

The effect of potassium on the selective oxidation of *n*-butane and ethane over Al₂O₃-supported vanadia catalysts

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The catalytic properties of undoped and K-doped (K/V atomic ratio of 0.5) Al₂O₃-supported vanadia catalysts (~4.5 wt% of V₂O₅) for the oxidation of *n*-butane and ethane were studied. Isolated tetrahedral V⁵⁺ species are mainly observed in both undoped and K-doped samples. The incorporation of potassium decreases both the reducibility of surface vanadium species and the number of surface acid sites. Potassium-free vanadium catalysts show a high selectivity during the oxidative dehydrogenation (ODH) of ethane but a low selectivity during the ODH of *n*-butane. However, the presence of potassium on the vanadium catalysts strongly influences their catalytic properties, increasing the selectivity to C₄-olefins from *n*-butane and decreasing the selectivity to ethene from ethane. The role of the acid–base characteristics of catalysts on selectivity to ODH reactions is proposed.

Keywords: undoped and potassium-doped alumina-supported vanadia catalysts; oxidative dehydrogenation of ethane and *n*-butane

1. Introduction

Supported metal oxides exhibit interesting catalytic properties depending on the composition of the catalyst and on the nature of the support [1–3]. The catalytic properties of supported vanadium catalysts for the oxidative dehydrogenation of alkanes depend on the nature of support and the fed alkane [4]. While V₂O₅/γ-

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Al_2O_3 catalysts show a high selectivity during the oxidative dehydrogenation (ODH) of ethane and propane [4–6], and a poor selectivity in the ODH of *n*-butane [4,7], the opposite is true for $\text{V}_2\text{O}_5/\text{MgO}$ catalysts which can be considered as basic catalysts [4]. These results have been explained on the basis of the role played by the acid–base characteristics of catalysts on the reaction mechanism [4,7].

The influence of the presence of potassium on catalytic properties of TiO_2 -supported vanadia based catalysts has been studied [2,3,8,9]. In these cases, potassium decreases both the activity and the selectivity of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts for oxidation reactions, as well as the reducibility of surface vanadium species. However, little information on the influence of promoters on the catalytic properties for the oxidative dehydrogenation of alkanes of supported vanadium catalysts is available [10].

If the selectivity during the oxidative dehydrogenation of ethane and *n*-butane over alumina-supported vanadia catalysts is related to the acid character of catalyst, the addition of potassium on $\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts must change their catalytic properties for both oxidation reactions. Thus, the importance of the acid–base characteristics of catalysts on the selectivity to oxydehydrogenation reactions could tentatively be proposed.

2. Experimental

Alumina-supported vanadium oxide catalyst (V/AL) was prepared by “wet” impregnation of a Girdler T126 $\gamma\text{-Al}_2\text{O}_3$ ($S_{\text{BET}} = 145 \text{ m}^2 \text{ g}^{-1}$) support with an ammonium metavanadate aqueous solution (pH = 7). Potassium-doped catalyst (V + K/AL sample) was prepared under the same conditions using mixed ammonium metavanadate and potassium carbonate aqueous solution. The impregnated samples were dried at 80°C and 27 kPa and then kept at 110°C for 16 h. Finally, they were calcined in air at 600°C for 4 h. The BET surface areas of calcined V/AL and V + K/AL samples were 137 and 138 $\text{m}^2 \text{ g}^{-1}$. Chemical analysis showed an V/AL atomic ratio of 4.8/95.2 (sample V/AL) and V/K/Al atomic ratio of 3.5/2.5/94.0 (sample V + K/AL).

Diffuse reflectance (DR) spectra in the UV–visible region were obtained with a Shimadzu UV-2101 PC spectrophotometer equipped with a reflectance attachment. Temperature-programmed reduction (TPR) data were obtained in a Micromeritics apparatus. Samples of 100 mg were contacted with an H_2/Ar mixture (H_2/Ar molar ratio of 0.15 and a total flow of 50 mol min^{-1}) and heated, at a rate of 10°C min^{-1} . Infrared spectra of adsorbed pyridine were obtained in a Nicolet 710 FTIR spectrophotometer. Wafers of 10 mg cm^{-2} , mounted in a pyrex vacuum cell fitted with CaF_2 windows, were degassed at 400°C for 2 h and then cooled at room temperature. Pyridine was firstly admitted at room temperature, degassed for 1 h, and finally desorbed at 150°C.

The catalytic experiments were carried out in a fixed bed, continuous stainless steel tubular reactor, working at atmospheric pressure. 0.2–0.5 g of catalyst (0.1–

0.5 mm particle size) was 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 (200–600 cm³ min⁻¹) in order to achieve different contact times ($W/F = 2\text{--}40 \text{ g}_{\text{cat}} \text{ h mol}_{\text{C}_4}^{-1}$, referred to the fed alkane) and different alkane conversion levels. The feed consisted of a mixture of ethane/oxygen/helium or *n*-butane/oxygen/helium with a molar ratio of 4 : 8 : 76 or 5 : 20 : 75, respectively. Experiments were carried out in the 500–550°C (*n*-butane) or 500–600°C (ethane) temperature interval. Blank runs showed that under the experimental conditions used in this work the homogeneous reactions can be neglected.

3. Results and discussion

The catalytic properties for the ODH of ethane and *n*-butane are shown in tables 1 and 2, respectively. Ethene or C₄-olefins, and carbon oxides were the main reaction products observed. Cracking products (C₁–C₃ hydrocarbons) are also observed on supported vanadium catalysts, but its selectivity is lower than 2%. In the case of pure $\gamma\text{-Al}_2\text{O}_3$, the selectivity to cracking products was about 5–10%.

Alumina presents a low activity and selectivity for the ODH of ethane. Alumina-supported vanadium catalyst shows a high ethane conversion and a high selectivity to ethene. Thus, it can be proposed that surface vanadium species are selective sites in the ODH of ethane. For the oxidative dehydrogenation of *n*-butane, alumina-supported vanadium catalyst presents a higher butane conversion than pure alumina, but the selectivity to C₄-olefins is low.

The presence of potassium on vanadium catalysts decreases the catalytic activity for the oxidative dehydrogenation of both ethane and *n*-butane. However, the selectivity to the corresponding olefins on V + K/AL shows an opposite trend to the undoped sample. In addition, the presence of potassium strongly decreases the

Table 1
Oxidative dehydrogenation of ethane on alumina-supported vanadia catalysts

Sample	Temp. (°C)	X_T^a (%)	Yield ^b (%)	Selectivity (%)		
				C ₂ H ₄	CO	CO ₂
Al ₂ O ₃	600	13.1	0.96	7.3	46.0	46.7
V/AL	530	24.8	13.3	53.7	40.7	5.5
	600	60.2	24.2	40.2	50.3	9.5
V + K/AL	530	6.2	2.42	39.1	34.7	26.0
	600	20.3	8.51	41.9	33.3	24.7

^a Conversion of ethane. Weight of sample = 0.5 g; total flow = 200 cm³ min⁻¹.

^b Yield of ethene.

Table 2
Oxidative dehydrogenation of *n*-butane on alumina-supported vanadia catalysts

Sample	Temp. (°C)	X_T^a (%)	Yield ^b (%)	Selectivity ^c (%)					
				1-C ₄ ⁼	c-2-C ₄ ⁼	t-2-C ₄ ⁼	BD	CO	CO ₂
Al ₂ O ₃	500	7.1	1.90	7.4	5.4	6.6	7.4	18.6	49.7
	550	10.4	3.16	9.0	6.6	8.4	5.4	23.3	37.9
V/AL	500	23.5	5.69	6.0	5.5	6.0	6.7	37.8	36.9
	550	46.5	4.93	2.7	1.9	2.4	3.6	51.7	36.5
V + K/AL	500	7.3	3.98	22.1	11.4	11.2	9.8	9.5	34.6
	550	13.7	8.80	25.5	11.9	10.7	16.1	10.9	22.6

^a Conversion of *n*-butane. Weight of sample: 0.2 g; total flow = 600 cm³ min⁻¹.

^b Yield of oxydehydrogenated products (C₄-olefins).

^c Selectivity to 1-butene (1-C₄⁼), cis-2-butene (c-2-C₄⁼), trans-2-butene (t-2-C₄⁼), butadiene (BD) and carbon oxides (CO and CO₂).

formation of ethene from ethane (table 1) but it increases the formation of C₄-olefins from *n*-butane (table 2).

We must indicate that the 1-butene/cis-2-butene/trans-2-butene/butadiene molar ratio also changes by the presence of potassium (table 2). The higher formation of 2-butene or 1-butene + butadiene was observed during the oxidation of *n*-butane on the V/AL or on the V + K/AL samples, respectively. It can also be noticed that the cis-2-butene/trans-2-butene ratio also changes depending on the catalysts. Thus, cis-2-butene/trans-2-butene ratios of 0.7, 0.8 and 1.1 are obtained on γ -Al₂O₃, V/AL and V + K/AL, respectively.

On the other hand, pure and potassium-doped γ -Al₂O₃ free of vanadium show the same catalytic properties, indicating that the catalytic properties of vanadium-containing samples are related to the presence of vanadium species.

Fig. 1 shows the variation with the conversion of *n*-butane and ethane of the selectivity to the corresponding olefins. In all cases the selectivity to olefins decreases with the alkane conversion. At the same alkane conversion, the V/AL sample shows a higher selectivity to ethene but a low selectivity to C₄-olefins, while the K-doped sample presents an opposite trend: a high selectivity to C₄-olefins and a low selectivity to ethene.

The diffuse reflectance spectra of calcined samples in the 200–600 nm region are shown in fig. 2. We must notice that the presence of V⁴⁺ species, with characteristic bands in the 530–800 nm region [11,12], were not observed. Both the undoped and the K-doped samples show a high-intensity charge transfer band at 280 nm. According to previously reported data [11–13], this band is related to the presence of V⁵⁺-species, highly dispersed on the surface of the support, with a tetrahedral coordination. In addition, it can be concluded that the presence of potassium does not change the nature of vanadium species.

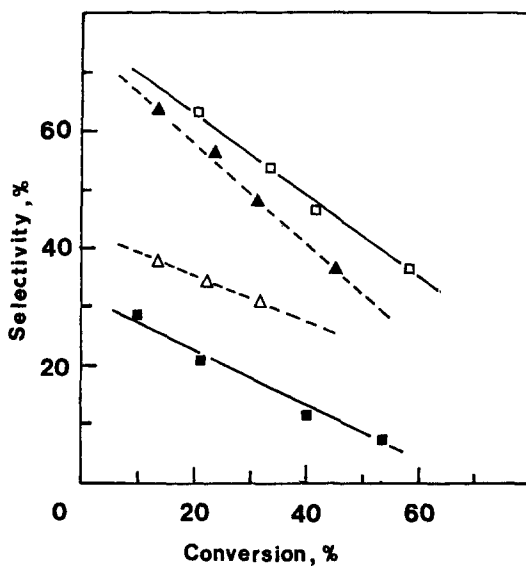


Fig. 1. Variation of the selectivity to ethene (\square , \triangle) or C_4 -olefins (\blacksquare , \blacktriangle) with the conversion of ethane (at 570°C) or *n*-butane (at 550°C), respectively. Catalysts: V/AL (\square , \blacksquare); V + K/AL (\triangle , \blacktriangle). Experimental conditions in text.

Fig. 3 shows the infrared spectra of pyridine adsorbed on $\gamma\text{-Al}_2\text{O}_3$ (fig. 3a), V/AL (fig. 3b) and V + K/AL (fig. 3c) after evacuation at 150°C . The appearance of bands at 1492 and 1596 cm^{-1} is not specific of a given population of acid sites [14].

The adsorption bands at 1445 and 1578 cm^{-1} corresponding to Lewis acid sites can be observed in Al_2O_3 and V/AL. The low intensity of these bands in the K-

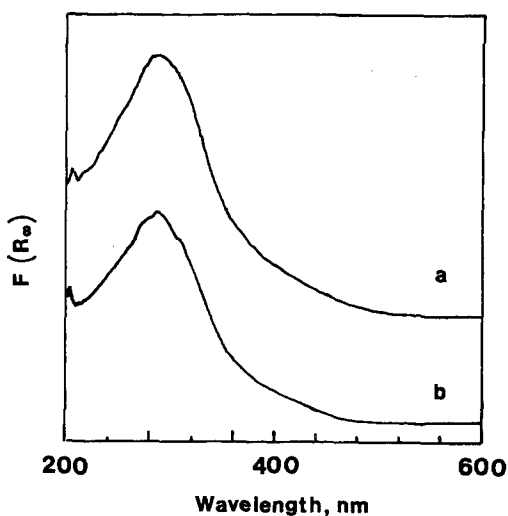


Fig. 2. UV-visible DR spectra of calcined samples: (a) V/AL, (b) V + K/AL.

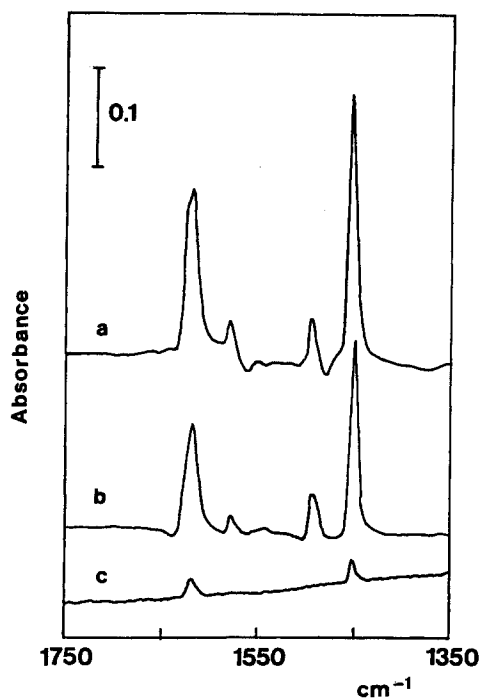


Fig. 3. FTIR spectra of adsorbed pyridine on γ - Al_2O_3 (a), V/AL (b), V + K/AL (c). Spectra were recorded after evacuation at 150°C .

doped sample indicates that the main of the surface acid sites disappear with the potassium incorporation. On the other hand, a band at 1543 cm^{-1} due to Brønsted acid sites (with a very low intensity) is observed in the V/AL sample. We must indicate that on alumina-supported vanadia catalysts the intensity of the latter band increases with the vanadium loading, indicating that the incorporation of vanadium favours the formation of Brønsted acid sites [14]. For this reason the presence of Brønsted acid sites in the V/AL sample cannot be ruled out.

TPR patterns of samples with and without potassium are shown in fig. 4. The V/AL sample shows two peaks: the first one, more intense, at 475°C ; the second one, a broad peak with a very low intensity, at temperatures higher than 600°C . These peaks correspond to surface vanadium species and bulk-like vanadia species, respectively [13]. In the case of the K-containing sample, a peak at 500°C in addition to a small peak at 385°C are related to surface vanadium species, the latter non-interacting with potassium. In addition, the broad peak at temperatures higher than 600°C observed on the K-doped catalysts can be related to the presence of bulk-like vanadia species. According to these results it can be proposed that the presence of potassium decreases the reducibility of most of the surface vanadium species. For this reason, the lower catalytic activity of the K-doped sample can be

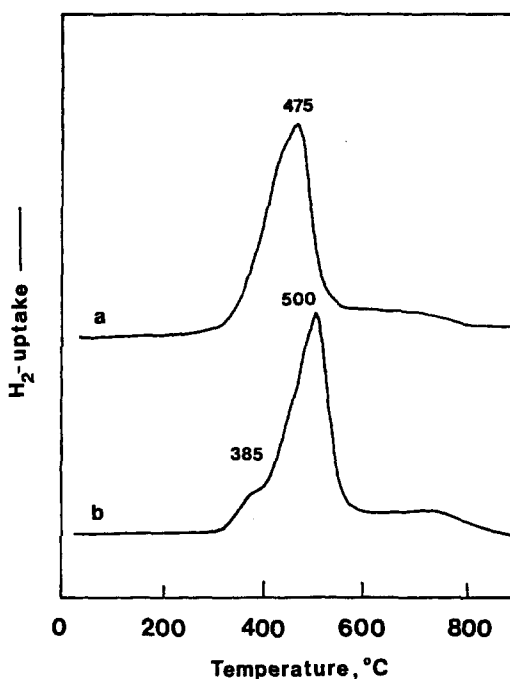


Fig. 4. TPR patterns of alumina-supported vanadia catalysts: (a) V/AL, (b) V + K/AL.

explained on the basis of the low reducibility of its redox sites. This effect has also been proposed on potassium-doped V_2O_5/TiO_2 catalysts [2,3,8,9].

It has been proposed that isolated tetrahedral V^{5+} species are the selective sites in the ODH of alkanes [4,5,7,11,12,15]. On the other hand, the different selectivity to C_4 -olefins obtained during the ODH of *n*-butane over supported vanadium catalysts has been explained on the basis of the different acid–base characteristics of catalysts: the higher the acid character the lower the selectivity to C_4 -olefins [4,5]. In this way, we must indicate that the selectivity to ethene during the oxidative dehydrogenation of ethane on vanadium containing molecular sieves is enhanced by the presence of acid sites [11,16].

The effect of potassium on V/Al_2O_3 can be explained from the fact that the acid sites of the undoped sample are not present on the K-doped sample. We must indicate that the effect of potassium in the oxidation of butane on V/Al catalysts is similar to that of cesium on silica-supported vanadium catalysts [10], but it is quite different from that observed on basic catalysts, i.e. V/MgO. In the latter case, a selective catalyst in the ODH of *n*-butane, the presence of potassium modifies the Mg-vanadate phases and decreases the selectivity to C_4 -olefins during the ODH of *n*-butane [17].

The presence of potassium on alumina-supported vanadia catalysts, and probably the presence of cesium in ref. [10], decreases both the reducibility of vanadium species and the number of surface acid sites. The lower reducibility of vanadium

species the lower the catalytic activity is, independently of the fed alkane. However, the selectivity to oxydehydrogenated products depends on both the acid–base character of catalysts and the length of the fed alkane. Catalysts with acid character favour the selective oxydehydrogenation of ethane while catalysts with basic character favour the oxydehydrogenation of *n*-butane.

On the other hand, it has been proposed that potassium in V/TiO₂ could interact with terminal V=O bonds and/or vanadium–oxygen–support bridging bonds [9], decreasing the catalytic activity of the surface vanadium oxide redox sites for oxidation reactions. From our results it is not possible to indicate the mechanism of potassium incorporation, but both of the mechanisms proposed above could operate in V₂O₅/Al₂O₃ catalyst. In this way, a more extensive study on the influence of both potassium and/or vanadium content on the selectivity to ODH reactions can optimize the catalytic properties of these catalysts.

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