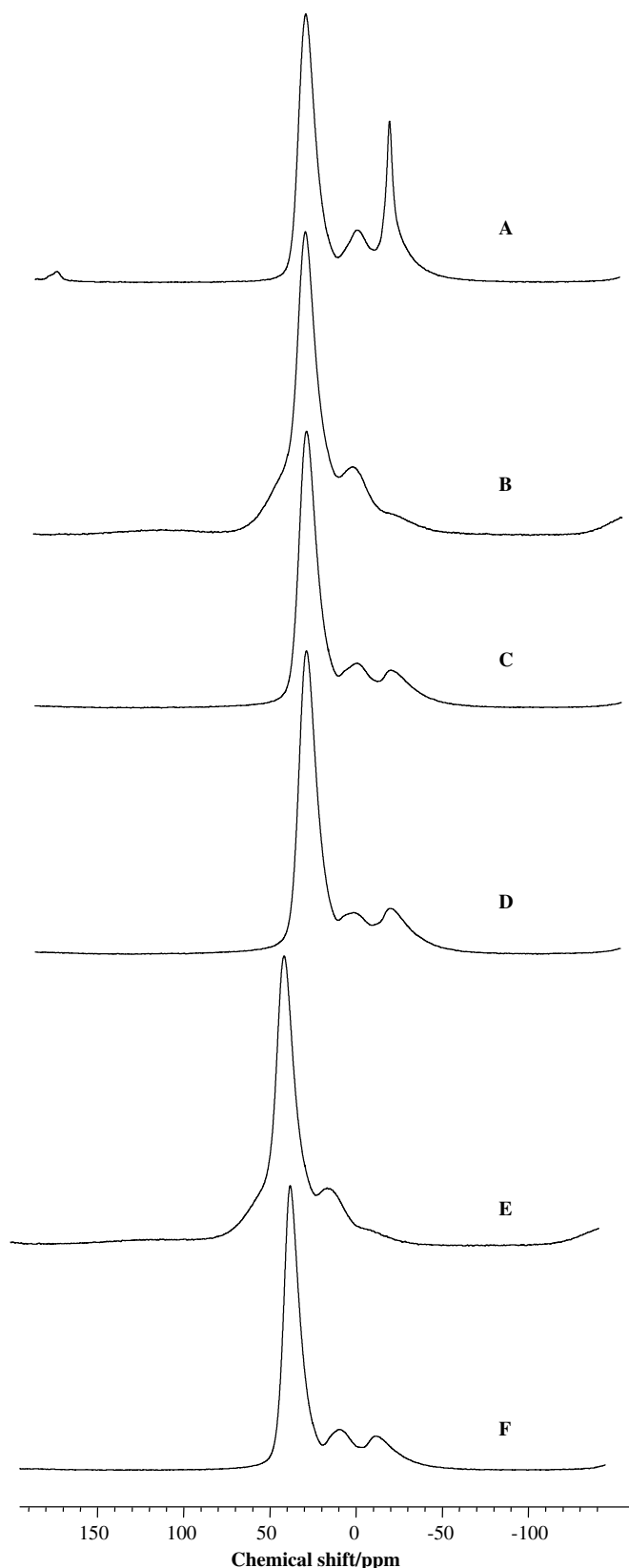


Fig. 5.  $^{27}\text{Al}$  MAS NMR spectra of the as-synthesized (A)  $\text{AlPO}_4\text{-5}$ , (B)  $(\text{Co}, \text{V})\text{APO-5-0.10-0.03}$ , (C)  $(\text{Cr}, \text{V})\text{APO-5-0.05-0.03}$ , (D)  $\text{CrAPO-5-0.05}$ , (E)  $(\text{Co}, \text{Cr})\text{APO-5-0.10-0.03}$  and (F)  $\text{VAPO-5-0.03}$ .

the lattice Al sites would lead to a shift of tetrahedral  $^{27}\text{Al}$  line [40]. On the other hand, the possibility for the incorporation of  $\text{Cr}^{3+}$  in the framework could not be excluded [16,21,25,26,31] as the framework incorporation of  $\text{Cr}^{3+}$  in  $\text{AlPO-5}$  was recently evidenced by the XAFS technique [32]. In addition, it is also supported by chemical analysis. The observation of  $\text{Cr}^{3+}$  ion in an octahedral coordination in general originates from its  $3d^3$  configuration, which strongly makes the distorted tetrahedral coordination state transform into the more stable sixfold coordination environment by bonding two water molecules located in the channel [32].

### 3.2. Catalyst testing

Since the type, content, valence and coordination state of transition metal ions in aluminophosphates have a significant influence on the catalytic property of the prepared materials, it is necessary to perform an extensive study of the catalytic performance of M- and (M, N)APO-5 molecular sieves with different compositions. It was shown that all samples exhibited catalytic activity with cyclohexanone and cyclohexanol as major products. Table 2 summarizes the typical catalytic results of MAPO-5 and (M, N)APO-5 molecular sieves for the selective oxidation of cyclohexane at a reaction time of 40 h. In agreement with the intrinsic nature of transition metal ions, the activity over the MAPO-5 molecular sieves decreased in the sequence  $\text{CrAPO-5} > \text{VAPO-5} > \text{CoAPO-5}$ , while no activity could be detected with the  $\text{AlPO-5}$  molecular sieves. For each series of catalyst materials, the activity, as expected, depended on the content of incorporated transition metal ions.  $\text{VAPO-5-0.05}$  and  $\text{CrAPO-5-0.05}$  are the most active catalysts among the prepared  $\text{VAPO-5}$  and  $\text{CrAPO-5}$

Table 2  
Catalytic results of the MAPO-5 and (M, N)APO-5 molecular sieves for the oxidation of cyclohexane<sup>a</sup>

Catalyst	Conversion (%)	Selectivity (%)			One/ol
		One <sup>b</sup>	Ol <sup>c</sup>	Others <sup>d</sup>	
$\text{AlPO}_4\text{-5}$	0.0	–	–	–	–
$\text{VAPO-5-0.03}$	2.9	57.9	30.3	11.8	1.9
$\text{VAPO-5-0.05}$	4.0	55.5	32.1	12.4	1.7
$\text{CoAPO-5-0.05}$	2.9	63.0	34.2	2.8	1.8
$\text{CoAPO-5-0.15}$	2.8	56.1	32.2	11.7	1.7
$\text{CrAPO-5-0.05}$	7.8	61.8	34.1	4.1	1.8
$\text{CrAPO-5-0.03}$	2.6	66.7	33.3	–	2.0
$(\text{Co}, \text{V})\text{APO-5-0.05-0.01}$	5.2	63.6	32.2	4.2	2.0
$(\text{Co}, \text{V})\text{APO-5-0.05-0.05}$	3.3	63.4	34.2	2.4	2.0
$(\text{Co}, \text{Cr})\text{APO-5-0.05-0.03}$	3.9	62.0	33.0	5.0	1.9
$(\text{Co}, \text{Cr})\text{APO-5-0.05-0.05}$	6.0	57.8	31.8	10.4	1.8
$(\text{Cr}, \text{V})\text{APO-5-0.05-0.01}$	8.1	58.6	32.9	8.5	1.8
$(\text{Cr}, \text{V})\text{APO-5-0.05-0.03}$	9.8	61.2	29.1	9.7	2.1
$(\text{Cr}, \text{V})\text{APO-5-0.05-0.05}$	7.4	56.6	32.8	10.6	1.7

<sup>a</sup> Reaction conditions: 60 °C, 40 h, 0.1 g catalyst, 10 mL acetone, 18.5 mmol cyclohexane, 18.5 mmol  $\text{H}_2\text{O}_2$  (30% in aqueous solution).

<sup>b</sup> Cyclohexanone.

<sup>c</sup> Cyclohexanol.

<sup>d</sup> Cyclohexandiol, cyclohexene and so on.

molecular sieves, respectively. It is not very clear why the activity obtained for CoAPO-5 was independent on the Co content in the experimental range. A decrease in site isolation of  $\text{Co}^{2+}$  at high cobalt content might be one reason since the site isolation is the key factor to achieve active and truly heterogeneous catalyst [41]. It is worth noting that simultaneous incorporation of appropriate amounts of vanadium and cobalt in the AFI framework, i.e. for the (Co, V)APO-5-0.05–0.01 sample, resulted in a significant improvement in activity, suggesting a synergistic effect may exist between Co and V. This is further confirmed by the result that the mechanical mixture of CoAPO-5-0.05 and VAPO-5-0.01 showed a conversion of 4.1% under the same reaction conditions, which is lower than that (5.2%) obtained on the (Co, V)APO-5-0.05–0.01. This also holds for (Cr, V)APO-5 molecular sieves.

The extensive investigation of the catalytic performance of the prepared MAPO-5 and (M, N)APO-5 molecular sieves shows that (Co, Cr)APO-5-0.05–0.05, (Co, V)APO-5-0.05–0.01 and (Cr, V)APO-5-0.05–0.03 gave the highest cyclohexane conversion for each series of (M, N)APO-5 molecular sieves. Therefore, hereafter the catalytic performance of these three samples was mainly explored, and a comparison was further made with CrAPO-5-0.05 as this sample was the most active single metal ion-incorporated MAPO-5 molecular sieves.

The solvent effect was first studied since a solvent could strongly affect the catalytic performance of transition metal ion-substituted molecular sieves. Fig. 6 shows that acetone and acetonitrile are favorable solvents for the oxidation of cyclohexane, whereas 1,2-dichloroethane and carbon tetrachloride as solvents led to a cyclohexane conversion of 0.05% and 0.8%, respectively. This is contrary to the liquid-phase oxidation of cyclohexane with *tert*-butylhydroperoxide over Ce-exchanged zeolite Y [6]. This shows

that basic and aprotic acetonitrile as a solvent not only favored the production of cyclohexanone but also showed a higher activity, while the polar solvent methanol gave a low cyclohexane conversion as a result of strong hydrophilicity of transition metal ion-substituted aluminophosphates [42]. As we know, the solvent could play an important role in assisting the adsorption/desorption of substrates/products [29]. To acquire a high activity, it is needed to make the hydrophobic substrate of cyclohexane and the hydrophilic oxidant of  $\text{H}_2\text{O}_2$  adsorb in equivalent amounts [29,43]. Since  $\text{H}_2\text{O}_2$  could easily enter into the channels of hydrophilic (M, N)APO-5 molecular sieves, it is required to select a suitable solvent which could assist the adsorption of an appropriate amount of cyclohexane, and simultaneously lead to a ready desorption of the formed products. Fig. 6 shows that acetone should be the solvent of choice. In addition, the interaction of the solvent with the oxidant and/or intermediate species cannot be neglected, as revealed by the formation of side-product of HCHO in methanol solvent. This may orientate the different reaction mechanism [29].

As expected, a high temperature increased the cyclohexane conversion as a result of an increasing reaction rate, which depended on the type of incorporated metal ions (Fig. 7). The conversions obtained for the (Co, V)APO-5-0.05–0.01 and CrAPO-5-0.05 catalysts both increased with increasing reaction temperature up to 75 °C. Attempts to further increase the activity by increasing the reaction temperature failed. In contrast, for the (Co, Cr)APO-5-0.05–0.05 and (Cr, V)APO-5-0.05–0.03 samples, the highest conversion was achieved at 90 °C. An increment of the reaction temperature to 100 °C resulted in a slight reduction in the cyclohexane conversion by more than 5%. This

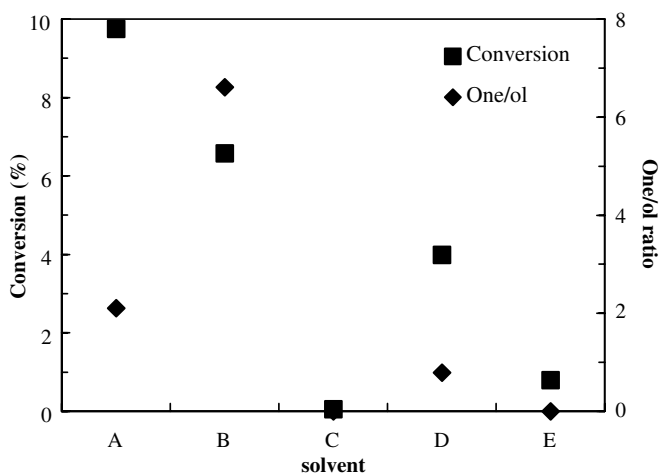


Fig. 6. Catalytic results of (Cr, V)APO-5-0.05–0.03 for the oxidation of cyclohexane with  $\text{H}_2\text{O}_2$  in different solvents: (A) acetone, (B) acetonitrile, (C) 1,2-dichloroethane, (D) methanol and (E) carbon tetrachloride (reaction conditions: 60 °C, 40 h, 0.1 g catalyst, 10 mL acetone, 18.5 mmol substrate, 18.5 mmol  $\text{H}_2\text{O}_2$  (30% in aqueous solution)).

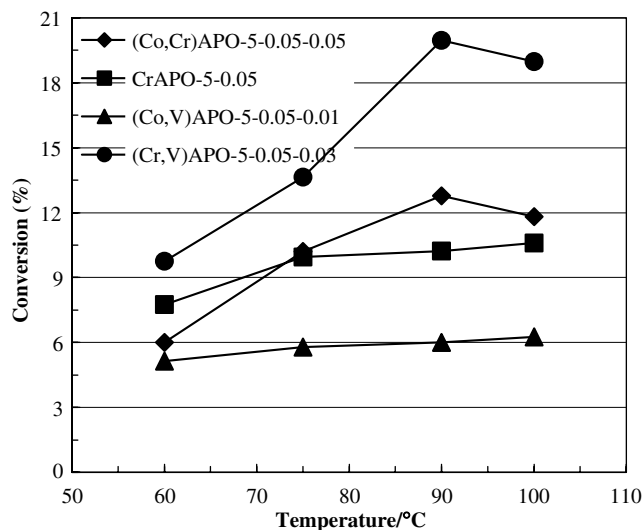


Fig. 7. Dependence of cyclohexane conversion on the reaction temperature for the CrAPO-5-0.05, (Co, V)APO-5-0.05–0.01, (Co, Cr)APO-5-0.05–0.05 and (Cr, V)APO-5-0.05–0.03 catalysts (reaction conditions: 40 h, 0.1 g catalyst, 10 mL acetone, 18.5 mmol substrate, 18.5 mmol  $\text{H}_2\text{O}_2$  (30% in aqueous solution)).

is because the high reaction temperature inevitably led to a severe decomposition of  $\text{H}_2\text{O}_2$ . Irrespective of this, the one/ol ratio in the products increased with the reaction temperature for all samples (not shown for brevity). Considering both the activity and selectivity, the optimum reaction temperature should be  $90^\circ\text{C}$ .

The relationship between cyclohexane conversion and reaction time shows that the activity increased with reaction time for all samples (Fig. 8). When the reaction was carried out for 50 h, the cyclohexane conversion obtained for (Cr, V)APO-5-0.05–0.03 increased to about 27%, which is about 1.5 times as high as that achieved on the CrAPO-5-0.05 catalyst under the same reaction conditions (18%). As for the (Co, Cr)APO-5-0.05–0.05 and (Co, V)APO-5-0.05–0.01 molecular sieves, a significant increase in the cyclohexane conversion was also observed within 20 and 40 h, respectively. Nevertheless, a further increase in the reaction time had no positive effect despite of the increase in the one/ol ratio of the products.

The catalytic stability of these four samples was further explored. The reactant composition was kept at the level of:  $\text{C}_6\text{H}_{12}/\text{H}_2\text{O}_2 = 1$  (mol/mol), catalyst/ $\text{C}_6\text{H}_{12} = 1/180$  (g/mmol) and acetone/ $\text{C}_6\text{H}_{12} = 5/9$  (mL/mmol). The reaction was conducted at  $90^\circ\text{C}$  for 10 h for each run. After one run, the catalyst was regenerated by washing with fresh acetone for three times. It is clear in Fig. 9 that within five reaction cycles, both the activity and selectivity of all samples did not decline. This indicates that (M, N)APO-5 molecular sieves are reusable catalysts. The enhancement in the activity of CrAPO-5-0.05 and (Co, V)APO-5-0.05–0.01 in the last two runs is possibly correlated with the change of the metal content in these catalysts since some leaching of metal ions occurred after five recycles, as

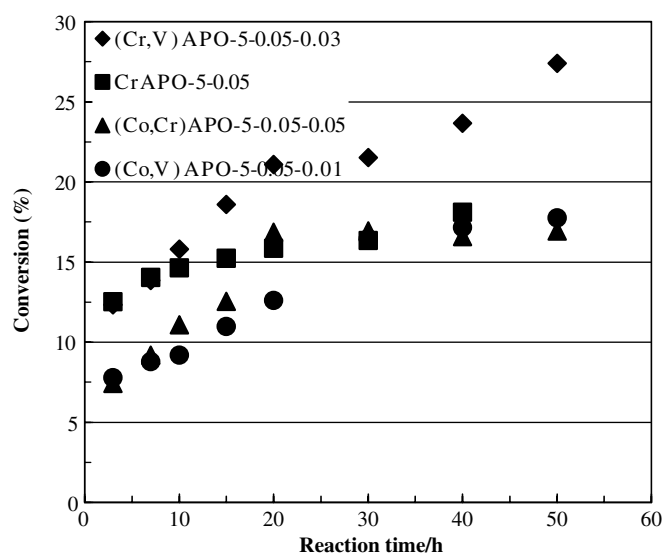


Fig. 8. Relationship between cyclohexane conversion and the reaction time for the CrAPO-5-0.05, (Co, V)APO-5-0.05–0.01, (Co, Cr)APO-5-0.05–0.05 and (Cr, V)APO-5-0.05–0.03 catalysts (reaction conditions:  $90^\circ\text{C}$ , 0.1 g catalyst, 10 mL acetone, 18.5 mmol substrate, 18.5 mmol  $\text{H}_2\text{O}_2$  (30% in aqueous solution)).

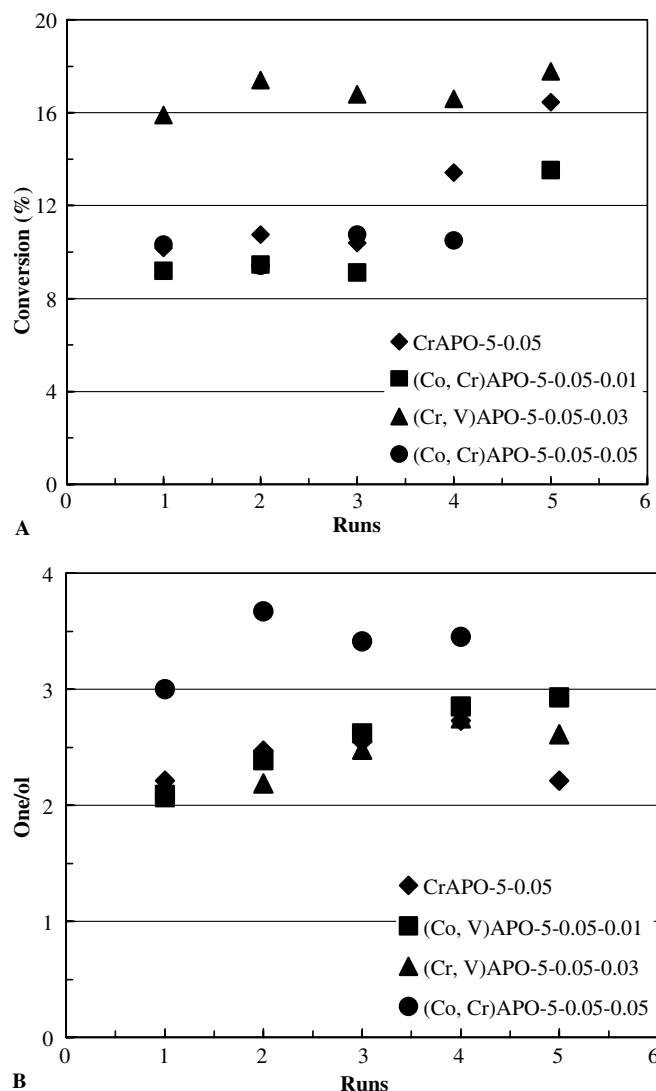


Fig. 9. (A) Cyclohexane conversion and (B) one/ol ratio in the product obtained within five repeated reaction runs for the CrAPO-5-0.05, (Co, V)APO-5-0.05–0.01, (Co, Cr)APO-5-0.05–0.05 and (Cr, V)APO-5-0.05–0.03 catalysts (reaction conditions:  $90^\circ\text{C}$ , 10 h, the reactant composition was kept at the level of:  $\text{C}_6\text{H}_{12}/\text{H}_2\text{O}_2 = 1$  (mol/mol), catalyst/ $\text{C}_6\text{H}_{12} = 1/180$  (g/mmol) and acetone/ $\text{C}_6\text{H}_{12} = 5/9$  (mL/mmol)).

revealed by ICP analysis (Table 3), and the metal ion content strongly influences the catalytic performance of MAPO-5 and (M, N)APO-5 molecular sieves (Table 2).

To check whether the oxidation of cyclohexane over the prepared MAPO-5 and (M, N)APO-5 catalysts in the presence of  $\text{H}_2\text{O}_2$  is a heterogeneous or a homogeneous reaction, we did the following experiments, and the results of which are depicted in Fig. 10. As reported by Belkhir and Lempers et al. [43,44] in the case of Co- and CrAPO-5 that an on-going reaction in the filtrate was indeed observed after the removal of the catalyst (the catalyst was separated by centrifugation under hot conditions so as to avoid the re-adsorption of possibly leached metal ions) although lower conversions were obtained at the same reaction time. This is consistent with an autoxidation mechanism [43,44],



Table 3  
Chemical composition of the CrAPO-5-0.05, (Co, V)APO-5-0.05–0.01, (Co, Cr)APO-5-0.05–0.05 and (Cr, V)APO-5-0.05–0.03 samples before and after five reaction recycles

Catalyst	Before			After			Loss caused by leaching		
	Co (%)	Cr (%)	V (%)	Co (%)	Cr (%)	V (%)	Co (%)	Cr (%)	V (%)
CrAPO-5-0.05	–	1.32	–	–	1.04	–	–	21.21	–
(Co, V)APO-5-0.05–0.01	2.82	–	0.20	2.06	–	0.15	26.95	–	25.00
(Co, Cr)APO-5-0.05–0.05	1.90	1.18	–	1.66	0.84	–	12.63	28.81	–
(Cr, V)APO-5-0.05–0.03	–	1.77	0.98	–	1.76	0.66	–	0.56	32.65

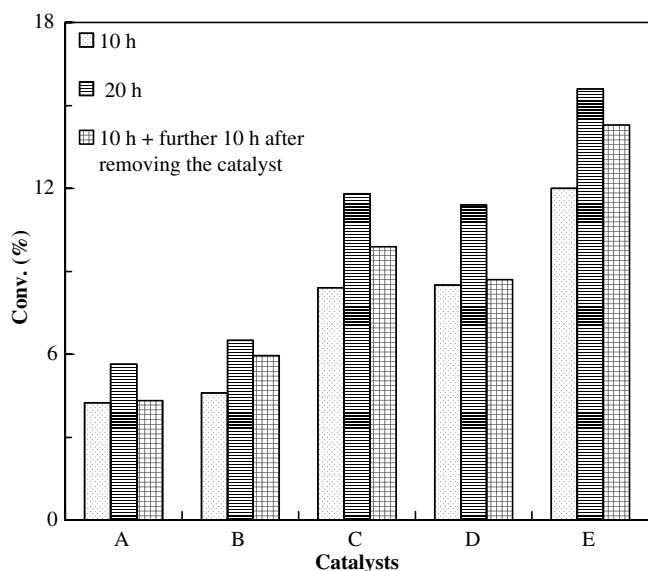


Fig. 10. Cyclohexane conversion obtained at different reaction conditions over the (A) VAPO-5-0.03, (B) CoAPO-5-0.05, (C) CrAPO-5-0.03, (D) (Co, V)APO-5-0.05–0.05 and (E) (Cr, V)APO-5-0.05–0.05 catalysts (reaction conditions: 90 °C, 0.1 g catalyst, 10 mL acetone, 18.5 mmol substrate, 18.5 mmol H<sub>2</sub>O<sub>2</sub> (30% in aqueous solution)).

*viz.* a very low concentration of leached metal ions homogeneously catalyzed the reaction. However, this is not true for the VAPO-5-0.03 molecular sieve although it was found by Haanepen and co-workers that the small amount of leached V<sup>5+</sup> ions in VAPO-5 also largely contributed to the observed activity [45]. When the reaction was carried out for 10 h, the cyclohexane conversion was 4.25% over the VAPO-5-0.03 sample. This is basically the same as that (4.32%) obtained by allowing the filtrate to further react for another 10 h after removing the catalyst. In contrast, a conversion of 5.65% was obtained at the reaction time of 20 h in the presence of VAPO-5-0.03. With respect to (M, N)APO-5 molecular sieves, in agreement with the VAPO-5-0.3, no obvious variation in activity (8.5% *vs.* 8.7%) was observed for the (Co, V)APO-5-0.05–0.05 sample, either, after filtering the catalyst and further proceeding the reaction, whereas (Cr, V)APO-5-0.05–0.05 showed the similar behavior to Co- and CrAPO-5. The difference of our experimental results from those of Haanepen and co-workers might be due to the different substrates. Cyclohexane is an apolar molecule, while both 3-phenyl-2-propen-1-ol and 3-octanol are large polar molecules, which

could extract framework metal ions too [46,47]. Thus, more V<sup>5+</sup> ions would be leached in the reactant solution when oxidizing these bulky alcohols, resulting in a more apparent continuation of the reaction after the removal of the catalyst. Regardless of this, the extraction of a little amount of V<sup>5+</sup> ions also occurred during the oxidation of cyclohexane as a result of the interaction of vanadium with H<sub>2</sub>O<sub>2</sub>, as revealed by ICP-AES analysis (Table 3). The observation of catalytic activity after separating the catalyst could not exclude the possibility of leached V<sup>5+</sup> ions acting as active sites since a low concentration of metal ions leads to a very long induction for initiating the reaction [43].

#### 4. Conclusions

(Co, Cr)APO-5, (Co, V)APO-5 and (Cr, V)APO-5 molecular sieves have been hydrothermally synthesized. It was shown that Co<sup>2+</sup> replaced the lattice Al<sup>3+</sup>, whereas V<sup>4+</sup> anchored to the sample via coordinating to two framework oxygen atoms and most probably substituted for P<sup>5+</sup> ions, respectively. The probability for framework incorporation of the studied transition metal ions decreased in the sequence: Co<sup>2+</sup> > V<sup>4+</sup> > Cr<sup>3+</sup>. Upon calcination, all V<sup>4+</sup> ions were oxidized to V<sup>5+</sup>, while Cr<sup>3+</sup> cations were oxidized to Cr<sup>5+</sup> and Cr<sup>6+</sup>. The simultaneous incorporation of two types of transition metal ions in the AFI framework showed higher activity, compared to single metal ion-substituted analogues in the selective oxidation of cyclohexane in the presence of H<sub>2</sub>O<sub>2</sub>. The reaction conditions, including solvent, reaction temperature and reaction time, had a strong influence on the catalytic performances. Acetone should be the solvent of choice. (M, N)APO-5 molecular sieves are stable to retain their activity and selectivity at least for five repeated runs although the leached metal ions may play a significant role in catalyzing the oxidation of cyclohexane.

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