On the nature of V and Mg ions in V, Mg-containing AlPO$_4$-5 catalysts

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Abstract

The location of both Mg and V ions in V, Mg-containing AlPO$_4$-5 samples and the influence of the magnesium ions on the nature, location and redox properties of the vanadium species have been studied by combining several physico-chemical characterisation techniques (TPR, XPS, NMR and ESR). While homogeneously distributed V^{5+} ions in framework positions have been observed on calcined VAPO-5, extraframework V^{5+} species are mainly observed in calcined VMgAPO-5 sample. XPS and ^{31}P MAS NMR indicate isomorphous incorporation of magnesium ions in as-synthesised VMgAPO-5 sample. A partial extraction of magnesium ions from lattice position is observed after calcination. However, Mg^{2+} ions remain partially in framework positions as suggested by the presence of Brönsted acid sites in the calcined VMgAPO-5 sample. The presence of magnesium decreases the reducibility of V^{5+} ions, although the amount of reduced vanadium ions in VMgAPO-5 was higher than those in VAPO-5. A correlation between physico-chemical characteristics and catalytic behaviour is also discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Aluminophosphate molecular sieves have received special attention due to the possibility of introducing acid and/or redox properties by means of isomorphous substitution of metals into the framework. In this way, the substitution of divalent metals (Mg^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, etc.) for Al^{3+}, or te-

travalent Si^{4+} for P^{5+} in the electroneutral AlPO-n framework gives MeAPOs [1] and SAPOs [2] molecular sieves, in which the generated negative charge can be protonated to form Brönsted acid sites producing interesting catalysts for acid reactions. On the other hand, transition metal ions with redox properties (V, Cr, etc.) can also be incorporated into framework positions giving catalyst with active sites for redox reactions [3–6].

Metal-containing AlPO$_4$-5, i.e. MeAPO-5 (Me = Cr or V) are active and selective in liquid phase oxidation processes [3–5]. However, the metal leaching process observed during the reaction, in addition

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to the high activity of these metal ions in solution, are negative factor against the use of these materials [5].

Nevertheless, they could be used as catalysts in gas phase selective oxidation reactions. This is the case of the oxidative dehydrogenation (OXDH) reactions, in which VAPO-5 appears to be a selective catalysts in the transformation of propane into propene at 550°C in the presence of molecular oxygen [6,7].

One interesting alternative could be the synthesis of AlPO-n materials with different functions, i.e. acid and redox properties. Following this approach, it has been reported the introduction of Mg and V, Si and V, or Ti and V in AlPO$_4$-5 (AFI type) structure to give VMgAPO-5 [8], VSAPO-5 [9a,9b] or VTAPO-5 [10]. In the case of V, Mg-containing AlPO$_4$-5, both acid and redox properties, and a high selectivity to ethylene during the OXDH of ethane, have been observed [8,11]. Although differences in the redox properties between VAPO-5 and VMgAPO-5 materials have been reported, their different catalytic behaviour in OXDH reactions have been related to the presence of Brönsted acid sites in VMgAPO-5 [12].

In this paper, we present a more detailed study on the location of both Mg and V ions in V,Mg-containing AlPO$_4$-5 samples by combining several physico-chemical characterisation techniques (temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), NMR and ESR). The influence of the magnesium ions on the nature of the vanadium species will also be studied.

2. Experimental

2.1. Preparation of samples

VAPO-5 and MgVAPO-5 materials were obtained from hydrothermal synthesis using triethylamine (TEA) as template [7,10]. 0.8Al$_2$O$_3$: P$_2$O$_5$:1.76TEA:xV$_2$O$_5$:yMgSO$_4$:47H$_2$O gels with appropriate molar compositions were heated in Teflon-lined stainless-steel autoclaves at 200°C for 16 h and then centrifuged, washed, and dried at 80°C. The samples were calcined in air, at 550°C for

8 h. Some characteristics of the samples are presented in Table 1.

2.2. Methods

X-ray diffraction (XRD) was performed on a Phillips 1060 diffractometer provided with graphite monochromator employing nickel-filtered Cu Kα radiation ($\lambda = 0.1542$ nm). Crystallinity was determined by measuring the intensity of the peaks appearing at $2\theta \approx 9.8$, 21.1 and 22.4 and comparing them with the uncalcined AlPO$_4$-5.

TPR results were obtained in a Micromeritics apparatus. Samples (100 mg) were first treated in argon at room temperature for 1 h, and subsequently contacted with a H$_2$/Ar mixture (molar ratio of 0.15, total flow of 3 l h^{-1}) and heated at a rate of 10°C min^{-1}, to a final temperature of 1000°C.

^{31}P solid state NMR spectra were recorded with a Varian VXR-400 S WB spectrometer at 161.9 MHz. A 5-mm VT CP/MAS Varian probe was used to acquire the ^{31}P spectra. Samples were packed into zirconia rotors and span at the magic angle (MAS) at a rate of c.a. 7 kHz. The standard inversion recovery pulse sequence was applied to determine the ^{31}P longitudinal relaxation time T_1 using $\pi/2$ rad pulses of 6.5 μs. Conventional ^{31}P Bloch decay spectra were measured using recycle delay times long enough to ensure the total recovery of magnetization ($\approx 5T_1$ for pulses of $\pi/2$ rad). All spectra were acquired using high power proton decoupling.

XPS spectra were acquired on a VSW100 spectrometer, using an Al anode at 600 W, a pass energy of 22 eV, and a step increment of 0.06 eV. During spectra acquisition, the vacuum was better than 10^{-8} mbar.

Electron spin resonance spectra (ESR) were recorded at 77 K on a Bruker ER-200 spectrometer working at the X-band and calibrated with a DPPH standard ($g = 2.0036$). Quantitative analysis was carried out by double integration of the ESR signals, using copper sulfate (CuSO$_4 \cdot$ 5H$_2$O) for calibration. Before the spectra were recorded, the calcined sample were reoxidised at 500°C with 400 mbar of oxygen for 1 h. The reduced samples were prepared by heating the calcined materials (previously evacuated at 25°C) with 133 mbar of H$_2$ in the 100–500°C

Table 1
Characteristics of calcined (C), as-synthesised (AS) and reduced at 500°C (R) V and/or Mg-containing AlPO$_4$-5

Sample	Metal amount[a]			Crist[b] (%)	H$_2$-TPR results[c]		$(V^{4+}+V^{3+})/V_t$[d]		T_1 (s)[e]		NMR P/Mg[f]	XPS results		
	Mg (%)	V (%)	P/Mg		T_M (°C)	H$_2$-uptake	AS	R	AS	R		Al/P	(Al+Mg)/P	P/Mg
AlPO$_4$-5 (C)	0	0	–	100	–	–	–	–	–	–	–	1	–	–
VAPO-5 (C)	0	1.2	–	89	470	1.033	29	66	7	1.5	–	0.92	–	–
VMgAPO-5 (AS)	–	–	–	100		–	32	11	26.27	13	8.0	0.72	1.02	3.40
VMgAP0-5 (C)	2.9	1.2	7.7	100	550,590	1.510	–	–	–	–	–	0.70	1.13	2.30

[a] Determined by A.A.S.
[b] Cristallinity of the samples referred to the as-synthesised AlPO$_4$-5.
[c] Temperature of the maximum hydrogen consumption (T_M) and H$_2$-consumption in 10^4 mol H$_2$ g^{-1}.
[d] $(V^{4+}+V^{3+})/V_t$ ratio on VAPO-5 and VMgAPO-5 determined by ESR spectroscopy. The reduced samples were exposed to ambient atmosphere after reduction treatment.
[e] ^{31}P NMR longitudinal relaxation time (T_1).
[f] P/Mg atomic ratio in as-synthesised VMgAPO-5 sample determined by NMR spectroscopy.

temperature range for 1 h. All samples (whether re-oxidised or reduced) were degassed at room temperature until a final pressure of 10^{-8} mbar was reached prior to spectra acquisition. A total of 20 mg of sample was employed in all cases.

3. Results and discussion

X-ray powder diffraction of the as-synthesised VAPO-5 and VMgAPO-5 samples shows the presence of highly crystalline materials with AFI structure, which remain stable after oxidation and reduction treatments at high temperatures.

The influence of the presence of Mg^{2+} ions on the redox properties of the vanadium ions in VMgAPO-5 has been determined by TPR and ESR spectroscopy. The TPR results of the VAPO-5 and VMgAPO-5 samples are included in Table 1. The different onset temperature for hydrogen reduction indicates a different reducibility of the vanadium species in both samples, the presence of Mg^{2+} ions increases the reduction temperature (decreases the reducibility of the vanadium ions). In addition, a higher hydrogen consumption during the TPR experiments is also observed on VMgAPO-5 sample.

According to previous results [13], two kinds of isolated V^{4+} species in a square pyramidal or distorted octahedral environment can be inferred from the ESR spectra of as-synthesised VAPO-5 sample. These species can be attributed to vanadyl in a distorted octahedral environment forming a complex of type $VO(H_2O)_3^{2+}$ coordinated to two framework oxygen (V1 signal) and to vanadyl species of type $(H_2O)_2VO(OH)\ldots RH^+$ linked to two framework oxygens and interacting with amine templates (V1a signal) [14]. In the case of VMgAPO-5 sample, isolated (V1) and associated V^{4+} (V2) cations are mainly observed, while the species (V1a) is hardly detected. Quantitative analysis of the ESR signals indicate that the amount of V^{4+} ions in both VAPO-5 and VMgAPO-5 as-synthesised materials is quite similar and around 30%. Calcination lead to an almost complete oxidation of the V^{4+} ions to V^{5+} in both samples.

Fig. 1 shows the variation of the amount of V^{4+} species determined "in situ" by ESR during the
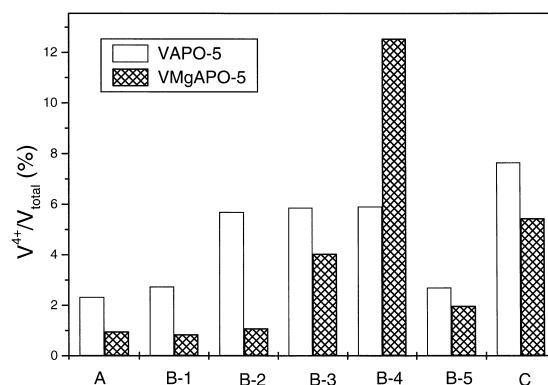

Fig. 1. V^{4+}/V_{total} atomic ratio (in %) determined by ESR spectroscopy in VAPO-5 and VMgAPO-5 samples after calcination at 500°C (A), reduction at 100°C (B-1), 200°C (B-2), 300°C (B-3), 400°C (B-4), 500°C (B-5), and reoxidation at 200°C (C).

reduction steps. For comparative purpose the amount of V^{4+} obtained on calcined and reoxidised samples are also included. A different behaviour between VAPO-5 and VMgAPO-5 is observed during the reduction step. The concentration of V^{4+} ions in VMgAPO-5 increases with the reduction temperature showing a maximum on the sample reduced at 400°C, while a low amount of V^{4+} species is observed in VAPO-5 sample. On the other hand, the amount of V^{4+} ions decreases at a reduction temperature of 500°C due to a subsequent reduction to V^{3+} species. This conclusion is in agreement with results obtained by IR spectroscopy of CO adsorption at low temperatures on the same sample [15].

^{31}P solid state NMR has been used to obtain some evidence of the Al^{3+}/Mg^{2+} substitution in several AlPO$_4$-*n* structures [16–19]. The ^{31}P MAS NMR spectra of as-synthesised and calcined VMgAPO-5 sample are shown in Fig. 2. In the as-synthesised sample (Fig. 2a) a signal at -30 ppm due to P(4Al) together with a second signal at -24 ppm ascribed to P(3Al, 1Mg) are clearly observed. Simulation of the ^{31}P MAS NMR spectra leads to estimate a P/Mg atomic ratio of 8.0. The good agreement between this value and that obtained from chemical analysis indicate that most of the magnesium ions substitutes for Al^{3+} ions in framework positions. The ^{31}P MAS NMR spectra of calcined VMgAPO-5 sample (Fig. 2b) is broadened and asymmetric and the presence of resonances of P(*n*Mg) units cannot be clearly estab-
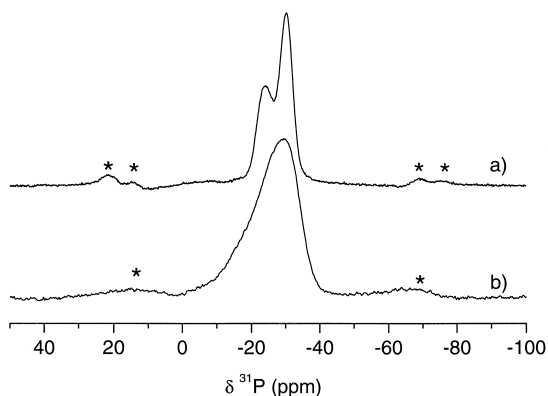
Fig. 2. ^{31}P NMR spectra of as-synthesised (a) and calcined (b) VMgAPO-5.

lished. The ^{31}P MAS NMR spectrum of the VAPO-5 sample, consists of a broad resonance with a maximum at ca. −30 ppm, with some asymmetry at low fields. The strong dipolar coupling with the unpaired electron of the V^{4+} paramagnetic species could impair the observation of any spectral feature, which could indicate the presence of vanadium in the P environment. Therefore, conventional ^{31}P and ^{27}Al MAS NMR cannot be used to prove the presence of vanadium in framework positions. In this case, a decrease on the longitudinal relaxation time of the nuclear magnetization of ^{31}P has been used as evidence of the incorporation of paramagnetic cations in framework positions [20]. The ^{31}P T_1 longitudinal relaxation time measured for the VAPO-5 and VMgAPO-5 samples, using the inversion recovery technique, and the concentration of paramagnetic V^{4+} ions are shown in Table 1. The concentration of V^{4+} ions (determined by ESR) in the as-synthesised VAPO-5 and VMgAPO-5 samples are quite similar, however a much slower longitudinal relaxation of ^{31}P (three to four times) is observed in the VMgAPO-5 sample. The different relaxation behaviour in both samples cannot be ascribed to V^{4+} concentrations but rather to its location. V^{4+} ions not incorporated in framework positions can be assumed in the VMgAPO-5 samples, as also supported by the presence of associated V^{4+} ions observed by ESR spectroscopy.

Further evidence of the different redox properties of vanadium in both materials is given in Table 1. When reduced samples are exposed to the ambient atmosphere, both the oxidation state of vanadium and the ^{31}P relaxation behaviour are different. Paramagnetic V^{4+} is predominant in VAPO-5, while it only accounts for around a 10% in the V,Mg-containing sample. This V^{4+} will be formed by oxidation of V^{3+}. The difference between both samples is probably due to an incomplete reduction of V ions in VMgAPO-5. The very short ^{31}P T_1 relaxation time in VAPO-5 suggests that paramagnetic species are incorporated in the framework. Therefore vanadium is still occupying framework positions after oxidation and subsequent reduction in VAPO-5.

In XPS the use of the C1s-signal as internal reference does not lead to successful calibration [21]. Therefore a value of 531.6 eV, taken as an average of the O1s XPS data reported in the literature for phosphate compounds, has been chosen as internal reference. The binding energies of O1s, Al2p and P2p on VAPO-5 material are quite similar to those reported for AlPO$_4$-5 [22], and then, the presence of vanadium in framework positions seems to have little influence on the adjacent atoms. The intensity of the line at 517 eV, due to V2p$_{3/2}$ [23], in the XPS spectra of calcined VAPO-5 was very low and, therefore, hard to determine (Fig. 3a–c) probably due to the low vanadium concentration and its homogeneous distribution over the entire sample.

Lines corresponding to O1s, Al2p, P2p and Mg2p are also observed in both as-synthesised and calcined VMgAPO-5 samples. On the other hand, a very weak V2p$_{3/2}$ band is hardly detected on the as-synthesised VMgAPO-5 sample (Fig. 3b), while it is clearly observed on the calcined VMgAPO-5 sample (Fig. 3c and 3(a–c)). Since the two samples have similar vanadium contents, the increase of the intensity of the V2p signal in the calcined VMgAPO-5 sample seems to indicate the formation of some extraframework vanadium species during the calcination.

Two additional oxygen bands at BEs of 529.7 and 533.8 eV appear on the calcined VMgAPO-5 sample (Fig. 3c and 3(a–c)). The higher BE component (533.8 eV), with a low intensity, can be attributed to surface chemisorbed –OH groups, whereas the lower BE component (529.7 eV) is related to more basic oxygen species [22]. The presence of basic oxygen atoms could be explained by the substitution of framework Al^{3+} ions by the less electronegative
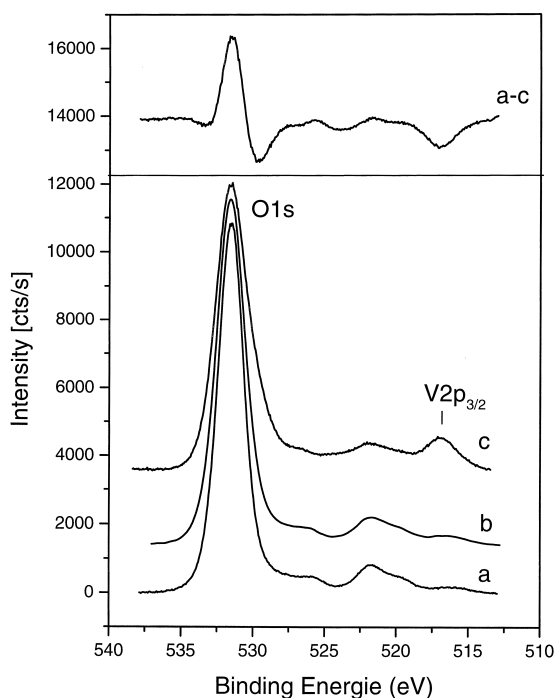
Fig. 3. XPS spectra of the calcined VAPO-5 (a), as-synthesised VMgAPO-5 (b) and calcined VMgAPO-5 (c) samples. The difference spectra of calcined VAPO-5 and VMgAPO-5 samples are also included (a–c).

atomic ratio lower than 1 (0.72) and an $(Al + Mg)/P$ surface atomic ratio of almost 1 (1.02) are observed in the as-synthesised VMgAPO-5. This is in agreement with the substitution of the Mg^{2+} for Al^{3+} in framework positions deduced from ^{31}P NMR, and with the presence of Brönsted acid sites previously reported [11]. On the other hand, the P/Mg surface atomic ratio of 3.40 is much lower than that obtained from chemical analysis (7.7) and ^{31}P NMR. The P/Mg ratio of as-synthetised VMgAPO-5 sample (determined by NMR) corresponds to framework composition. The low P/Mg surface atomic ratio must be due to an heterogeneous distribution of the Mg^{2+} ions in the sample, in agreement with the SEM-EDX results of this sample [11], in which heterogeneous crystals sizes and magnesium distributions were observed.

In the calcined VMgAPO-5, an $(Al + Mg)/P$ surface atomic ratio higher than 1 (1.13) and a P/Mg atomic ratio of 2.30 are observed. These results are consistent with the partial extraction of Mg ions from lattice positions to the catalyst surface during the calcination step. In this way, it has been observed that the number of Brönsted acid sites (related to Mg^{2+} ions in framework positions) is partially reduced after calcination [11], indicating the presence of extraframework Mg^{2+} ions.

4. Conclusions

The isomorphous incorporation of metal ions in aluminophosphate molecular sieves is not well established in many cases and the combined use of a variety of spectroscopic techniques is employed to gain some insight in the substitution mechanism. The XPS results presented here suggest a homogeneous distribution of the vanadium species in both as-synthesised and calcined VAPO-5. However, strong differences have been observed between as-synthesised and calcined VMgAPO-5 materials. XPS and ^{31}P MAS NMR indicate isomorphous incorporation of magnesium ions in the as-synthesised VMgAPO-5 sample, while calcination leads to a partial extraction of magnesium ions from lattice positions. This is evidenced by the appearance of more basic surface oxygen species as determined by XPS measurements

Mg^{2+} ions, which may increase the electron density of the adjacent oxygen ions and consequently decrease the BE of this oxygen species. However, the presence of a highly disperse MgO extraframework phase can also account for a higher basicity of the oxygen species. As the signal at 529.7 eV is practically absent in the XPS spectra of the as-synthesised VMgAPO-5 sample (Fig. 3b), it will be more probably related to extraframework oxygen species in a highly disperse MgO phase rather than to lattice oxygen species. In fact, NMR results show the presence of framework Mg ions in the as-synthesised VMgAPO-5 sample, whereas extraframework Mg phases must be formed after calcination.

The surface compositions of VAPO-5 and VMgAPO-5 have been determined by XPS and the results are given in Table 1. In VAPO-5, the Al/P surface atomic ratio is close to 1 (like in the pure $AlPO_4$-5), which agrees with the low vanadium concentration on the catalyst surface. An Al/P surface

and a strong decrease in the intensity of the $P(n\text{Mg})$ resonances in the ^{31}P MAS NMR spectra. However, some Mg ions must remain in framework positions, as suggested by the presence of Brönsted acid sites in the calcined sample. In addition to this, an increase in the intensity of the V2p signal in the XPS spectrum of the calcined VMgAPO-5 sample, compared to the corresponding original sample, indicates some extraction of the vanadium species to the catalyst surface during the calcination.

On the other hand, TPR experiments show different redox properties of the vanadium species in the VAPO-5 and VMgAPO-5 samples. In this way, V^{5+} ions in VMgAPO-5 are less reducible than those in VAPO-5. This agrees with the different nature of the vanadium species present in both samples. ESR experiments on VAPO-5 and VMgAPO-5 samples reduced at different temperatures strongly suggest the formation of V^{3+} species at high temperatures, whereas V^{4+} species seem to be more stabilised on VMgAPO-5 samples at intermediate reduction temperatures.

Based on our results, V ions are mainly occupying framework sites in calcined VAPO-5, while they are mainly located in extraframework positions in calcined VMgAPO-5 samples. This difference can be explained by the presence of Mg ions, which induce a lower stabilisation of the vanadium species in the framework. The higher temperature required to reduce V ions in VMgAPO-5 can explain its lower catalytic activity in OXDH reactions. However, the higher selectivity to ethylene from ethane observed on VMgAPO-5 can be attributed to the presence of Brönsted acid sites (related to Mg ions in framework positions).

Acknowledgements

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