Cyclohexane oxidation using transition metal-containing aluminophosphates (MAPO-VFI)

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Abstract

The preparation of Co-, Cr-, Fe-, Mn-, Ti-, and V-containing aluminophosphates (MAPO) with VFI structure is described. Physico–chemical techniques were used to characterize the solids synthesized. The MAPO-VFI were compared to AlPO-VFI impregnated with the various metals confirming the isomorphous substitution of Co, Cr, Fe, and Ti into the structure. V is coordinated to defect sites and Mn probably precipitated as oxide on the crystal surface. V- and CrAPO-VFI are active catalysts for the oxidation of cyclohexane with *tert*-butyl hydroperoxide producing cyclohexanone with some cyclohexanol and cyclohexene. CrAPO-VFI was recycled twice without significant loss of activity. On the other hand, VAPO-VFI showed significant metal leaching.

Keywords: VPI-5; Metallaluminophosphates; VFI-structure; Cyclohexane; Catalytic oxidation; *tert*-butyl hydroperoxide

1. Introduction

Right after his account of the first synthesis of an aluminophosphate molecular sieve with channels formed by 18 atom rings and pore diameters of 1.2 nm [1], Davis et al. [2] found that it was possible to isomorphously substitute silicon and cobalt into its framework. The new molecular sieve was named VPI-5, and the IZA eventually decided upon the symbol VFI to describe its structure. In this work, the aluminophosphate VPI-5 will be referred to as AlPO-VFI. VPI-5 containing other isomorphously substituted metals M will be called

MAPO-VFI. Since Davis' discovery, the incorporation of small amounts (less than 5% wt/wt) of metals such as magnesium [3], iron [4,5], and cobalt [6], which substitute aluminum isomorphously, has been reported. The incorporation of manganese into AlPO-VFI has been published as well [7], but isomorphous substitution is unlikely. Although much energy has been devoted to the study of synthesis conditions and the characterization of AlPO-VFI, only a few reports [6,7] can be found on its use, or on the use of MAPO-VFI, in catalysis, probably because of its relative thermal instability. For molecular sieves with the VFI structure, the removal of zeolitic water is an essential step that has to be done prior to any application-oriented studies such as catalysis. The thermal

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treatment requires carefully controlled conditions, otherwise the VFI structure will readily decay to the AlPO-8 phase [8,9].

Transition metal-containing aluminophosphates have great potential as heterogeneous oxidation catalysts for a variety of organic substrates [10]. MAPO-5 (AFI structure), a more stable aluminophosphate with a smaller pore diameter (0.73 nm), has been successfully applied in the oxidation of alkanes, as reported for CoAPO-5 [11], VAPO-5 [12,13], CrAPO-5 [14], and TiAPO-5 [15]. The use of MAPO-VFI takes advantage of the known catalytic properties of metallaluminophosphates combined with a larger pore diameter, allowing the processing of bulkier organic molecules.

This work describes the synthesis of the novel aluminophosphates TiAPO-VFI, VAPO-VFI, and CrAPO-VFI, and reports their catalytic activity in the oxidation of cyclohexane in comparison with Mn-, Fe-, and Co-containing AlPO-VFI, and with AlPO-VFI impregnated with Cr and V.

2. Experimental

2.1. Synthesis of the catalysts

MAPO-VFI were synthesized according to a modified version of the published procedure [2]: Pseudoboehmite (Condea), phosphoric acid (Aldrich) and distilled water were mixed in a molar ratio of 1:1:40 and aged for 2 h. One equivalent of di-n-propylamine (Aldrich) was added and the gel aged for another 2 h. The metal source, 0.04 equivalents of $Mn(CH_3COO)_2 \cdot 4H_2O$ (Fluka), $Co(CH_3COO)_2 \cdot 4H_2O$ (Fluka), $VOSO_4 \cdot 3H_2O$ (Aldrich), $Cr(NO_3)_3 \cdot 9 \ H_2O$ (Aldrich), or $FeCl_3$, (Aldrich), was dissolved in ca. 5 ml of water and added to the gel, which was vigorously stirred for 15 min. For the synthesis of TiAPO-VFI, $Ti(C_2H_5O)_4$ (Aldrich) dissolved in ethanol (Ti ~ 20%) was added to the gel. The gel was then transferred to a teflon-lined autoclave and crystallized by heat-

ing at 150°C for 3.5 h. The crystals were separated from the remaining gel by washing with plenty of distilled water on a 250 Tyler mesh sieve. After filtration, the crystals were dried at room temperature in a desiccator, giving a yield of ca. 5 g. The metal-free $AlPO_4$-VFI was prepared by the same method, but without adding the metal source. The metal impregnated AlPO-M were prepared by stirring AlPO-VFI in a solution of the metal ions (1 mol/L) for 2 h at 40–50°C. The AlPO-M were then filtered, washed and dried at room temperature in a desiccator.

2.2. Catalyst characterization

The samples were characterized as synthesized by X ray diffraction (XRD) using a Shimadzu XD-3A diffractometer with Cu K α radiation. Scanning electron micrographs were recorded on a JEOL JSM-T 300 microscope, and the mapping of the metal surface distribution was performed using an energy dispersive X-ray spectrometer (EDS), which provides the semi-quantitative metal content of the samples. Diffuse reflectance UV–visible spectra in the range between 200 and 800 nm were obtained for powdered samples adhering to a sample holder using a Perkin Elmer Lambda-9, 1645 series, spectrophotometer. High proton decoupled magic angle spinning ^{27}Al and ^{31}P NMR spectra were recorded on a Bruker AC 300/P spectrometer. The ^{27}Al NMR spectra were obtained at a frequency of 78.2 MHz and sweep width of 25,000 Hz. Chemical shifts are relative to $Al(NO_3)_3$. The ^{31}P NMR spectra were obtained at a frequency of 121.5 MHz and sweep width of 35,714 Hz. Chemical shifts are relative to 85% H_3PO_4. Infrared spectra were obtained on a Perkin Elmer 1600 FTIR M-80 Specord spectrophotometer from KBr waffers containing samples of MAPO-VFI. CHN analyses were performed with a Perkin Elmer 2401 analyzer, and the metal contents were determined using a Spectrace TX-5000 X-ray fluorescence spectrometer, comparing with standard curves pre-

pared from the various metal oxides. Thermogravimetric analyses of the MAPO-VFI were carried out with a DuPont 951 instrument.

2.3. Catalytic reactions

Approximately 0.3 g of MAPO-VFI was dried at 80°C under vacuum (0.1 mbar) for 2 h. 0.20 g of the dry catalyst was immediately suspended in 15.6 g cyclohexane (99.5%, washed with concentrated sulfuric acid, water, 5% sodium bicarbonate solution, and water and then distilled). 10 mmol tert-butyl hydroperoxide (TBHP) dissolved in 1.1 g cyclohexane, were added and the reaction mixture was magnetically stirred in open air for 24 h. Runs with chromium acetylacetonate (Cr(acac)$_3$, Ventron) followed the same procedure. For the autoxidation of cyclohexane using CoAPO-VFI, a suspension of 0.20 g of the catalyst in 15.6 g of cyclohexane was introduced into a 100 ml autoclave, pressurized with 25 bar of oxygen, and kept at 110°C for 24 h.

2.4. Chromatographic analysis

The reaction mixture was filtered, approximately 10 mg of cyclooctane (internal standard weighed to 0.1 mg precision) was added, and the sample was diluted with pure cyclohexane (1:5). The samples were analyzed with an HP 5890 series II gas chromatograph equipped with a 4 m × 3.2 mm i.d. column packed with 10% Carbowax 20 M on Chromosorb W-HP, coupled to a flame ionization detector, interfaced to an HP Vectra VL pentium workstation. The temperature was programmed at 10°C min^{-1} from 70 to 170°C. The products were identified by co-injection of authentic samples. The efficiency with respect to TBHP was calculated taking into account that 1 mol of TBHP is necessary to produce 0.5 mol of cyclohexanone(one), 1 mol of cyclohexene(ene) or 1 mol of cyclohexanol(ol). The amounts of oxidized products given in the tables have been corrected for blanks. The turnover numbers are

given as mmol of oxidized products per mmol of metal present in MAPO-VFI.

3. Results and discussion

The X-ray diffraction analyses show that the metallaluminophosphates (MAPO) synthesized have the VFI structure and are highly crystalline. Scanning electron microscopy confirms the presence of a single phase. It also reveals that the MAPO-VFI crystallize in long needles agglomerated into spheres or sphere segments with a radius of 50–75 μm, typical for aluminophosphates with the VFI structure. The impregnation of AlPO-VFI with the several metal ions does not affect its crystallinity. The UV–visible spectra of Fe- and CoAPO-VFI indicate that the metals are tetrahedrally coordinated in the framework. On the other hand, the spectrum of VAPO-VFI indicates the presence of VO^{2+} cations which are probably coordinated to defect sites. The spectrum of TiAPO-VFI shows that, besides the tetrahedrally coordinated Ti, some anatase is present in the material. The UV–visible spectrum of CrAPO-VFI indicates the presence of octahedrally coordinated chromium. On the other hand, the FTIR spectrum of this material gives no indication of chromium oxide, suggesting that the chromium substitutes aluminum in the framework and is additionally coordinated to two water molecules, as suggested by Chen and Sheldon [14]. The UV–visible spectrum of MnAPO-VFI is not different from the transition metal-free material, but the broad shoulders in the FTIR spectrum at 850 and 1050 cm^{-1} indicate that manganese is present as MnO. The increased peak width combined with a lowering of the chemical shift, which is observed in the ^{31}P NMR spectra of Co-, Cr-, Fe- and TiAPO-VFI, is a further indication for the isomorphous substitution of these metals into the framework. The ^{31}P MAS NMR spectra for V- and MnAPO-VFI are very similar to that of AlPO-VFI. However, a slight decrease in the chemical shift observed for VAPO-VFI

suggests an interaction of vanadyl cations with the framework. This interaction is confirmed by an additional shoulder of the peak observed in the ^{27}Al MAS NMR spectrum of VAPO-VFI at 40 ppm. Similar additional shoulders are also observed for Cr- and CoAPO-VFI. The NMR spectra of MnAPO-VFI and the transition metal-free AlPO-VFI are very similar, suggesting that manganese is not substituted into the framework but probably precipitated as MnO on the crystal surface/pores.

The CHN analyses of all MAPO-VFI show that only ca. 2.5% of the template remains in the pores, as it was already observed by Schmidt et al. [9]. According to the thermogravimetric analysis, the porous system of the as synthesized material contains between 15 and 20% of zeolitic water. Drying of the MAPO-VFI at 80°C under vacuum (0.1 mbar) reduces the water content to less than 3%, which is low enough to allow the diffusion of cyclohexane into the pore system, thus permitting the catalytic oxidation reaction to occur. Higher drying temperatures should be avoided because the VFI structure partially collapses to AlPO-8.

MAPO-VFI activated as described above were used as catalysts for the oxidation of cyclohexane under rather mild conditions. The results are shown in Table 1. As expected, titanium and manganese show very low activity for cyclohexane oxidation at 70°C. Under the conditions employed, iron does not form a high valence oxo complex and therefore also shows low activity. The conditions used for the autoxi-

dation of cyclohexane with CoAPO-VFI were too mild to produce a reasonable conversion of cyclohexane. V- and CrAPO-VFI, however, form rather reactive oxo complexes at 70°C, which convert cyclohexane with high turnover numbers. For both catalysts, the efficiency with respect to TBHP was found to be higher than 100%, implying that molecular oxygen takes part in the reaction. The reaction temperature used is lower than that used by Chen and Sheldon (115°C) [14] to autoxidize cyclohexane with CrAPO-5 in the presence of cyclohexyl hydroperoxide. They observed turnover numbers of 4 h^{-1} compared to 17 h^{-1} found for CrAPO-VFI at 70°C. This shows that Cr- and VAPO-VFI are very active oxidation catalysts which deserve a more profound investigation.

Both Cr- and VAPO-VFI produce mostly cyclohexanone together with some cyclohexanol and cyclohexene. Similarly high cyclohexanone/cyclohexanol ratios have been reported for the autoxidation of cyclohexane in the presence of CrAPO-5 [14]. The amount of cyclohexene formed is probably smaller than the value reported, since acetone, formed in trace amounts by TBHP decomposition, is not separated from cyclohexene under the chromatographic conditions used. On the other hand, cyclohexene was positively identified as a product by gas chromatography coupled to a mass detector. A kinetic study of cyclohexane oxidation with VAPO-VFI (Fig. 1) shows that the amounts of cyclohexanone and cyclohexanol increase approximately linearly during the reaction time,

Table 1
Product distribution for MAPO-VFI-catalyzed cyclohexane oxidation

Metal	Metal content (%)	One (mmol)	Ol (mmol)	Ene [a] (mmol)	Turnover number	Efficiency (%)
Ti	1.43	0.12	0.03	0.20	6	4.7
V	0.74	7.2	0.47	0.25	281	151
Cr	0.43	5.7	0.54	0.65	418	126
Mn	0.76	0.10	0.01	0.24	11	4.5
Fe	1.11	0.11	0.08	0.23	11	5.3
Co	0.99	0.14	0.02	0.28	13	5.8

Reaction conditions: 200 mg of catalyst, 15.6 g of cyclohexane, 10 mmol of TBHP, 24 h, 70°C, except for CoAPO-VFI: 200 mg of catalyst, 15.6 g of cyclohexane, 25 bar of O_2, 110°C, 24 h.
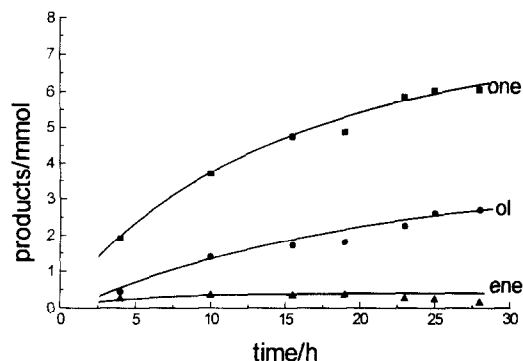[a] Contains some acetone from TBHP decomposition.

Fig. 1. Time dependence of cyclohexane oxidation with VAPO-VFI (■ cyclohexanone (one), ● cyclohexanol (ol), △ cyclohexene (ene)). Reaction conditions: 200 mg of catalyst, 15.6 g of cyclohexane, 10 mmol of TBHP, 70°C.

while cyclohexene is produced at the beginning of the reaction and subsequently levels off.

During the reactions, approximately 10% of the Cr- and VAPO-VFI is transformed to the AlPO-8 phase. Drying the used catalysts under the conditions used initially does not restore their activity. Therefore the catalysts were simply reused after decantation of the products and addition of fresh portions of cyclohexane and TBHP. This procedure allows both catalysts to be used for three consecutive cycles. After the third cycle the crystals were completely disintegrated, probably due to friction with the magnetic stirrer Fig. 2. The amount of oxidized products obtained with CrAPO-VFI in three consecutive cycles is compared in Table 2 with those obtained with Cr(acac)$_3$ in homogeneous phase and AlPO-Cr. Cr(acac)$_3$ shows low activity, indicating that the cyclohexanone is not formed in a homogeneous catalyzed reaction. Impregnated AlPO-Cr forms mainly cyclohexanol, while cyclohexanone is the principal product with CrAPO-VFI.

The amount of isomorphously substituted Cr present in CrAPO-VFI does not vary significantly during recycling, as shown by an only slight loss of activity. This is confirmed by the chromium content in CrAPO-VFI after 2 cycles, which is the same as found in the as-synthesized catalyst within the experimental error. Interestingly, the chromium sites that are active for
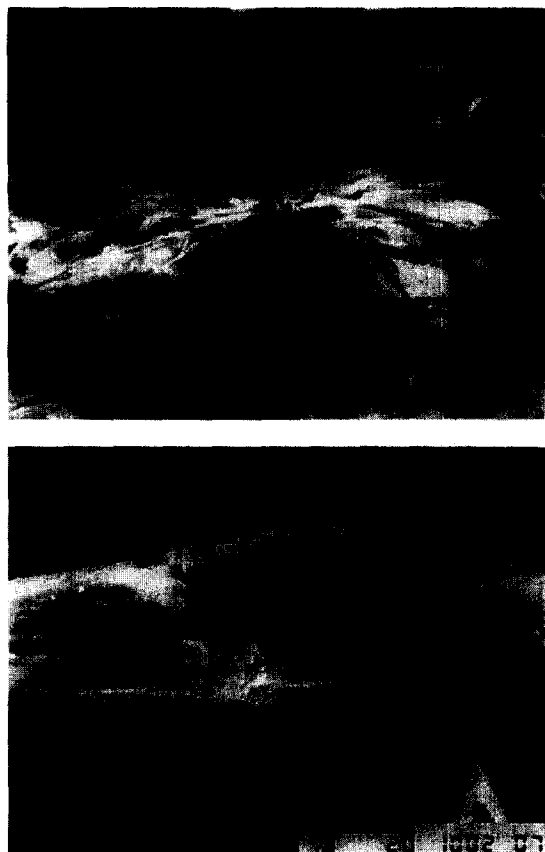

Fig. 2. Electron scanning micrographs of CrAPO-VFI before and after two catalytic reactions.

cyclohexanol formation and which are found in larger amounts in AlPO-Cr leach easily from the catalyst since the amount of cyclohexanol found in the second and third cycle of CrAPO-VFI is nearly zero. Further evidence that

Table 2

Product distribution from cyclohexane oxidation with chromium containing catalysts

Catalyst	One (mmol)	Ol (mmol)	Ene [a] (mmol)
CrAPO-VFI	5.7	0.54	0.65
CrAPO-VFI (2nd cycle)	5.6	0.02	0.72
CrAPO-VFI (3rd cycle)	5.2	0.01	0.51
AlPO-Cr impregnated	0.04	1.2	0.64
Cr(acac)$_3$	0.58	0.10	0.26

Reaction conditions: 200 mg of catalyst, 15.6 g of cyclohexane, 10 mmol of TBHP, 24 h, 70°C, except for Cr(acac)$_3$, when 5 mg of Cr(acac)$_3$ was used as catalyst.

[a] Contains some acetone from TBHP decomposition.

Table 3
Product distribution from cyclohexane oxidation with vanadium containing catalysts

Catalyst	One (mmol)	Ol (mmol)	Ene [a] (mmol)
VAPO-VFI	7.1	1.5	0.25
VAPO-VFI (2nd cycle)	4.1	0.6	0.19
VAPO-VFI (3rd cycle)	1.9	0.42	0.10
AlPO-V impregnated	0.21	0.80	0.20

Reaction conditions: 200 mg of catalyst, 15.6 g of cyclohexane, 10 mmol of TBHP, 24 h, 70°C.

[a] Contains some acetone from TBHP decomposition.

chromium leaches significantly from the impregnated AlPO-Cr is shown by a reduction of the metal content from 0.13 to 0.06% after the reaction. The surface metal content of CrAPO-VFI was also analyzed by scanning electron microscopy coupled to energy dispersive X-ray spectrometry, which gives information on the nature of the elements present in a 1 μm deep layer. Only a slight reduction in the chromium content in the surface layer was observed after the reactions.

The results of three consecutive cycles of cyclohexanol oxidation with VAPO-VFI are compared with those obtained with the impregnated AlPO-V in Table 3. As found for chromium, VAPO-VFI forms mainly cyclohexanone, while AlPO-V is much less reactive and cyclohexanol is the principal product. Furthermore, VAPO-VFI looses its catalytic activity more rapidly than CrAPO-VFI, which can be explained by the leaching of approximately 15% of vanadium during each cycle. Scanning electron microscopy coupled to energy dispersive spectrometry also detected a decrease of the vanadium content in the surface layer of the catalyst.

4. Conclusions

AlPO-VFI with titanium, chromium, iron, or cobalt isomorphously substituted into the structure are easily prepared, while vanadium is coordinated as vanadyl cations to defect sites and

manganese precipitated as MnO. Only V- and CrAPO-VFI show high activity for cyclohexane oxidation with tert-butyl hydroperoxide under mild conditions forming cyclohexanone as the principal product. While CrAPO-VFI can be recycled three times without significant loss of activity, V leaches from the crystals reducing its catalytic activity to 27% in the third cycle. Isomorphously substituted chromium in CrAPO-VFI appears to produce mainly cyclohexanone, while precipitated chromium forms cyclohexanol. However, this hypothesis still requires further study.

Acknowledgements

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