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Alumina-supported catalysts for propane oxidative dehydrogenation from mixed $V_XM_{(6-X)}O_{19}{}^{n-}$ (M = W, Mo) hexametalate precursors

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Abstract

γ-Al_2O_3 supported vanadium oxides were modified by tungsten and molybdenum oxides in order to improve dispersion and selectivity towards olefins in propane oxidative dehydrogenation (ODH). Both vanadium–tungsten and vanadium–molybdenum catalysts were obtained by adsorption of mixed isopolyanions ($VW_5O_{19}{}^{5-}$, $V_2W_4O_{19}{}^{4-}$, $VMo_5O_{19}{}^{5-}$ and $V_2Mo_4O_{19}{}^{4-}$) from aqueous solutions. The isopolyanion solutions were characterized by UV-Vis and ^{51}V NMR spectroscopy. Vanadium, vanadium–tungsten and vanadium–molybdenum precursors and catalysts were also characterized by UV-Vis (diffuse reflectance) and solid state ^{51}V NMR spectroscopy. An improved selectivity to propene in the presence of tungsten and molybdenum in VO_x/γ-Al_2O_3 was observed and attributed to dilution of vanadium by tungsten or molybdenum oxides on the γ-Al_2O_3 surface.

Keywords: Propane oxidative dehydrogenation; Supported vanadium oxides; Hexametalates

1. Introduction

Oxidative dehydrogenation (ODH) of hydrocarbons is an important reaction catalyzed by vanadium oxide supported catalysts. Many works presented in the literature have discussed the molecular structure of vanadia species and modifications provoked by supports and others elements added for promoting conversion and selectivity towards olefins. Numerous techniques, such as UV-Vis DRS [1–3], XANES/EXAFS [4], ^{51}V NMR [5–9] and Raman spectroscopy [10,11] have been applied to investigate how these modifications influence hydrocarbon activation and selectivity to olefins. A few other studies have also been devoted to kinetics of hydrocarbon oxidation [12,13] in order to achieve a better understanding of the reaction mechanism and the influence of modifications. The role of acid–base properties of the active site is generally stressed as fundamental in determining catalytic properties; however, the concept of site isolation has recently been proposed as a key one for hydrocarbon oxidation [14].

Vanadium is also known for its capacity of forming a wide variety of polynuclear metal–oxygen complexes containing one or more transition elements [15]. Complexes of general formula $V_XM_{(6-X)}O_{19}{}^{n-}$—Linqvist anions—(M = Mo, W), have been described in aqueous solution [16–19]. In this work, aqueous solutions containing those polyanions were utilized to prepare modified vanadium supported catalysts,

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aiming at increasing dispersion and enhancing the interaction between the different elements on the surface of the support. Catalysts were prepared by adsorption on the support from aqueous mixed hexametalates $VW_5O_{19}{}^{3-}$, $V_2W_4O_{19}{}^{4-}$, $VMo_5O_{19}{}^{3-}$ and $V_2Mo_4O_{19}{}^{4-}$.

2. Experimental

2.1. Synthesis of V–W and V–Mo isopolyanions

Solutions of vanadium and tungsten ($VW_5O_{19}{}^{3-}$, $V_2W_4O_{19}{}^{4-}$) mixed isopolyanions of Linqvist structure were prepared as in Flynn and Pope [16]. Vanadium and molybdenum ($VMo_5O_{19}{}^{3-}$, $V_2Mo_4O_{19}{}^{4-}$) mixed isopolyanions solutions were prepared at atomic ratio V:Mo equal to 1:5 and 1:2, respectively, using the pH range suggested by Maksimovskaya and Chumachenko [17]. Solution characterization was performed by UV-Vis and ^{51}V NMR.

2.2. Preparation of catalysts

Alumina-supported catalysts were prepared by the equilibrium adsorption method in aqueous solution. Commercial gamma alumina (Engelhard, BET surface area 200 $m^2\,g^{-1}$) was added to each solution (1 g/100 ml) with stirring for 2 h at room temperature.

Both vanadium–tungsten and vanadium–molybdenum catalysts were obtained by adsorption of the mixed isopolyanions from 0.010 M aqueous solutions prepared as mentioned above. This concentration corresponds to 0.060 M of total metal elements in the solution. Two alumina-supported vanadium oxides were also obtained as references, by using ammonium metavanadate (minimum 99.5%, Carlo Erba) solutions with concentrations of 0.030 M at pH = 7 and 0.060 M at pH = 4, respectively. Alumina-supported molybdenum oxides and alumina-supported tungsten oxides were prepared using, respectively, a 0.060 M sodium tungstate (Grupo Química, 99%) solution and a 0.060 M Mo(VI) solution (ammonium heptamolybdate, Vetec, 80% in MoO_3), at pH = 7 in both cases. After adsorption, the solids were filtered off, dried at 100 °C overnight (precursors), then progressively at 150 and 250 °C for 3 h and calcined at 500 °C for 5 h. The precursors were denominated from the polyanion composition and the total metal concentration in solution, as shown in Table 1. The letter "c" was added when referring to the catalysts obtained after calcination.

Table 1
pH values used in sample preparation

Catalyst	pH
V30c	7
V60, V60c	4
VW560	2
V2W460, V2W460c	4
VMo560	3
V2Mo460, V2Mo460c	5
W60c	7
Mo60c	7

2.3. Catalysts characterization

UV-Vis diffuse reflectance spectra were recorded over a wavelength range from 200 to 800 nm on a Varian Cary |5| spectrometer equipped with a Harrick Diffuse Reflectance attachment with Praying Mantis geometry. Gamma alumina was used as the reference material for the catalysts.

^{51}V NMR spectra were obtained at a ^{51}V frequency of 78.95 MHz on a Bruker DRX300 spectrometer. The field-frequency stabilization (lock) during the acquisition of the aqueous solution spectra was maintained by placing a sealed capillary containing D_2O into 5 mm cylindrical tubes. In solid state NMR experiments samples were packed in a 4 mm diameter cylindrical zirconia rotors with Kel-F end-caps. MAS spectra were recorded between 8 and 15 kHz in order to identify the isotropic chemical shifts in a Bruker 4 mm CP-MAS probe. Single pulsed excitation of 1 μs ($\pi/12$); a dead time of 10 μs and 1 s recycle delay were used both in static and MAS spectra. Free induction decays (FIDs) were acquired with a sweep width of 200 kHz and an acquisition time of 10.9 ms. The spectra were zero filled to 4096 data points and processed with a 500 Hz Lorentzian line broadening, applied before Fourier transformation. Both for solution and solid state ^{51}V spectra the chemical shifts were externally referenced to the signal of $NaVO_3$ (0.16 M) at −574.28 ppm [20] as secondary reference, with less negative values in the high frequency direction.

2.4. *Catalytic experiments*

The solids were tested for propane ODH in a conventional flow system. The catalyst (200 mg) was deposited on a porous fixed bed in a Pyrex reactor in U tube form operating under atmospheric pressure and fed with a 1% (V%) propane/air mixture. The catalytic zone was isothermal. Complete, on line analysis of reactants and products (C_3H_8 and CO, CO_2, C_3H_6) was done in a single step using a Shimadzu GC-17AAF chromatograph with FID detection. The gas sample ran through a MTN-1 metanizer after elution on a Porapak Q column and before detection. In all cases, carbon balances attained 100%, within the experimental precision of the system.

3. Results and discussion

3.1. *Characterization of isopolyanions in solution*

UV-Vis spectra of both vanadium–tungsten isopolyanions solutions (not reported here) showed maximum and minimum values close to literature values, as listed in Table 2. The spectra of vanadium–molybdenum isopolyanions could not be observed, since these species decompose at the low concentrations that are necessary for UV analysis [17].

The chemical shifts observed from solution ^{51}V NMR are given in Table 3. The values are at about 2 ppm upfield compared with the literature [17,21], except for the isopolyanion $V_2W_4O_{19}^{4-}$, that appeared 9 ppm upfield. Literature data [17,19,21] have shown that ^{51}V NMR chemical shifts of vanadium–tungsten isopolyanions are pH dependent, e.g., they move to low frequency as the pH of the solution moves to low values. This was attributed to protonation of the species. Thus, we consider that $HV_2W_4O_{19}^{3-}$ was probably obtained instead of $V_2W_4O_{19}^{4-}$. Moreover, the ^{51}V spectrum of $VMo_5O_{19}^{3-}$ isopolyanion solution presented two signals; the first one at −504 ppm (high intensity) corresponds to the expected polyanion, while another one at −509 ppm (low intensity), was attributed to the protonated species $HV_2Mo_4O_{19}^{3-}$. In the spectrum of $V_2Mo_4O_{19}^{4-}$ solution, only one signal was observed at −496.5 ppm, as expected from this polyanion.

Table 2
UV-Vis maximum and minimum values for hexametalates in aqueous solution

λ (nm)	$VW_5O_{19}^{5-}$		$HV_2W_4O_{19}^{3-}$	
	Literature[a]	Experimental	Literature[a]	Experimental
λ_{max}	385	382	374	368
λ_{min}	333	332	328	323
λ'_{max}	267	264	–	–

[a] Flynn and Pope [16].

Table 3
^{51}V NMR chemical shifts observed for isopolyanions solutions

Sample	Chemical shift (ppm)	
	Experimental	Literature
$V_2W_4O_{19}^{4-}$	−516.6	−507[a]
$VW_5O_{19}^{3-}$	−523.8	−522[a]
$V_2Mo_4O_{19}^{4-}$	−496.5	−494[b]
$VMo_5O_{19}^{3-}$	−504/−509	−502[b]

[a] O'Donnell and Pope [21].
[b] Maksimovskaya and Chumachenko [17].

From the results of both, UV and NMR spectroscopies, it is clear that the solutions used in the preparation of the catalyst mainly contained the specified polyanions.

3.2. *Characterization of the catalysts*

Fig. 1 shows the UV-Vis diffuse reflectance spectra of the precursors and catalysts. The spectra of pure vanadium catalysts, reported in Fig. 1a, present intense bands in the 200–500 nm region, attributed to ligand to metal charge transfer (LMCT) bands, and confirming the presence of V^{5+} (d^0) in the samples. The spectra of V60 and V60c are similar; with the absorption band near 450 nm in both spectra pointing to the presence of highly polymerized V^{5+} species [2]. On the other hand, V30c catalyst absorbs in the 300 nm region, with a shoulder at higher wavelength, indicating less condensed V^{5+} species, maybe in tetrahedral coordination.

The spectra of pure tungsten and molybdenum precursors are shown in Fig. 1b. Strong absorptions are observed under 300 nm, which are related to LMCT bands. No modification on the corresponding spectra was observed after calcination. Fig. 1c shows the spectra of the precursor and catalyst prepared from

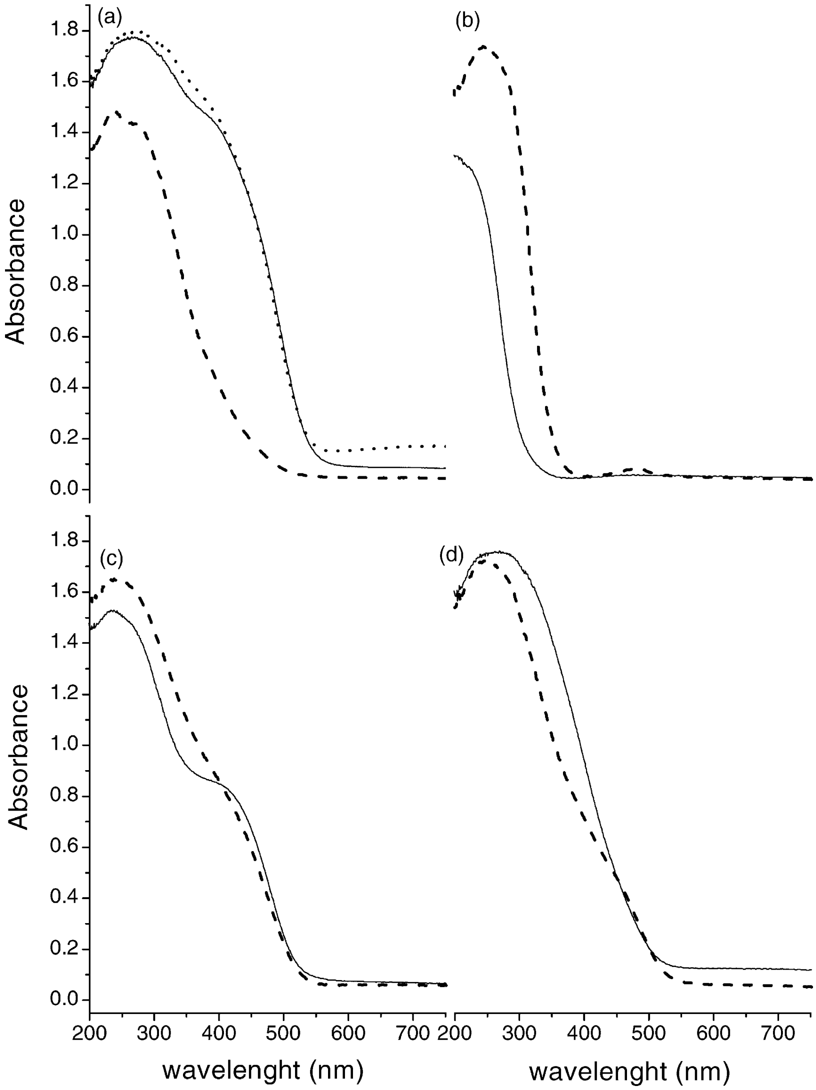

Fig. 1. UV-Vis spectra of the precursors and catalysts: (a) V60 (—), V60c (· · ·), V30c (- - -); (b) W60 (—), Mo60 (- - -); (c) V2W460 (—), V2W460c (- - -); (d) V2Mo460c (—), V2Mo460 (- - -).

$V_2W_4O_{19}{}^{4-}$. A well-defined absorption is seen at 450 nm in the spectrum of the precursor, in accordance with the octahedral coordination of vanadium in the initial polyanion. The profile of the band in the solid is very similar to that of the solution. The band is softened after calcination, suggesting that structural modifications of the polyanion should only occur during calcination. In contrast, the spectra of V2Mo460 and V2Mo460c catalysts, shown in Fig. 1d, show less difference. The presence of vanadium in octahedral coordination is already small in the precursor, suggesting early decomposition of the polyanion during the preparation.

^{51}V solid state static NMR spectra of some dried catalysts are shown in Fig. 2. The chemical shifts obtained for all, dried samples and catalysts are listed in Table 4. The spectrum of sample V60 showed a broad signal centered at −420 ppm, whereas for the sample V30, the signal was observed at −540 ppm. These signals can be attributed to octahedral (six-coordinated)

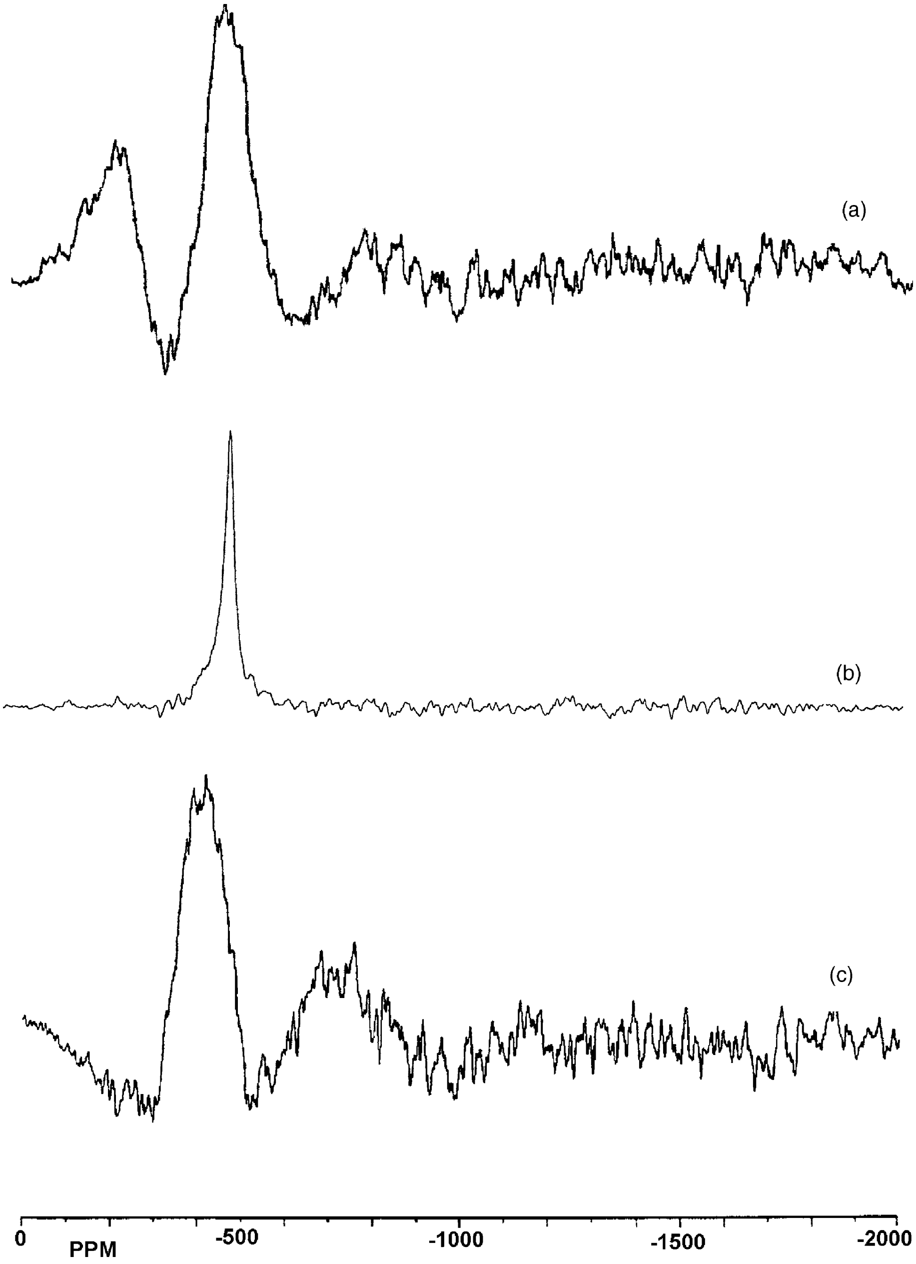

Fig. 2. ^{51}V solid state NMR static spectra of catalysts: V2Mo460 (a), V2W460 (b) and V60 (c), dried at 100 °C.

and tetrahedral (four-coordinated) species, respectively [2,6]. The experimental conditions used to prepare the samples V60 and V30 (lower pH and higher vanadium amount in V60 compared with V30) were more favorable to forming condensed vanadium species in V60, thus justifying the chemical shifts obtained. It was also observed that the presence of W and Mo in mixed samples shifted the signal of vanadium towards higher frequency. The static spectrum of V2Mo460 showed the same shape observed for

Table 4
^{51}V MAS NMR isotropic chemical shifts obtained for dried (100 °C) and calcined (500 °C) γ-Al_2O_3 supported catalysts

Sample	Chemical shift (ppm)
V30[a] (dried)	−583
V30c[a] (calcined)	−582
V60[b] (dried)	−504, −584
V60c[b] (calcined)	−500, −571
VW560 (dried)	−510.5
VMo560 (dried)	−583
V2W460 (dried)	−507, −584 (small)
V2W460c (calcined)	−506, −576
V2Mo460 (dried)	−510 (small), −587
V2Mo460c (calcined)	−591.5

[a] Nominal concentration of V = 0.003 mol.
[b] Nominal concentration of V = 0.006 mol.

sample V60, reinforcing the evidence of polyanion decomposition got from UV spectra. Surprisingly, the static spectra of precursors V2W460 and VW560 (not shown) presented a sharp signal, indicating a high degree of order in the local neighborhood of vanadium. The static spectra of calcined catalysts, shown in Fig. 3, presented similar values of chemical shifts (Table 4) and shapes already observed in dried samples, except for drastic broadening of the line shape for V2Mo460c. That spectrum is characteristic of axially symmetric chemical shielding tensor patterns; however, due to low signal to noise ratio the values of the principal tensor components could not be determined.

^{51}V MAS NMR spectra are exhibited in Fig. 4. The comparison of chemical shifts of vanadium–tungsten solutions with those obtained after supporting on γ-Al_2O_3 (Table 4) showed that these hexametalate isopolyanions are adsorbed by the support without significant structural modification. The isotropic chemical shifts obtained for samples VW560 and V2W460, at −511 and −507 ppm, respectively, indicate the presence of $V_2W_4O_{19}^{4-}$ in both dried catalysts. According to Flynn and Pope [16], the anion $VW_5O_{19}^{3-}$ decomposes through the following reaction in alkaline medium:

$$2VW_5O_{19}^{3-} + 10\,OH^- \rightarrow V_2W_4O_{19}^{4-} + 6WO_4^{2-} + 5H_2O$$

Indeed, the alumina support present in suspension in the solution could act as an alkaline promoter, increasing the pH of the medium during the impregnation step of $VW_5O_{19}^{3-}$ and leading to possible decomposition of the anion.

In the case of vanadomolybdates, the isotropic chemical shifts obtained by MAS NMR spectra showed the presence of two signals, indicating some modification of the species during the adsorption process. Again, the increase in pH value due to γ-Al_2O_3 could lead to hydrolysis of the polyanion, with decomposition to tetrahedral species. Maksimovskaya and Chumachenko [17] pointed out that aqueous equilibria of vanadium–molybdenum species are very fast (formation, decomposition and inter-conversion between species) and their presence in solution depends on concentration and pH. Our results are in agreement with those statements.

^{51}V MAS NMR spectra of the catalysts are shown in Fig. 5. Although the spectrum of V60c is very similar to that of its dried precursor V60, the spectra of mixed catalysts V2W460c and V2Mo460c evidenced thermal decomposition of the polyanions. In the case of vanadium–tungsten solids, a broad signal could be detected at −579 ppm, corresponding to a new V species formed during the calcination; however, a narrow signal at −505.5 ppm, probably due to the precursor polyanion is still present. On the other hand, the small signal at −510 ppm observed in the spectrum of vanadium–molybdenum precursors completely disappeared after calcination, and only a broad signal at −596 ppm was observed for this sample. The chemical shifts obtained before and after calcination are comparable to those given by pure γ-Al_2O_3 supported vanadium oxides, confirming the results obtained by electronic spectroscopy.

3.3. Propane ODH

Results for propane conversion and selectivity to propene in ODH are given in Figs. 6 and 7, respectively. No oxygenates could be detected in any case. Catalysts prepared from monosubstituted polyanions, $VMo_5O_{19}^{3-}$ and $VW_5O_{19}^{3-}$ showed very low activity; the results are not reported in this work.

Fig. 6 shows that propane conversion is much higher for V60c catalysts, which have the highest vanadium content. This is in accordance with the known potential of vanadium oxides for paraffin activation. Also in accordance is the observation that

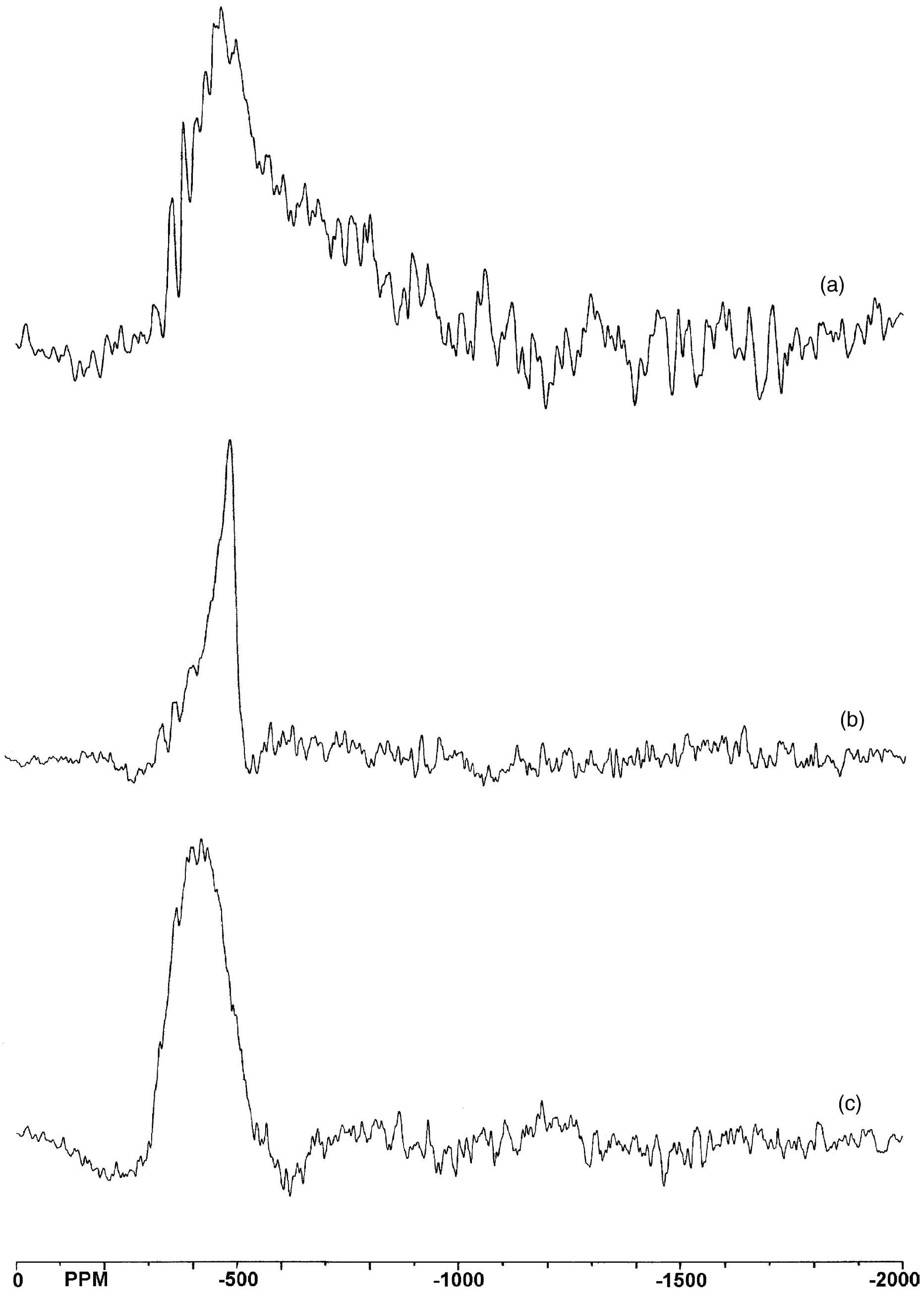

Fig. 3. ^{51}V solid state NMR static spectra of catalysts: V2Mo460c (a), V2W460c (b) and V60c (c), calcined at 500 °C.

pure molybdenum and tungsten oxides showed the lowest activity among these materials. V30c showed intermediate activity, well correlated with its lower vanadium content. Interestingly, V2Mo460c gave higher conversion than V2W460c, which presented the same activity level as pure molybdenum and tungsten oxides. In the case of vanadium–molybdenum oxides, NMR results indicated strong decomposition

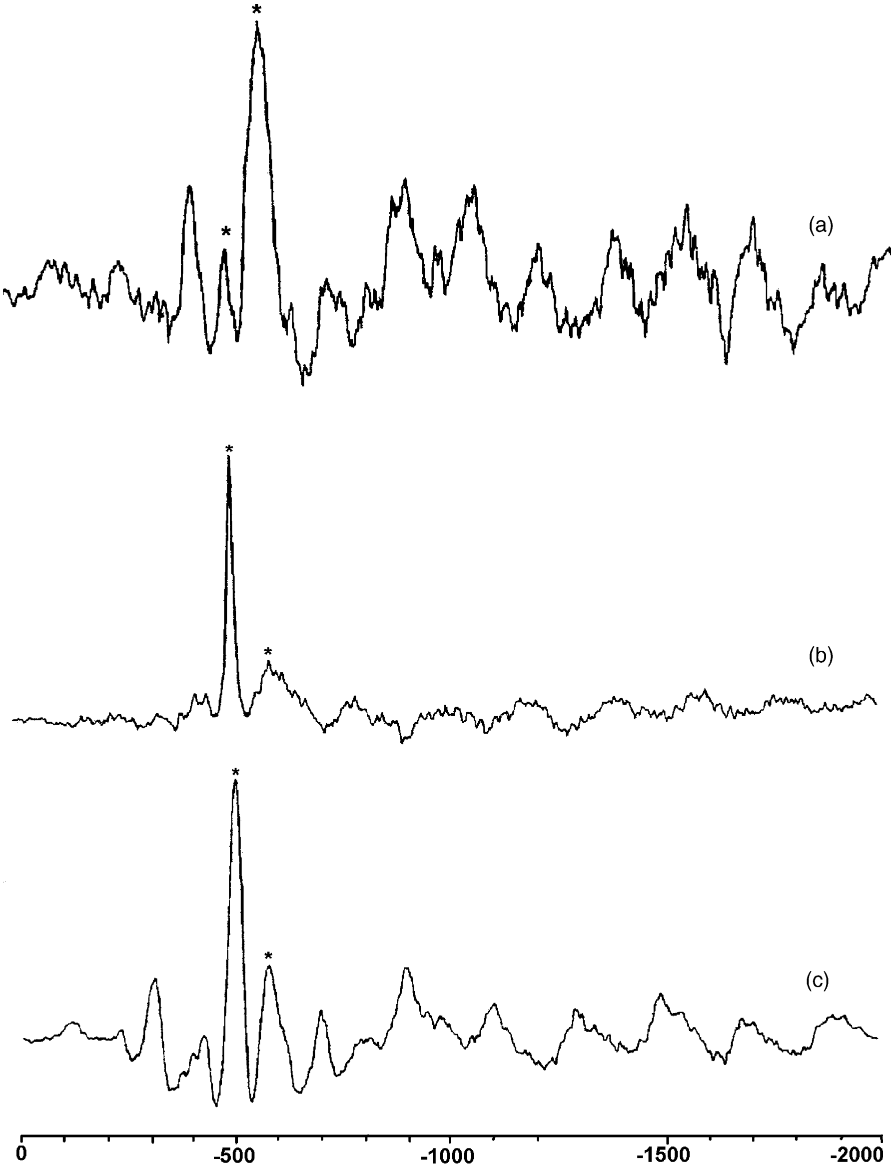

Fig. 4. ^{51}V solid state MAS NMR (15 kHz) spectra of catalysts: V2Mo460 (a), V2W460 (b) and V60 (c), dried at 100 °C. $*$ denotes the isotropic signals.

of the precursor polyanion, with formation of vanadate species comparable with those observed in pure supported vanadium oxides. The observed catalytic activity of this material is therefore in agreement with its vanadium content. In contrast, the low activity of vanadium–tungsten oxides suggests the absence of free superficial vanadium oxide.

Fig. 7 shows that selectivity is a decreasing function of conversion for all catalysts, as expected from the kinetical model developed by Khodakov et al. [12]. However, initial selectivity above 80% is obtained only for V60c and mixed catalysts. In the latter case, and more particularly in the case of vanadium–tungsten oxides, a synergetic effect between the two transition

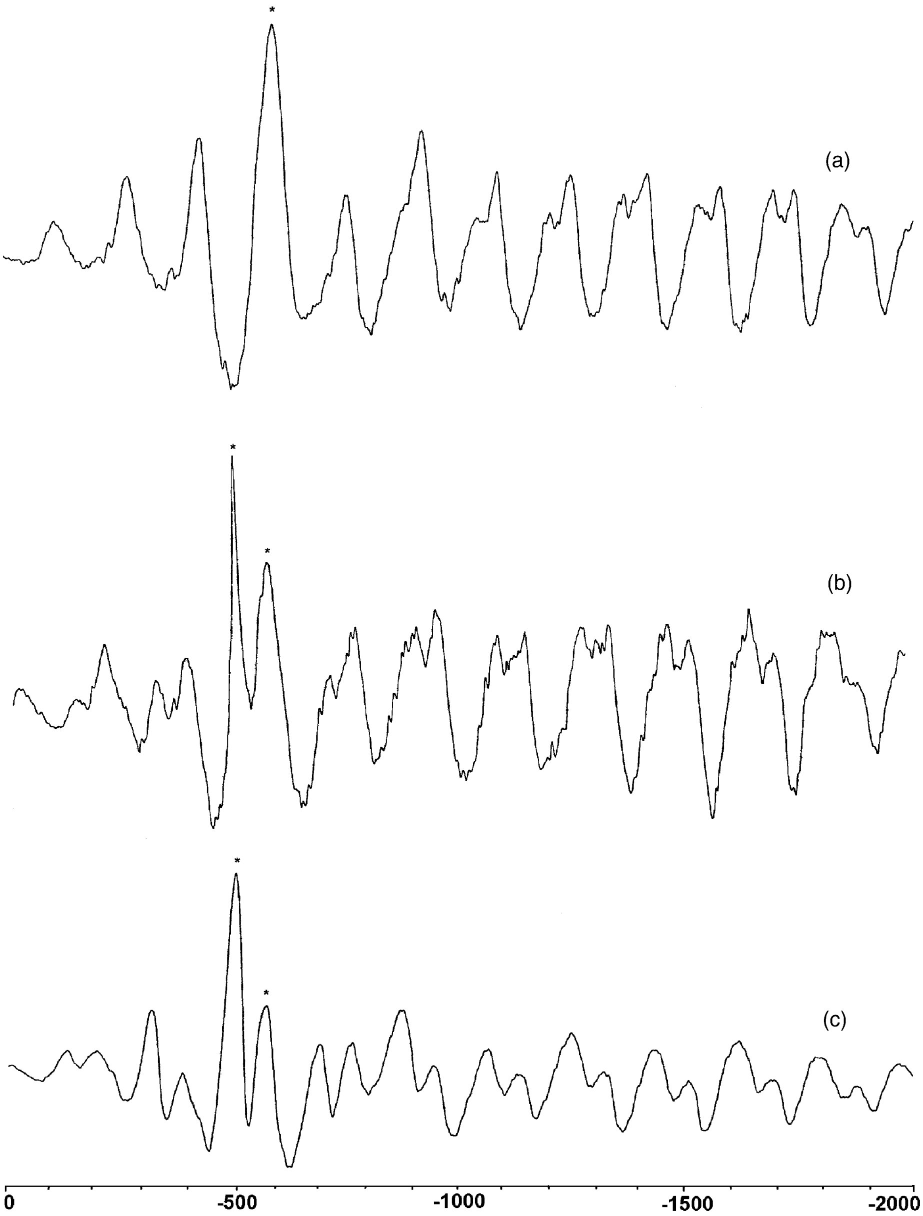

Fig. 5. ^{51}V solid state MAS NMR (15 kHz) spectra of V2Mo460c (a), V2W460c (b) and V60c (c), calcined at 500 °C. $*$ denotes the isotropic signals.

metal oxides is manifested by the lower slope of the selectivity function. As a result, selectivity values up to 50% were obtained at 20% conversion, nearly twice the value given by pure supported vanadium oxides.

It could be argued that selectivity, as a function of the ratio between rate constants for selective and non-selective reaction channels, might be temperature dependent and should be determined at constant temperature to draw firmer conclusions regarding the influence of structural parameters. However, the very low selectivity given by tungsten oxides in the whole temperature region suggests that chemical parameters,

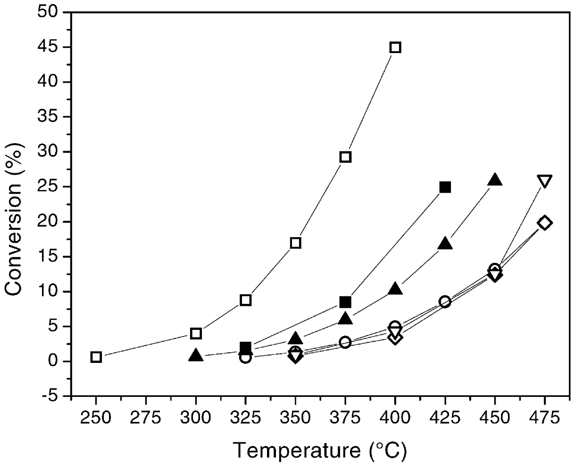

Fig. 6. Conversion as a function of temperature for catalysts: V60c (□), V2W460c (○), V2Mo460c (▲), W60c (▽), Mo60c (◇), V30c (■).

i.e. composition and local structure, do control the selectivity.

Participation of bare surface of the alumina support to propene combustion was excluded since pure vanadium catalysts with different vanadium contents showed the same selectivity/conversion curve. The synergetic effect was thus attributed to dilution of vanadium oxide by non-active oxide species and possibly to the presence of bridging bonds V–O–M (M = W, Mo) in mixed oxide structures. NMR results evidenced the stability of $V_2W_4O_{19}{}^{4-}$ polyanions on the alumina surface in the conditions used for drying the catalysts. Even after calcination the presence of this polyanion was detected, suggesting that superficial mixed oxides might indeed be present in the conditions of catalysis. Although $V_2Mo_4O_{19}{}^{4-}$ polyanions appear to be less stable, we propose that some synergetic effect should be attributed to the formation of V–O–Mo bridging species on the surface of the support. Thus, the less stable polyanion gives way after calcination to higher amounts of free vanadium oxides, producing a more active but less selective catalyst.

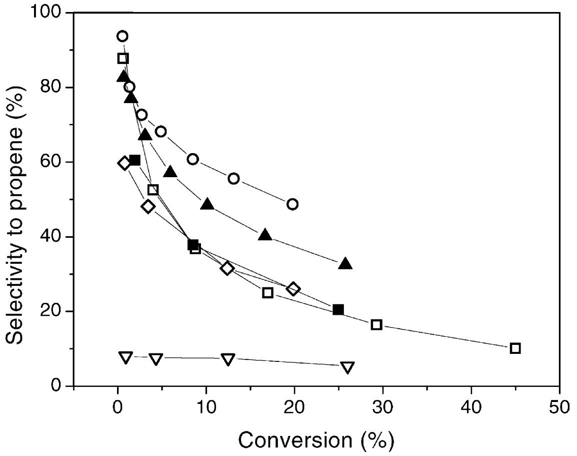

Fig. 7. Selectivity to propene for catalysts: V60c (□), V2W460c (○), V2Mo460c (▲), W60c (▽), Mo60c (◇), V30c (■).

4. Conclusion

Vanadium–molybdenum and vanadium–tungsten hexametalate polyanions prepared in aqueous solution were used as precursors of modified alumina-supported vanadium oxides for application in propane ODH. Catalytic and spectroscopic results have shown that incomplete decomposition of the supported polyanion during calcination enhances the selectivity of the resultant oxide towards the olefin. In contrast, activity of the catalysts was well correlated with the amount of free supported vanadium oxides. The results suggest that the concept of site isolation applies to propane ODH.

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