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Role of potassium on the structure and activity of alumina-supported vanadium oxide catalysts for propane oxidative dehydrogenation

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Abstract

The influence of potassium on the structure and properties of alumina-supported vanadium oxide catalysts has been studied by in situ Raman spectroscopy, temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), a probe reaction of acid/base–redox sites (methanol chemisorption) and tested in oxidative dehydrogenation (ODH) of propane. Potassium coordinates to surface vanadium oxide species altering its structure but does not form bulk compounds, possibly because the total V + K coverage does not reach the monolayer coverage on alumina. The interaction of K with V weakens the terminal V=O bond. K-doped alumina (KAl)-supported vanadia catalysts show lower acidity, a decrease of reducibility and a decrease of propane conversion values. These trends do not correspond with the changes in the terminal V=O bond energy. Thus, it appears that the terminal V=O bond of surface vanadium oxide species is not the active site for propane ODH, oxidation of methanol to formaldehyde and for the reduction of surface vanadium oxide species by hydrogen. Potassium also changes the acid–base characteristic of the system and decreases the acidic character of surface vanadia. This shift in the acid–base character to a more basic system must also account for the better selectivity in propane ODH due to a variation in the interaction between the intermediates and the surface.

Keywords: VO_x/Al_2O_3 catalysts; Doping by potassium; In situ Raman; Vanadia; Propane; Oxidative dehydrogenation; XPS; Temperature-programmed reduction

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1. Introduction

The oxidative dehydrogenation (ODH) of light alkanes to alkenes possesses great industrial relevance and it has extensively been studied [1–5]. Vanadium oxide is present in most of the catalysts for selective oxidation of alkanes, which afford higher productivity and higher yield at lower temperatures. A rational catalysts design requires detailed information on the nature of the active sites and their role in the catalytic cycle. The catalytic properties of supported vanadia for selective oxidation reactions are strongly influenced by the preparation method, nature of the support and of the promoter. Alumina-supported vanadium oxide catalysts afford best performance of propane ODH at half monolayer coverage [6]. The acid–base character of the metal oxide support can determine both the nature of vanadium species and the catalytic behavior of these catalysts [6,7]. Alkali metals, in particular potassium, are often mentioned as promoters for industrial

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catalysts for selective oxidation processes since they afford higher selectivity for partial oxidation reactions [8–18]. However, the role of alkali dopants on the structure and properties of supported vanadia is not fully understood. Titania-supported vanadia shows a strong dependence on the sequence of preparation so that V oxide on K-doped titania appears to cover K sites and the molecular structures of vanadia resemble those of surface vanadia [10]. However, K oxide added to titania-supported vanadia shows higher exposure of K and the formation of potassium vanadates [10,19]. At low coverage, the presence of K does not lead to the formation of vanadates, but its interaction with surface vanadia results in weaker V=O bonds in the surface vanadia species [9,19].

In this work, undoped and K-doped VO_x/Al_2O_3 catalysts have been prepared by different methods, tested for propane ODH, and characterized by in situ Raman spectroscopy, temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and by the adsorption and temperature-programmed reaction of probe molecule methanol, sensitive to acid, basic and redox sites.

2. Experimental

The catalysts were prepared by impregnation of a commercial γ-Al_2O_3 (Girdler Südchemie, 160 $m^2\,g^{-1}$) support with an aqueous solution of ammonium metavanadate. Due to modest solubility of the vanadium salt, the solution was heated to 60 °C. The content of vanadium in the catalysts corresponds to half monolayer coverage of VO_x, i.e. near 4 V atoms nm^{-2} (16 wt.% V_2O_5); this catalyst is labeled 16VAl. The K-doped catalysts were prepared from aqueous solution of potassium hydroxide by sequential impregnation (V–*x*K-doped alumina (KAl) and *x*K–VAl) and by co-impregnation (*x*KV–Al). Concentration of K_2O in this series was to 1, 3, and 6 wt.%, which correspond to a K/V atomic ratio of 0.1, 0.3 and 0.8, respectively. After drying at 120 °C for 2 h, the samples were calcined at 450 °C for 4 h. The chemical analyses of the catalysts were carried out by inductively coupled plasma analysis (ICP-AES) using a Perkin-Elmer Optima 3300 DV spectrometer.

The BET area of the catalysts was measured with a Micromeritics ASAP-2000 apparatus from N_2 adsorption isotherms. The reducibility of catalysts was studied by TPR in a Micrometrics apparatus model TPR/TPD-2900 fitted with a TCD detector. Samples of ca. 20 mg each were used. Treatment in Ar flow at 250 °C for 1 h preceded each TPR experiment. After cooling at room temperature the TPR experiment was carried out under a flow of 10% H_2/Ar mixture, with a heating rate of 10 °C min^{-1} up to 1000 °C with a flow rate of 80 $cm^3\,min^{-1}$. The X-ray photoelectron spectra were recorded on a VG ESCALAB 200R photoelectron spectrometer using Mg Kα (1253.6 eV)/Al Kα (1486.6 eV) radiation from an X-ray source operating at 12 kV and 10 mA. Working pressure was lower than 5×10^{-9} Torr.

In situ Raman spectra were run with a Renishaw Micro-Raman System 1000 equipped with a cooled CCD detector and a holographic super-Notch filter that removes the elastic scattering. The samples were excited with the 514 nm Ar line in an in situ cell (Linkam, TS-1500), which allows temperature treatments up to 1500 °C under flowing gases. The spectra of the dehydrated catalysts were obtained after the samples were calcined at 300 °C under O_2/He for 1 h. The laser power on the samples was ca. 12 mW and acquisition time was 120 s.

Methanol chemisorption and its temperature-programmed surface reaction (TPSR) were followed by mass spectroscopy experiments were performed in a conventional fixed bed apparatus using a quartz reactor coupled to a quadrupole mass spectrometer equipment, model Balzers QMG 125. The samples (100 mg) were pretreated with a mixture of Ar/He (5/95% molar) by heating to 100 °C for 1 h in a fixed bed quartz microreactor. Methanol chemisorption was performed treating the sample with a 2000 ppm methanol in Ar/He stream at 100 °C until saturation is reached. The signal of methanol is followed so that it is possible to determine the number of methanol molecules that chemisorb. Quantitative methanol chemisorption determine the density of surface active sites in bulk metal oxides [20,21]. Infrared and TPSR studies show that the nature of surface methoxy species depends on the adsorption temperature. Methanol adsorption at 100 °C generates only metal–methoxy (M–OCH_3) groups through a chemisorption process, whereas methanol adsorption is mainly molecularly physisorbed at low temperature [22]. Thus, the sample was purged with an Ar/He mixture at 100 °C to remove any trace of physically adsorbed molecular methanol and then it was heated up to 500 °C at 6 °C min^{-1}. The effluent gases were continuously monitored with an on-line mass spectrometer. The reaction products were dimethyl ether, formaldehyde, carbon monoxide, carbon dioxide and water.

The activity of catalysts for propane ODH were conducted at atmospheric pressure in a conventional fixed bed quartz microreactor. The catalysts (100 mg) were tested between 300 and 500 °C. The reactant gas mixture of $C_3H_8/O_2/He$ (1/6/4) was used with a total flow rate of 45 cm^3 min^{-1}. Analysis of products and unreacted propane was performed by on-line CG (HP-5890 Series II). Propene, carbon monoxide, and carbon dioxide were found to be the main reaction products.

3. Results

The BET specific area values and catalyst composition are presented in Table 1. Addition of potassium to the oxide support results in a moderate decrease of the specific area compared to non-doped 16VAl. The BET area of the catalysts decreases with increasing potassium content. The addition of K to alumina decreases the BET area values to 135 m^2 g^{-1}. The addition of V to alumina decreases BET area to 144 m^2 g^{-1}. The addition of both, V and K, reduces the BET area values to a similar extent than the previous series. Thus, the preparation procedure does not appear to have a strong effect on the BET area values.

The reducibility of bulk V_2O_5 and of the V–K–O/Al_2O_3 catalyst series are shown in Table 2. The bulk V_2O_5 showed three reduction peaks that can be attributed to sequential reduction of bulk V_2O_5 [23,24]. Alumina-supported vanadia and K-doped vanadia–alumina catalysts exhibit a single reduction peak. The temperature for this maximum (T_{max}) increases with K loading on VO_x/Al_2O_3 from 482 to 547 °C, irrespective of the preparation method. T_{max} is lowest for 16VAl (480 °C), which is characteristic of surface vanadia species on alumina. On the other hand, the preparation method does have an effect on the extent of reduction of vanadium sites after TPR. Thus, KV–Al series shows a continuous decrease of H_2/V values with K loading. K–VAl series shows a sharp decrease of H_2/V values on addition of K, these series show H_2/V values ranging from 0.6 to 0.8. However, the trends are different for V–KAl, series, where the extent of reduction is less affected (1.0, 0.8 and 0.7) with increasing K content. Thus, the interaction between V and K oxides appears to be less intense for V–KAl series.

The surface K/V atomic ratio is determined by XPS (Fig. 1). As expected, the K/V ratio increases with K loading in all the series. However, co-impregnated KV–Al series shows the highest atomic K/V atomic ratio values. The K–VAl series shows moderate values, but V–KAl series shows the lowest K/V atomic ratio

Table 1
Catalyst composition and BET area

Catalyst	V_2O_5 (wt.%)	K_2O (wt.%)	Surface density (V atoms nm^{-2})	Surface density (V atoms nm^{-2})	BET area (m^2 g^{-1})
Al_2O_3	–	–	–	–	160
1KAl	–	0.8	–	0.4	143
3KAl	–	2.7	–	1.3	141
6KAl	–	5.6	–	2.7	135
16VAl	15.8	–	4.0	–	144
1K16V–Al	16.8	0.7	4.0	0.4	141
3K16V–Al	14.5	0.9	4.0	1.3	135
6K16V–Al	14.6	1.7	4.0	2.7	127
1K–16VAl	16.1	0.8	4.0	0.4	139
3K–16VAl	14.9	1.0	4.0	1.3	137
6K–16VAl	14.4	1.9	4.0	2.7	136
16V–1KAl	15.0	0.8	4.0	0.4	141
16V–3KAl	14.6	0.8	4.0	1.3	138
16V–6KAl	14.9	1.5	4.0	2.7	135

Table 2
H_2-TPR of V–K–O/Al_2O_3 catalyst and methanol chemisorption data

Catalyst	V_2O_5 (wt.%)	T_{max} (°C)				H_2 uptake (μmol g^{-1})	H_2/V (μmol ratio)	Methanol chemisorption (μmol per 100 mg)
		T_1	T_2	T_3	T_4			
16VAl	15.8	480	–	–	–	1636	0.9	144
1K16V–Al	16.8	487	–	–	–	1513	0.8	117
3K16V–Al	15.5	507	–	–	–	1057	0.7	109
6K16V–Al	14.6	538	–	–	–	921	0.6	79
1K–16VAl	16.1	491	–	–	–	1098	0.6	102
3K–16VAl	14.9	504	–	–	–	1031	0.6	99
6K–16VAl	14.4	547	–	–	–	906	0.6	90
16V–1KAl	15.0	482	–	–	–	1592	1.0	116
16V–3KAl	14.6	506	–	–	–	1204	0.8	92
16V–6KAl	14.9	540	–	–	–	1149	0.7	97
V_2O_5	100	–	678	711	841	11 129	1.0	–
Al_2O_3	0	–	–	–	–	–	–	203
1KAl	–	–	–	–	–	–	–	174
3KAl	–	–	–	–	–	–	–	149
6KAl	–	–	–	–	–	–	–	134

at each K content. The V–KAl series shows the lowest exposure of K sites.

The in situ Raman spectra of the dehydrated catalysts are shown in Fig. 2. The catalyst 16VAl exhibits a Raman band near 1027 cm^{-1}, characteristic of the stretching mode of terminal V=O in surface isolated and terminal V=O in surface polymeric vanadium oxide species (Fig. 2A). The broad Raman band between 880 and 920 cm^{-1} is characteristic of the V–O–V stretching mode of surface polymeric vanadium oxide species. The other bands near 340, 620 and 780 cm^{-1} are characteristic of the bonds V–O–V and O–V–O [25,26]. The incorporation of potassium in the 16VAl (Fig. 2A) shifts the band at 1027–990 cm^{-1} (K–VAl series). The new band at 990 cm^{-1} does not correspond to that of crystalline V_2O_5, since it should also present additional Raman bands that are not observed. The Raman spectra of the dehydrated V–KAl series (Fig. 2B) and of the co-impregnated KV–Al series (Fig. 2C) show an analogy with the former series. However, the shift of the Raman band at 1027 cm^{-1} as K content increases is less evident for V–KAl series. A comparison of the Raman spectra of the catalysts prepared by different methods is shown in Fig. 2D. The shift of the Raman band from 1027 cm^{-1} to lower wavenumbers evidences a weakening of the terminal V=O bond due to the interaction between surface vanadia and surface K oxide, similar effect has been observed by using FT-Raman spectroscopy Bulushev et al. [19] and it has also been observed with IR spectroscopy [9]. Some broad features appear to develop in the 800–1000 cm^{-1} window that may correspond to the incipient formation of potassium vanadate [19].

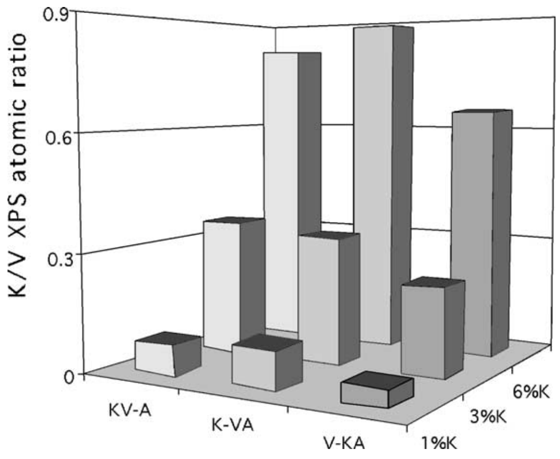

Fig. 1. K/V XPS atomic ratio for the V–K–O/Al_2O_3 catalysts vs. K loading and preparation method.

The amount of methanol chemisorbed (μmol 0.1 g_{cat}^{-1}) at 100 °C on the catalysts is shown in Table 2. It decreases with potassium or vanadium content on alumina. The presence of both, K and V, over alumina decreases methanol adsorption to larger extent, and this is most evident for 6K–16VAl. The K content strongly decreases the chemisorption of

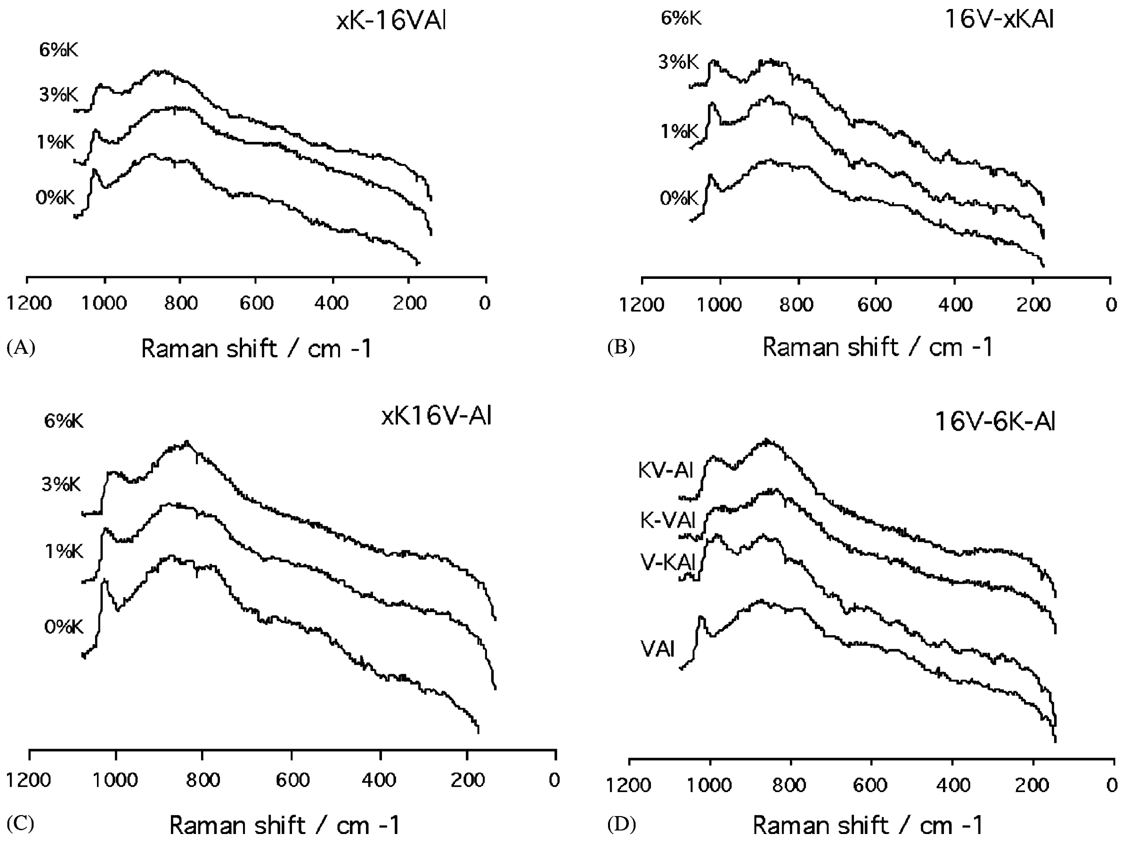

Fig. 2. Raman spectra of dehydrated V–K–O/Al_2O_3 catalysts.

methanol. The V–KAl series shows a trend similar to that of K–VAl and KV–Al series. The TPSR profiles are illustrated in Fig. 3. The TPSR products of methanol chemisorbed over surface sites of K-doped VO_x/Al_2O_3 are described as follows: HCHO (redox sites); DME (acid sites); CO_2 (basic sites). Along the spectra, water was also released from the surface through the reactions of chemisorbed methanol with redox, basic and acidic sites. Therefore, water profile is not discussed. CO is a secondary product and it has also been removed from the figures. Methanol TPSR on alumina support shows desorption of chemisorbed methanol at ca. 140, 210 and 300 °C. Acid sites form DME. The production of CO_2, due to basic sites, is very low. Undoped (Al_2O_3) and KAl show no yield to formaldehyde due to the lack of redox sites. Addition of K to alumina significantly decreases the acidity (DME formation) and increases basicity (CO_2 formation) the presence of basic sites also decreases CO_2 onset temperature. A characteristic behavior of K loading is that it increases the amount of methanol that desorbs at ca. 300 °C with K content. The incorporation of vanadium on alumina (16VAl) promotes formaldehyde formation (redox sites) and decreases CO_2 formation (basic sites). When K is added to VAl, the presence of basic sites becomes evident by the increase of CO_2 production and the decrease of DME production. But K also affects the redox properties. Formaldehyde production presents a shift of its production maxima from 230 to 258 °C in V–KAl series (Fig. 3). Similar shifts are observed for K–VAl (from 239 to 292 °C) and for the co-impregnated KV–Al (from 234 to 285 °C), not shown for the sake of simplicity.

The preparation method does show a moderate effect on formaldehyde production. Fig. 4 illustrates the

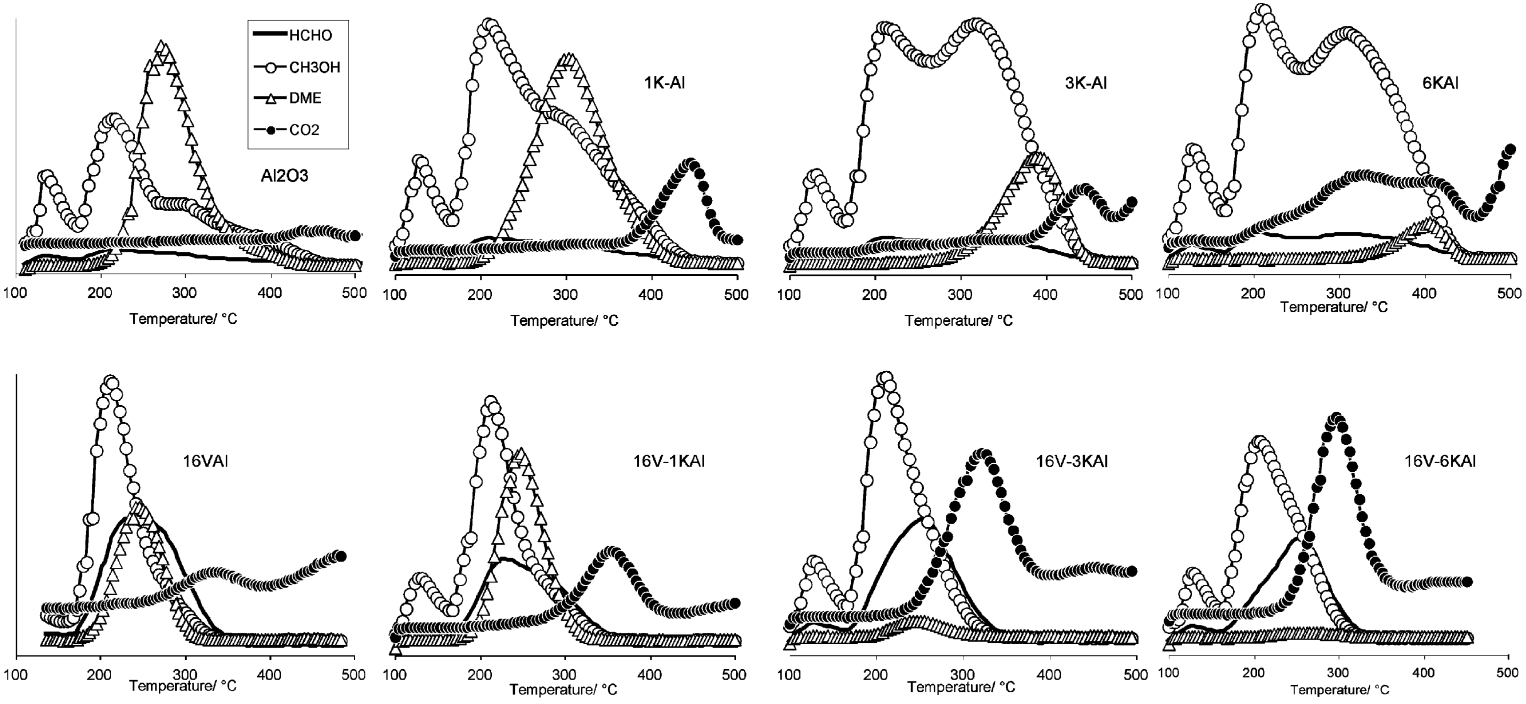

Fig. 3. Methanol TPSR on the V–K–O/Al_2O_3 catalysts.

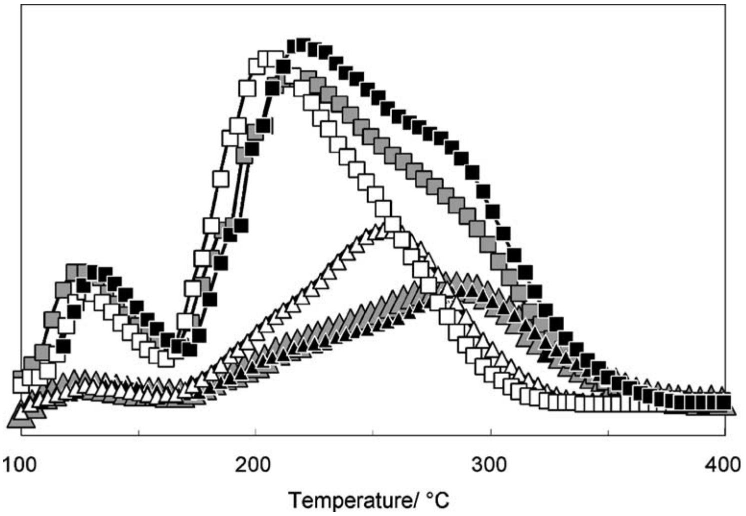

Fig. 4. Effect of preparation method and K loading on formaldehyde and methanol profiles in the TPSR experiments on samples with 6 wt.% K_2O and 16 wt.% V_2O_5, methanol desorption (squares), formaldehyde formation (triangles). White: V–KAl series; gray: K–VAl series; black, KV–Al series.

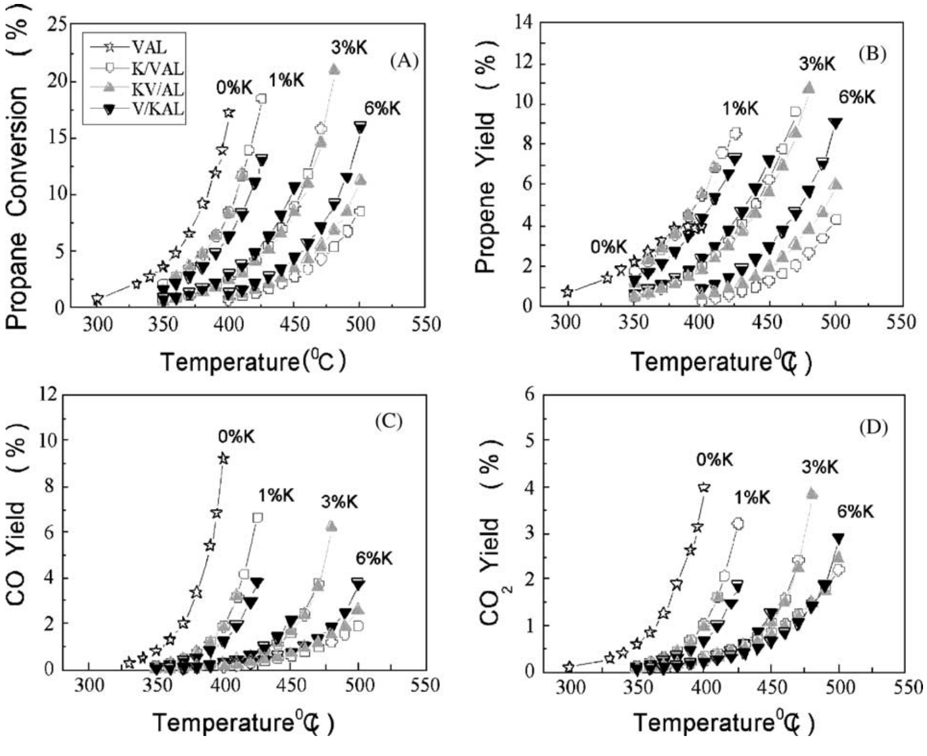

Fig. 5. Propane ODH on V–K–O/Al_2O_3 catalysts: (A) propane conversion; (B) propene yield; (C) CO yield; (D) CO_2 yield.

formaldehyde profile of catalysts with 6 wt.% K_2O and 16 wt.% V_2O_5 on alumina for the different preparation procedures. The V–KAl series shows the lowest effect on formaldehyde production. The effect of preparation method is most evident on methanol desorption profiles (Fig. 4), namely, the methanol desorption component around 300 °C increases in the sequence V–KAl $<$ K–VAl $<$ KV–Al. As this component appears related to K exposure, which is lowest for V–KAl series.

The results of catalytic activity for the ODH of propane as a function of reaction temperature are shown in Fig. 5. The temperature required to reach 10% conversion of propane, increases with potassium content (Fig. 5A). The decrease in activity is mainly due to a decrease in the formation of non-selective CO and CO_2. The yield to propene increases with the addition of potassium and reaches a maximum yield for 3K–16VAl and 3K16VAl. The increase in the production of propene with the decrease in the acidity could be due to the easier desorption of propene from the less acidic surface, preventing the consecutive total combustion of propene to carbon oxides [16].

4. Discussion

The nature of surface vanadium oxide species is affected by the presence of potassium and the impregnation sequence. This is evident in the reducibility, methanol chemisorption/TPSR, Raman and XP spectra and catalytic performance. The Raman spectra evidences an alteration in the nature of surface vanadium oxide species by K. Potassium may replace surface protons and giving rise to V–O–K and Al–O–K linkages of different types that cannot be determined by the techniques used here. Such scenario has been proposed for KAl-supported vanadia [29]. The Raman bands of surface vanadia species are most altered for 6K–16VAl, which evidences a larger disturbance structure of surface vanadia when potassium is added. The ^{51}V NMR-MAS spectra shows that the potassium addition strongly changes the environment of V sites and forms alkali vanadates on V/TiO_2 [10,30]. Bulk and in some cases, supported, mixed K and V oxides form potassium vanadates or bronzes [10,14,30,31]. In those cases, the total surface density of V is 10 and 20 V atoms nm^{-2} [10], which is above the monolayer coverage (monolayer coverage of vanadia on titania is ca. 8 V atoms nm^{-2}). Our results do not show the formation of bulk V–K–O compounds since total V + K coverage on alumina does not reach monolayer. It has been demonstrated for other alumina-supported vanadium oxides species with a dopant that the formation of tri-dimensional compounds requires a surface coverage of at least a monolayer [27,28]. Other authors report the formation of amorphous vanadates below monolayer coverage at a higher K/V atomic ratio (1:1) [19]. In the systems reported here, K and V do interact but do not appear to form bulk compounds. The main feature of the K-modified surface vanadia appears to be a weakening of the terminal V=O bond, as its Raman band shifts to lower wavenumber.

The TPR profiles and the Raman spectra show that the interaction between surface vanadia and surface K oxides decreases the reducibility of the surface vanadium oxide species. The relevance of K loading on the H_2/V values in the $V–K–Al_2O_3$ series depends on the preparation sequence. The V–KAl series exhibits the highest extent of reducibility: 1.0 H_2/V for 16V–1KAl that decreases with K content. The samples prepared by impregnation of V on a KAl exhibit higher reducibility. Formaldehyde production during TPSR experiments is also a probe of the redox properties of the $K–V–Al_2O_3$ series. The shifts of the T_{max} in the formaldehyde plots further support the modification of redox properties shown by H_2-TPR profiles. It is interesting to underline that Raman spectra show a weakening of the V=O bond with K-doping. Therefore, the changes in the strength of the terminal V=O bond does not correlate with change in reducibility and hence, the site for reduction cannot be the terminal V=O bond.

Methanol chemisorption shows that the addition of potassium decreases the quantity of methanol chemisorbed over $K–V–Al_2O_3$ catalysts. The TPSR profiles are very informative since they show a progressive decrease of DME formation with K loading and a concomitant increase of CO_2: both underline the replacement of acidic sites by basic ones. Methanol desorption shows low and a high temperature desorption components. The high temperature methanol desorption component shows two contributions around 220 and 280 °C. The second contribution is particularly intense on KAl samples, and it is quite intense for K–VAl and KV–Al series at high K loading, but not for V–KAl. Co-impregnated VK–Al and K–VAl series show higher exposure of K sites, likely as a consequence of the incipient formation of K–V–O compounds, where K and V would distribute in a more homogeneous way than for V–KAl series. It makes sense that K–VAl and co-impregnated KV–Al series show similar structures since V oxide species on alumina solubilize on exposure to the K-precursor impregnating solution. So, the impregnation stage would be very similar for these two series. Supported K does not appear to solubilize upon exposure to the V-precursor impregnating solution. Therefore, the number of exposed K sites would be lower for V–KAl series, which is consistent with a model of vanadia species deposited on top of surface K sites for V–KAl series. This is also consistent with the XPS data that show an exposure of K two or three-times higher than that of the V–KAl series.

The better performance of the 3K/16VAl and 3K16V/Al catalysts as compared with the others K-doped catalysts can be explained by changes in the nature of the surface sites. This maybe the result of a combined effect of K and V exposure, acid–base properties and redox properties. Any increase in K loading decreases the reducibility of surface vanadia species, and this correlates with a decrease in conversion values, mainly due to a decrease in non-selective CO and CO_2. The K loading produces the strongest effect, however, the preparation method also appears to have some effect on the performance. At low and medium K loading, the effect of the preparation method on propane ODH is not very intense, but for 6 wt.% K_2O loading, the preparation method does show differences, and 16V–6KAl is the most efficient catalyst among those with 6 wt.% K_2O. It therefore appears that there is an optimum exposure of K for propane ODH. However, the best catalytic results are afforded by the samples with 3 wt.% K_2O. In this case, the three preparation methods appear to reach similar catalytic performance. The Raman spectra shows a weakening of the V=O bond with K-doping. The changes in the strength of the terminal V=O bond does not correlate with change in reducibility or with the change in catalytic activity. Isotopic studies by Chen et al. show that the cleavage of the methylene C–H bond is the rate-determining step for propane dehydrogenation reactions [5]. They also propose that there are different lattice oxide sites for propane dehydrogenation and combustion [5]. The results presented above, strongly suggest that the terminal V=O bond is not the site directly involved in the activation of the methylene C–H bond during propane ODH.

Potassium also increases the basicity of the catalysts, and this could allow an easier desorption of propene from the less acidic surface, preventing the consecutive total combustion of propene to carbon oxides [16]. Thus, the modification of acid–basic properties, i.e. decrease in the acidity and increase in the basicity for $K–VO_x/Al_2O_3$, plays also an important role in the design of catalysts for the ODH of light alkanes. The presence of K appears to have a remarkable effect on the reaction mechanism for propane ODH since K free alumina-supported vanadia appears to produce CO_2 as a secondary product, while the addition of K results in the formation of CO_2 as a primary product [17]. The nature of the effect of potassium on such interaction with vanadia–alumina is presently under study [32].

5. Conclusions

The addition of potassium to VO_x/Al_2O_3 catalysts affects the structure and properties of surface vanadium oxide species. Potassium loading has a primary effect, and the preparation method has a secondary effect. Potassium removes surface acid sites, generates basic sites through its coordination with surface vanadia species. The most remarkable effect on surface vanadium oxide species is the weakening of the terminal V=O bond. The H_2-TPR and methanol TPSR show a decrease of reducibility with K content, that parallels the decrease in catalytic performance. These trends cannot be understood if the terminal V=O bond is the active site of vanadia species, since this bond becomes more labile upon interaction with potassium.

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