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Oxidative dehydrogenation of *n*-butane and 1-butene on undoped and K-doped VO_x/Al_2O_3 catalysts

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Abstract

The oxidative dehydrogenation (OXDH) of *n*-butane and 1-butene on undoped and K-doped alumina-supported vanadia catalysts has been studied. The low selectivity to OXDH products on alumina-supported vanadia catalysts is a consequence of the isomerization of olefins (low temperatures) and the formation of carbon oxides (high temperatures) on acid sites. The presence of potassium results in a decrease of the number of acid sites and a higher selectivity to OXDH products from both *n*-butane and 1-butene. Infrared spectroscopy data of 1-butene adsorbed on the catalysts suggest the presence of different adsorbed species: (i) O-containing species on the undoped catalyst, or (ii) adsorbed butadiene on K-doped catalyst. A reaction network including parallel and consecutive reactions is proposed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metal oxide supported vanadia catalysts have high selectivity for the oxydehydrogenation (OXDH) of short chain paraffins [1–5]. The acid–base character of the metal oxide support can determine both the nature of vanadium species and the catalytic behavior of these catalysts [2–5]. In particular, VO_x/Al_2O_3 is an active and selective catalyst in the OXDH of ethane [5–7], but it has low selectivity in the oxidation of butane [6]. The incorporation of potassium on VO_x/Al_2O_3 catalysts favors higher selectivity to C_4-olefins during OXDH of *n*-butane [7]. A similar promoting effect of alkali metals has also been observed during the OXDH of C_3 and C_4 on both VO_x/TiO_2 [8] and metal molybdate-based catalysts [9,10]. However, the role of potassium is still not clear.

Vibrational spectroscopy of adsorbed molecules on metal oxides can help to understand the mechanism of some oxidation reactions [11]. Although the adsorption of alkanes on supported vanadia catalysts is generally low [12], the adsorption of molecular intermediates, especially C_4-olefins, may be used to study the mechanism of the OXDH of *n*-butane.

The aim of this paper is to compare the catalytic results obtained during the oxidation of *n*-butane and 1-butene on well characterized undoped and K-doped VO_x/Al_2O_3 catalysts and to investigate the nature of adsorbed species formed on the catalyst surface during the adsorption of 1-butene by IR spectroscopy.

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2. Experimental

The VO_x/Al_2O_3 (3.5 wt.% V-atoms) catalyst was prepared by impregnation of a non-porous γ-Al_2O_3 support with an ammonium metavanadate aqueous solution (pH=7). The K-doped VO_x/Al_2O_3 catalyst (K/V atomic ratio of 0.7) was prepared by impregnation of the alumina-supported vanadia catalyst with an aqueous solution of potassium nitrate. The catalysts were calcined at 600°C for 6 h.

The catalytic experiments were carried out in a fixed bed continuous quartz tubular reactor (i.d. 20 mm, length 400 mm), working at atmospheric pressure. Catalyst samples (0.3–0.5 mm particle size) were introduced in the reactor and diluted with 8 g of silicon carbide (0.5–0.75 mm particle size) in order to keep a constant volume in the catalyst bed. The flow rate of the reactants was varied (100–600 $cm^3 min^{-1}$) to achieve different contact times ($W/F =$ 2–40 $g_{cat} h\, mol_{C_4}{}^{-1}$), and different *n*-butane or 1-butene conversions. The feed consisted of mixtures of *n*-butane/O_2/He with a molar ratio of 5/20/75 or 1-butene/O_2/He with a molar ratio of 2/20/78. Reactants and reaction products were analyzed by on-line gas chromatography [3]. Blank runs showed that under the experimental conditions used in this work the homogeneous reaction could be neglected.

IR spectroscopy studies were performed with a Bruker IFS-88 apparatus at a spectral resolution of 1 cm^{-1} collecting 128 scans. Self-supporting wafers were prepared from the sample powders and heated directly in the IR cell. Prior to each experiment, all samples were activated for 1 h in a flow of oxygen at 500°C, followed by 1 h evacuation at the same temperature. The experiments were performed by exposing the sample to 50 hPa (1 hPa=1 mbar) of 1-butene at room temperature in the IR cell. After 1 h, the temperature was increased from 25 to 400°C in steps of 50°C and stabilization times of 1 h at each temperature.

3. Results and discussion

Previous characterization results (DR-UV–VIS and ^{51}V NMR spectroscopy) of both undoped and K-doped catalysts indicated the presence of polymeric tetrahedral V^{5+} species [7,13]. On the other hand, while Lewis acid sites are observed on the undoped samples (determined by IR of adsorbed pyridine) they are completely removed after the incorporation of potassium [7,13]. The decreasing number of Lewis acid sites with the potassium loading may be a consequence of: (i) a direct interaction of acid sites with potassium, and/or (ii) a higher dispersion of vanadium species. Recent results indicated that, although the number of Lewis acid sites depends on the K-loading, the reduction of their acid site density is a consequence of the higher dispersion of V-species on the surface of the metal oxide support which is favored by the presence of potassium [14].

On the other hand, the incorporation of potassium decreases the reducibility of V^{5+} species. Thus, the temperature of maximum H_2-consumption, determined by TPR of hydrogen, shifts from 450°C (for the undoped catalyst) to 500°C for the K-doped catalyst.

3.1. Oxydehydrogenation of n-butane

Fig. 1 shows the variation of the selectivity to OXDH products with the conversion of *n*-butane at 500°C on both undoped and K-doped catalysts. It can be seen that the selectivity to OXDH products, i.e. 1-butene, 2-butenes and butadiene, on the undoped catalysts was lower than that on the K-doped catalyst. It must be noted that 2-butenes (at low temperature)

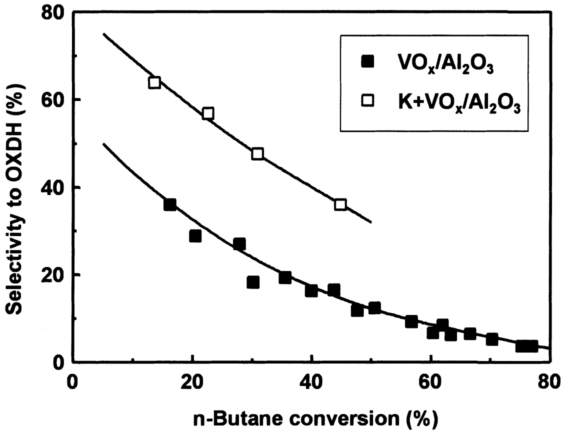


Fig. 1. Variation of the selectivity to oxydehydrogenation products (butenes and butadiene) with the *n*-butane conversion during the OXDH of *n*-butane on undoped and K-doped alumina-supported vanadia catalysts.

and CO_x (at high temperatures) were the most abundant reaction products on VO_x/Al_2O_3 sample (with a *trans*-/*cis*-2-butene ratio of 1.27–1.29). However, 1-butene (at low temperature) and butadiene (at high temperature) were the most important products when the reaction was carried out on the K-doped catalysts. In this case, a *trans*-/*cis*-2-butene ratio of 0.97–0.95 was obtained.

Although the selectivities to monoolefins decreased with the conversion of *n*-butane, the selectivity to butadiene showed different trends on the two catalysts. Thus, it decreased on the VO_x/Al_2O_3 but increased on the K-doped catalyst. However, the catalytic activity of K-doped catalyst was lower than that of the undoped catalyst.

3.2. Oxydehydrogenation of 1-butene

Butadiene and carbon oxides were observed during the oxidation of 1-butene on both catalysts. In addition, 2-butenes (which are formed by isomerization of 1-butene) were also obtained. Oxygenated compounds other than CO_x were not observed.

Fig. 2 shows the variation of the conversion of 1-butene and the selectivity to the main products with the reaction temperature for both undoped and K-doped catalysts. As it has been observed during the oxidation of *n*-butane, the K-doped catalyst shows a lower catalytic activity than the undoped catalyst.

2-Butenes and/or carbon oxides were the most important products during the oxidation of 1-butene on the undoped catalyst, while a selectivity to butadiene of 50% was obtained on the K-doped catalyst, since. 2-butenes are formed by acid catalysis [15,16] and butadiene and CO_x are formed by oxidation reactions, Fig. 3 shows the variation of the selectivity to butadiene, referred to as the butadiene/(butadiene+CO_x) ratio, with the conversion of 1-butene to oxidation products. It can be seen that 1-butene is selectively oxidized to butadiene on the K-doped catalysts. However, a low selectivity to butadiene is observed on the undoped sample. These results were observed independently of the reaction temperature.

It has been proposed that Lewis acid sites could favor the isomerization of olefins at low temperatures and the deep oxidation at high temperatures [15]. According to our results, it is clear that the presence of Lewis acid sites on VO_x/Al_2O_3 favors both the isomer-

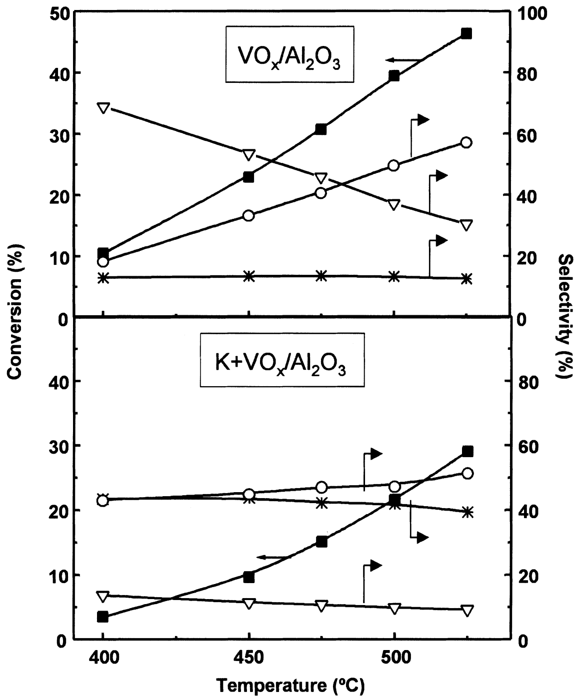


Fig. 2. Variation of the conversion of 1-butene (■) and the selectivity to the main reaction products, i.e. 2-butenes (▽), butadiene (∗) and CO_x (○), with the reaction temperature during the oxidation of 1-butene on undoped and K-doped VO_x/Al_2O_3.

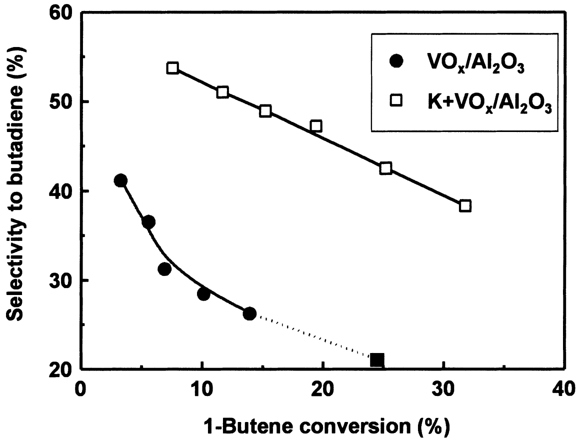


Fig. 3. Variation of the selectivity to butadiene, expressed as butadiene/(butadiene+CO_x) ratio, with the conversion of 1-butene during the oxidation of 1-butene at 500°C (□, ■) and 400°C (●) on both undoped and K-doped catalysts.

ization of 1-butene to 2-butenes and the deep oxidation on acid sites rather than the oxydehydrogenation of 1-butene on V-sites (redox catalysis). However, the incorporation of potassium eliminates these acid sites favoring the oxidative dehydrogenation of olefins rather than the isomerization or the deep oxidation reactions.

3.3. *Infrared studies of 1-butene adsorption*

The IR spectra in the low frequency region (1000–2000 cm^{-1}) of the adsorbed species resulting from the adsorption of 1-butene at room temperature on VO_x/Al_2O_3 and their evolution at increasing temperatures are reported in Fig. 4A. The room temperature spectrum is characterized by the presence of several bands. The sharp band at 1634 cm^{-1} is due to adsorbed unreacted 1-butene (ν(C=C)) while bands at 1692, 1463, 1378 and 1181 cm^{-1} can be assigned to adsorbed methyl-ethylketone (C=O stretching, asymmetric and symmetric CH_3 bending and C–C–C asymmetric stretching, respectively) [11]. Moreover, bands at 1667, 1634 and 1173 cm^{-1} can also be assigned to methyl-vinylketone [11]. The formation of the corresponding carbonyl compounds implies the formation of the corresponding alkoxide species. This species can later be oxidatively dehydrogenated to the corresponding carbonyl compound. However, no bands in the 1100 cm^{-1} region were detected, evidencing the absence of C–O bonds, and therefore of alkoxide species. This could be due to a quick oxidation of the alkoxide species to the corresponding carbonyl compound.

After heating at 100°C, the sharp band at 1634 cm^{-1} due to unreacted 1-butene disappears, whereas new bands at 1592 and 1393 cm^{-1} appear. These bands can be assigned to species containing carboxylate groups (COO^- asymmetric and symmetric stretching bending) [11]. However, the band at 1592 can also be related with: (i) the ν(C=C) stretching modes, shifted to lower frequencies with respect to the value of the free olefin due to perturbation by adsorption interactions [17]; therefore, surface σ-bonded allyl species may be proposed, and/or (ii) π-bonded allyl species [16]. In our case, surface σ-bonded allyl species (precursor of isomerization products) can be proposed according to the reaction products observed during the catalytic test.

Further heating causes a progressive disappearance of the bands at 1690 and 1667 cm^{-1} due to the carbonyl compounds, and an increase of strong broad bands at 1590 and 1457 cm^{-1} due to different carboxylate species. At temperatures >300°C, the bands at 1393 and 1378 cm^{-1} as well as a strong broad band centered at 1568 cm^{-1} tend to disappear. Also in the

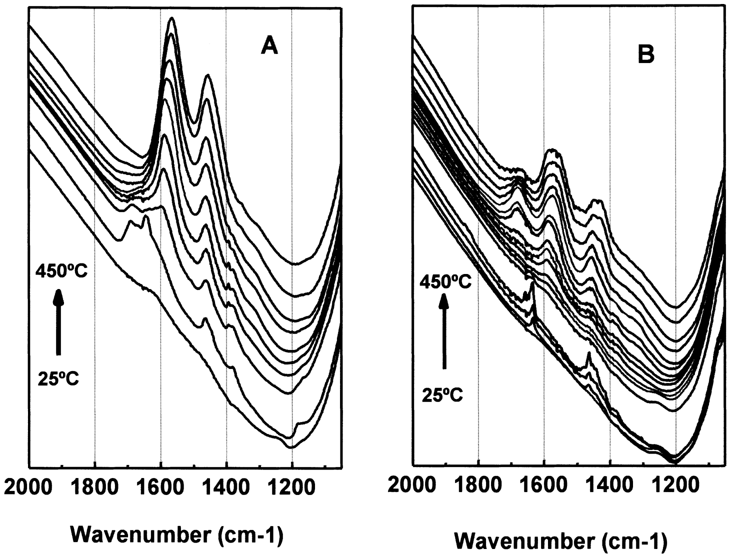


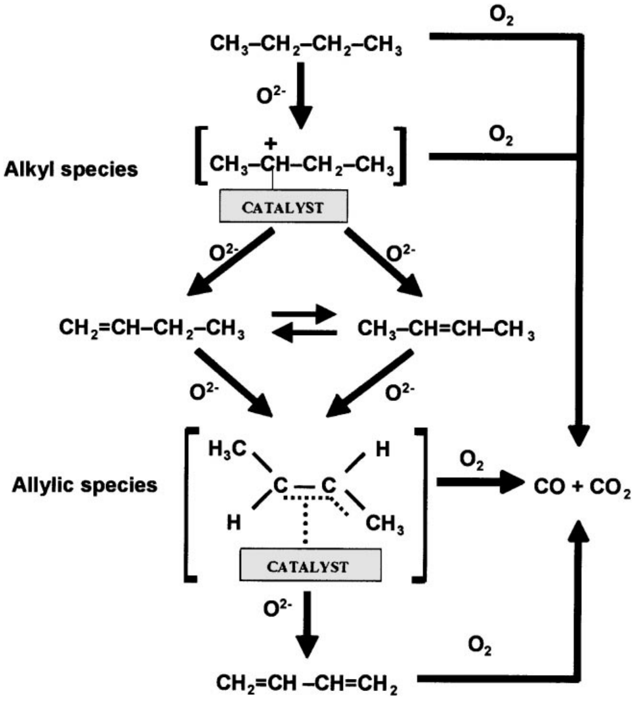
Fig. 4. IR spectra of 1-butene adsorbed on undoped (A) and K-doped VO_x/Al_2O_3 (B) catalysts at increasing temperature from 25 to 450°C.

C–H stretching region, a broad band appeared near 3050 cm^{-1}, typical of ν(CH) modes of unsaturated and/or aromatic compounds [18]. This may indicate that strongly bonded carbonaceous species began to grow at the surface at higher temperatures.

The spectra of the adsorbed species resulting from adsorption of 1-butene at room temperature on the K-doped catalyst and their evolution at increasing temperatures are reported in Fig. 4B. The room temperature spectrum is quite different from that observed for the undoped catalyst. Only bands due to unreacted adsorbed 1-butene species are observed. The shift to lower frequencies (1635 cm^{-1}) of the ν(C=C) stretching mode with respect to the gas phase and the corresponding perturbation of the OH bands indicate an interaction between the π-bonding orbital of the olefin and the hydrogen atom of the OH groups. This species is easily removed by increasing the temperature up to 100°C. No other bands assigned to carbonyl or alkoxide species as in the VO_x/Al_2O_3 are observed (strong bands expected in the region 1750–1650 or 1200–1000 cm^{-1}, respectively).

After increasing the temperature to 100°C, no bands are observed anymore. Further heating from 150 to 200°C shows the growth of two broad bands at 1590 and 1440 cm^{-1} and other weaker bands at 1390 and 1377 cm^{-1}. The bands at 1590 and 1440 cm^{-1} can be assigned to carboxylate species. However, considering the spectra recorded at increasing temperature, which show the growth of a strong band at 1682 cm^{-1} (assigned to carbonyl species), the assignation of these bands to carboxylate species is probably not correct. It is expected that carboxylate species are formed via consecutive oxidation of carbonyl species. Alternatively, the above mentioned bands could be attributed to surface σ-bonded allyl species [17], bonding to lattice oxygen, but no bands at 1200–1000 cm^{-1} assigned to C–O bonds have been observed. Therefore, π-bonded allyl species must also be considered.

As indicated before, increasing the temperature up to 200°C leads to the appearance of a strong band at 1682 cm^{-1} attributed to some carbonyl species. Further heating causes their progressive oxidation with



Scheme 1. Oxidative dehydrogenation of *n*-butane.

the growth of bands typical of carboxylates (broad maximum at 1580 and 1430 cm^{-1}).

In the OH region of the IR spectra, a shift of the bands of hydroxyl groups is observed at room temperature in both undoped and K-doped catalyst after the adsorption of 1-butene. However, while the number of OH groups decrease at room temperature on the undoped catalyst, they decrease only at high temperature on the K-doped catalyst. This decrease of the number of OH groups is parallel to the appearance of O-containing products indicating that the formation of these are more favored on the undoped catalyst.

4. Conclusions

The catalytic results on the oxydehydrogenation of *n*-butane and 1-butene on both undoped and K-doped VO_x/Al_2O_3 catalysts indicate that the presence of Lewis acid sites in VO_x/Al_2O_3 enhances the deep oxidation of both hydrocarbons. In the case of the transformation of 1-butene, the rate of the olefin isomerization (acid catalysis) is higher on K-free catalysts than the oxidation reactions by redox catalysis. However, the addition of potassium to the catalysts eliminates these acid sites favoring both the decrease in the isomerization reaction and the better selectivity to OXDH reactions. Scheme 1 shows a possible reaction network for the oxidation of C_4-hydrocarbons in which butadiene, selectively produced on K-doped catalysts, is formed by consecutive reaction (allylic mechanism) from butenes. It must be noted that according to previously reported results [19], lattice oxygen is only involved in the formation of monoolefins and diolefins, while adsorbed oxygen species are involved in the deep oxidation.

The infrared investigation presented here permitted the detection of surface reaction intermediates which justify, from a mechanistic point of view, the differences in the selectivity to the main reaction products observed during the oxidation of 1-butene and *n*-butane on both undoped and K-doped catalysts. These results correlate with the influence of the acid–base character of the catalyst surfaces on the selectivity to oxydehydrogenation products previously proposed [2,3]. A higher interaction between adsorbed intermediates and the active sites is obtained on catalysts with acid sites (undoped VO_x/Al_2O_3) favoring the isomerization of olefins at low temperature and the deep oxidation at high reaction temperatures. In this case, alkoxide species has been observed by IR spectroscopy of adsorbed 1-butene at room temperature.

On catalysts with a basic character (K-doped VO_x/Al_2O_3) a fast desorption of adsorbed intermediates occurs favoring a high selectivity to olefins and diolefins. In this case, π-bonded allyl species has been observed by IR spectroscopy at increasing temperatures after the adsorption of 1-butene. Thus, the second H-abstraction and/or the desorption of olefinic intermediates may be considered as the selectivity-determining steps in the oxydehydrogenation of *n*-butane.

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