Article

The Influence of the Amount and Impregnation Sequence of Potassium on the Catalytic Performance of VO$_x$/Al$_2$O$_3$ for the Non-Oxidative Dehydrogenation of n-Butane

María A. Volpe and Elba A. García*

Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, 8000-Bahia Blanca, Argentina

A dehidrogenação não-oxidativa de n-butano foi estudado usando catalisadores de vanádio suportados em alumina e potássio como promotor (a 873 K e pressão atmosfera), a fim de se explorar a influência da quantidade e da ordem de agregação do metal alcalino na atividade catalítica e seletividade de olefinas. A atividade e seletividade da dehidrogenação não-oxidativa diminuíram com o aumento da razão molar K/V. O melhor desempenho catalítico foi obtido com 1 wt.% de potássio e quando o promotor foi agregado pela primeira vez nos catalisadores de vanádio suportados em alumina. A ordem de agregação do promotor tem efeitos na atividade catalítica. Dados de TPR (redução à temperatura programada) indicam que menos espécies de vanádio são acessíveis à redução quando baixa quantidade (1 wt.%) de promotor metal alcalino foi impregnada no catalisador antes do vanádio. Após tratamento de regeneração, estes catalisadores não recuperam a plena atividade. Tendo em conta os resultados de TPR, essa desativação do catalisador pode estar relacionada com a transformação estrutural irreversível de espécies de óxido de vanádio superficiais pelo potássio.

The non-oxidative dehydrogenation of n-butane was studied over potassium-promoted supported vanadium alumina catalysts (at 823 K under atmosphere pressure) to explore the influence of the amount and the order of potassium aggregation on the catalytic activity and selectivity towards olefins. The non-oxidative dehydrogenation activity and selectivity decreased with increasing K/V molar ratio. The best catalytic performance was obtained with 1 wt.% of potassium loading and when the promoter was first aggregated in the supported vanadium alumina catalysts. The order of promoter aggregation has effects in the catalytic activity. TPR (temperature programmed reduction) data indicate that less vanadium species are accessible to the reduction when low amount (1 wt.%) of alkali metal promoter was first introduced in these samples. After regeneration treatment, these promoted catalysts did not recover the full activity. Taking in account TPR results, this catalyst deactivation may be related to the irreversible structural transformation of surface vanadium oxide species by potassium.

Keywords: non-oxidative dehydrogenation of n-butane, vanadium oxide, K promoter, TPR

Introduction

The dehydrogenation of paraffins yields olefins,[1] which are not a final product, but rather building blocks for manufacturing the most used chemical commodities. Petrochemical intermediates (propylene, butadiene, butylenes), components for the gasoline pool (methyl tertiary butyl ether (MTBE), alkylates) and for the diesel pool (high cetane diesel), are conveniently made through paraffin dehydrogenation.

The activation of alkanes is more difficult than that of the corresponding olefins, but their large reserves underline the economic interest in their conversion. The lower alkanes are the least reactive hydrocarbons, and this has preserved them over time. In addition, their low reactivity has hindered their use in industrial processes.[2]

Paraffin dehydrogenation is a strongly endothermic reaction that is limited by chemical equilibrium and, according with Le Chatelier's principle, higher conversion requires either higher temperatures or lower pressures.[3] The temperature required for the dehydrogenation of light paraffins is much higher than for heavy paraffins. For 40% conversion, the dehydrogenation of propane requires a temperature of at least about 853 K, while dodecane can be theoretically dehydrogenated to the same extent at only 723 K. The equilibrium conversion increases at higher

*e-mail: garciaea@criba.edu.ar

temperatures, but side reactions, coke formation and catalyst deactivation are also accelerated. The production of light olefins by the catalytic dehydrogenation of light paraffins must be able to maintain reasonable conversion levels and high olefin selectivity. Therefore, it is very important to produce olefins in high yields over long periods of time, and to minimize consecutive and side reactions.

There has been a strong interest to study the oxidative dehydrogenation of ethane, propane and butane because of the potential commercial interest to utilize alkane effectively. Ideally, for oxidative dehydrogenation, the formation of alkenes is the only reaction. In practice, however, non-selective oxidation to carbon oxides and other products also occurs.[4]

The huge number of works devoted to the oxidative dehydrogenation of paraffins is an indication of the scientific and industrial interest for alternatives to catalytic and thermal dehydrogenation/cracking reactions that suffer from energetic drawbacks.

Interest in the transformation of light alkanes to valuable oxygenated compounds and olefins by means of oxidation has been growing in recent years due to the possibility of developing new processes of lower environmental impact and of lower cost.[5]

Catalysis by oxides is extensively used.[2] In recent years, supported vanadium oxide catalysts have found wide commercial application as oxidation catalysts: selective oxidation of *o*-xylene to phthalic anhydride, ammoxidation of alkyl aromatics and selective catalytic reduction of NO_x with NH_3. Also, Sakurai *et al.*[6] and Vislowskiy *et al.*[7] investigated the dehydrogenation of ethylbenzene to styrene with carbon dioxide using various vanadium catalysts. In addition to these reactions, supported vanadia catalysts were also investigated for the oxidative dehydrogenation of short chain paraffins to olefins.[8]

The presence of additives affects the supported oxide. Alkaline additives tend to coordinate to acidic supported oxides (V, Mo, W, etc) by altering the M–O bonds. The additives affect the structure of the supported species since the support sites must be shared with a second component, resulting in an effective increase in the surface coverage.

The alkali doping can have the effect of increasing selectivity and activity while preventing phase transformations, inhibiting sintering and creating basic centers on the catalyst surface.[9] Abello *et al.*[10] showed a significant increase in selectivity on Mo/MgO-gAl$_2$O$_3$ with the addition of potassium.

Promoters, in particular alkali metal ions, are known to influence the redox and acid-basic properties of vanadium oxide catalysts. This is the case of Na-doped or K-doped

supported vanadia catalysts. Recently, Concepción *et al.*[11] observed that the incorporation of potassium strongly modifies the catalytic behavior of VO_x/Al_2O_3 catalysts.

Harlin *et al.*[12] studied alumina-supported vanadium oxide with and without promoters as catalysts in the oxidative dehydrogenation of n-butane. The authors reported selectivity values for this reaction to n-butenes in order of 41% for non-promoted catalysts. The modification of these catalysts with promoter caused an increase in the selectivity for dehydrogenation. The selectivity values were between 60-80%.

López Nieto *et al.*[13] observed that the reducibility of the V atoms can influence the selectivity to OXDH (oxidative dehydrogenation) products, and suggested that this could be explained by its effect on the rate of the selective redox processes involving V-species on the catalyst surface.

The aim of the present article is the attainment of the optimal K content and the better preparation method of promoted vanadium alumina catalysts for the non-oxidative catalytic dehydrogenation of n-butane to olefins, by the determination of the effective aggregation sequence between vanadium and promoter. Temperature programmed reduction (TPR) and chemical analysis were employed for the characterization of the catalysts. It was used the non-oxidative dehydrogenation of n-butane as test reaction.

Experimental

Several promoted supported vanadium alumina catalysts were prepared and investigated. A non-promoted vanadium-alumina sample was also prepared.

Commercial γ-Al$_2$O$_3$ (Rhône Poulenc, 120 m^2 g^{-1}) was used as a support. The most important reason to choose alumina as support material is its superior capability to maintain a high degree of vanadium dispersion, which is essential for achieving high dehydrogenation activity and selectivity.

The concentration of the solution was selected in order to obtain a V final concentration of 5 wt.% and the vanadium aggregate was always by grafting method from toluene solution of V(AcAc)$_3$. This vanadium loading was chosen because it is well below the loading required for full monolayer coverage of the support (12.6 wt.% V).[14] At this loading on alumina, the vanadium oxide should be well dispersed and, according with Clark *et al.*,[15] the activity of the catalyst should be near its optimum in dehydrogenation.

First, it was prepared a K free vanadium alumina catalyst. The alumina support was doped with 5 wt.% of vanadium by grafting method. It was accomplished by dissolving the necessary amount of vanadyl acetylacetonate

V(acac)$_3$ in toluene solvent. Then, the sample was filtered and washed with solvent. Finally, the sample was calcined in air at 873 K for 4 h. This catalyst was named as V5. The V concentration as determined by atomic absorption spectroscopy (AAS) was 4.8 wt.%.

Afterwards, two series of K-promoted vanadium catalysts were performed. In the first series of these promoted catalysts, the deposition of K was done over the V5 sample. V5 was treated by soak impregnation with an aqueous solution of potassium nitrate. The concentration of the potassium solutions were selected to achieve potassium loading in the range between 1 and 10 wt.%. Following 24 h of contact, the samples were dried in air at 383 K overnight and finally calcined at 873 K for 1 h. The different samples are designated by the nominal value of the corresponding element (1, 5 or 10 wt.%) and taking in account the order of aggregates. These catalysts are denoted further in the text by the symbols V5 Kx, where x = 1, 5 or 10 corresponds to K wt.%. Thus, for instance, the catalyst denoted V5 K1 contains 5 wt.% of vanadium and 1 wt.% of K as promoter. These samples were first impregnated with the vanadium solution and then with potassium solution.

Then, it was prepared a second series of catalysts, where the K promoter was first aggregated. The alkali metal promoter was introduced by adding appropriate amounts of potassium nitrate solutions to the γ-Al$_2$O$_3$ support, using the soak impregnation. The concentration of the potassium nitrate solution was selected in order to obtain a 1 or 10 wt.% concentration of the alkali metal. The samples were dried at 383 K overnight and finally calcined at 873 K for 1 h. Afterwards, they were impregnated with solution of V(AcAc)$_3$ in toluene, in which the concentration corresponds to a target loading of 5 wt.% of vanadium. Then, the material was filtered and washed with toluene. Finally, the samples were calcined in air at 873 K for 4 h. For the sample containing 1 wt.% of K, the actual V concentration was 4.9 wt.% as measured by AAS. This sample was named as K1 V5. For the sample with 10% of K, the amount of fixed V was too low (lower than 0.3 wt.%). This sample was named as

K10 V0. Chemical analyses of V and K were carried out in a Varian SpecAA-30. The chemical characteristics of the catalysts are listed in Table 1.

Temperature programmed reduction (TPR-H$_2$) was performed in an automatic equipment (Pulse Chemisorb 2705, Micromeritics) with a thermal conductivity detector. The fresh catalyst (80 mg) was submitted to a heat treatment (7 K min^{-1} up to 873 K) in a gas flow (60 ml min^{-1}) of the mixture H$_2$:Ar (10:90). Before the TPR experiments, the samples were heat treated under inert atmosphere at 673 K for 2 h to produce the decomposition of nitrate, which would lead a strong interference in the TCD (thermal conductivity detector) analysis of H$_2$.

The activity measurements were carried out at 823 K under atmospheric pressure in a quartz fixed-bed microreactor. The catalyst charge was 0.200 g. The catalyst was heated to the reaction temperature under air flow. The n-butane (Praxair, 99.9%) feed with a weight hourly space velocity (WHSV) of 4.29 h^{-1} was diluted with nitrogen (Aga, 99, 999%), being the molar ratio of nitrogen to butane 9:1. The catalytic tests were conducted at atmospheric pressure. Prior to each reaction run, the catalysts were activated *in situ* by flowing dry air at 773 K for 2 h.

The activity of the catalyst was followed for 60 min, after which the catalyst was flushed with argon and regenerated with diluted air. The analyses of reactants and products were carried out by on-line gas KoniK chromatography using a Chrom PAW 40/60 mesh capillary column and a flame ionization detector. Oxygenate products, other than carbon oxides, were not observed in this work. Blank runs showed that, under the experimental conditions used in this work, the contribution of reactions taking place in the void spaces of the reactor (homogeneous reactions) can be neglected. The amount of carbon on the support were measured by elemental analyzer.

Then, the catalyst was purged with argon at 873 K for 30 min to remove adsorbed reactant/products from the catalyst surface after the dehydrogenation reaction. The catalyst was then cooled to room temperature in a flow of argon, after which the gas flow was switched to 3% O$_2$/Ar and the catalyst was heated to 873 K at a programmed heating

Table 1. Analytical data and TPR results of all prepared samples

Catalyst	V / wt.%	K / wt.%	H$_2$ consumption / (mol g^{-1} cat.)	V / (mol g^{-1} cat.)	H$_2$/V (molar ratio)
V5	4.8	-	7.0×10^{-4}	9.4×10^{-4}	0.74
V5 K1	4.8	0.9	6.1×10^{-4}	9.4×10^{-4}	0.64
V5 K5	4.8	5.2	4.7×10^{-4}	9.4×10^{-4}	0.50
V5 K10	4.8	9.7	0.8×10^{-4}	9.4×10^{-4}	0.08
K1 V5	4.9	1.1	1.8×10^{-4}	0.9×10^{-3}	0.18

rate of 10 K min^{-1}. The temperature was maintained at 873 K until regeneration was complete.

Results

TPR data

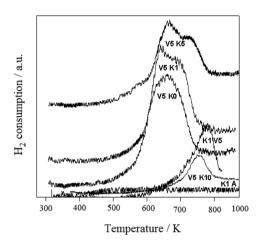The TPR profiles of all prepared catalysts are shown in Figure 1.

Figure 1. TPR profiles of promoted and non-promoted vanadium alumina catalysts.

The reduction peak temperature was taken as a measure of the reducibility of the catalytic system. The oxide support Al_2O_3 is not reduced during the reduction of the surface vanadia species in this temperature range.[8] Besides, it must be mentioned that no H_2 consumption was recorded either for K_2O or potassium alumina catalysts (K1 A).

The supported vanadium alumina catalyst spectrum reveals only one broad peak with a maximum temperature around 648 K, at vanadium loading of 5 wt.% (V5). This peak can be attributed to the reduction of a surface V-polymeric species on the alumina surface. Bond and Tahir[16] also reported the assignment of low temperature peak to surface species. The broadness of the TPR peak indicates the reduction of various surface vanadia species.

Besides Stobbe-Kreemers *et al.*[17] reported that at higher vanadium oxide loadings, vanadium oxide polymers are formed. In addition, these authors[17] within this paper showed by means of XPS (X-ray photoelectron spectroscopy) analysis that the binding energy of the vanadium atoms decreases upon increasing the vanadium oxide coverage. This decrease in binding energy is probably caused by a weakening of the vanadium-oxygen bond strength with increasing degree of polymerization of the vanadium oxide. The decrease in vanadium-oxygen bond strength is reflected in the lower reduction temperature.

On the other hand, Blasco *et al.*[18] and Deo *et al.*[19] proposed that the strength of the bridging V−O−support bond controls the reducibility and reactivity of the supported vanadium catalysts.

The TPR pattern of the V5 K1 catalyst shows a peak very similar to that of non-promoted vanadium catalysts, with a maximum temperature around 633 K. This temperature was shifted towards lower values in comparison with the non-promoted vanadium catalyst. In addition, on the high-temperature side of this peak, a new incipient signal appears as an increasing asymmetry around 693 K.

When the K content increases (V5 K5), the principal peak shifts towards higher temperature in comparison with V5 K1 catalysts and the shoulder is more evident.

It is only observed a defined reduction peak at 753 K when the K loading is 10 wt.% (sample V5 K10). This value is 100 K higher than the reduction temperature for the non-promoted vanadium catalyst.

The trend is different for the catalysts K1 V5, where the K was introduced before the vanadium content. The introduction of interacting surface additives such as K significantly retards the reduction of the surface vanadia species. In the case of K1V5 alumina supported catalysts, it clearly appeared that the peak was globally shifted towards a higher temperature range respecting the non-promoted catalysts. One might expect to observe the formation of potassium vanadate in this catalyst.

The K10 V0 sample (results not show in Figure 1, neither in Table 1) does not show any appreciable hydrogen consumption. This indicates that the low V fixed on the K-promoted alumina cannot be reduced in the 293-823 K temperature range. It could be envisaged that this sample is not active for the dehydrogenation reaction.

These TPR results reveal the potassium influence in the reduction of vanadium species. The promoter modifies the interaction between metallic species and the alumina support.

On the other hand, the order of the promoter introduction have an effect on the extent of reduction of vanadium sites. If it is compared the V5 K1 and K1 V5 samples, it can be seen that the TPR peak is minor and well-defined in the K1 V5 catalyst than in V5 K1. It is observed that the surface species in K1 V5 are more difficult to reduce than in V5 K1. Thus, the interaction between V and K oxides appears to be less intense for V K catalysts than in K V samples. The dependence of the vanadium reducibility on K content demonstrates the interaction between potassium and vanadium species.

The evaluation of the TPR patterns of these catalysts showed that the reducibility of V species is affected by the presence and amount of the promoter and besides by the order of promoter aggregation.

In conclusion, the TPR-H$_2$ data clearly reveal that potassium modifies the degree of contact interaction at the interface of vanadium and the support.

The hydrogen consumption and the H$_2$/V molar ratio are shown in Table 1.

It is observed that the hydrogen consumption diminished with the aggregation of the promoter in the supported vanadium alumina catalysts in which the potassium was introduced after the vanadium. The diminution of hydrogen consumption is related with the increase in potassium loading.

It should be also observed that the V5 K10 catalyst had the lowest value of hydrogen consumption.

The K1 V5 catalyst in which the potassium was aggregated prior to vanadium shows less hydrogen consumption than the V5 K1 sample.

Taking in account the H$_2$/V values of all prepared catalysts (Table 1), it was assumed for V5 K5 sample a reduction stoichiometry of 0.5 H$_2$/V from V^{5+} to V^{4+}. In addition, McGregor *et al.*[20] observed V^{4+} species by EPR (electron paramagnetic resonance) spectroscopy after reduction of VO$_x$ during the n-butane dehydrogenation reaction. The oxidation state of the vanadium was assumed to be +5 before reduction.

Catalysis and selectivity

The reaction test (non-oxidative n-butane dehydrogenation) was carried out in absence of diffusional influences through the choice of suitable operating variables. Before the catalytic measurements, all the samples were calcined at 823 K.

The main reaction in catalytic dehydrogenation is the formation of mono-olefins from the corresponding feed paraffin. Other secondary no desired reactions or consecutive reactions such as skeletal isomerization, cracking, oligomerization, polymerization of olefinic materials and coke formation also occurred.

Carbon oxides were the main products during the first minute on stream probably due to the reduction of vanadium oxide by n-butane. The dehydrogenated products formed were: n-butenes (1-butene, *cis*-2-butene and trans-2-butene) and 1,3-butadiene. These products were detected in the product stream later than CO and CO$_2$.

In these experimental conditions, the percentage of conversion in all catalysts was always lower than 20%.

The catalytic results obtained during the dehydrogenation of n-butane under oxygen free atmosphere at 823 K for all prepared catalysts are shown in Figure 2. The results corresponding to bare alumina K10 V0 are not reported. This sample was completely inactive for the title reaction.
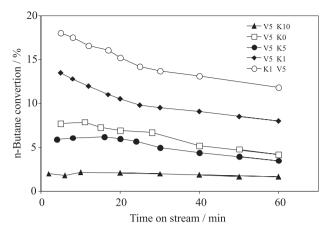

Figure 2. Variation of the conversion of n-butane *vs.* time on stream at 823 K for all prepared catalysts.

First, it is observed that, the non-oxidative n-butane dehydrogenation over V5 catalyst was low.

It was observed an improvement in the conversion of n-butane in the potassium-promoted supported vanadium alumina catalysts (K1 V5 and V5 K1) when a small amount of promoter was added. The addition of high potassium loading (V5 K10) caused a significant drop in the non-oxidative n-butane dehydrogenation.

Moreover, variations in the catalytic properties were observed with the order of promoter and vanadium aggregation (K1 V5 and V5 K1).

These results confirm the promoter effect of potassium on supported vanadium alumina catalysts for the non-oxidative dehydrogenation of n-butane at low metal loading (V5 K1).

It can be seen that the conversion of n-butane is dependent of the K loading. Results show that when the K content added to vanadium alumina catalysts is in low amount (1%), different effects are observed: (*i*) the initial conversion increases, (*ii*) the selectivity tends to increase, (*iii*) the deactivation also decreases and (*iv*) no oxygenated organic compounds were detected in these alkali-promoted vanadium catalysts.

All the catalysts lose activity during the course of the reaction and this phenomenon is more evident in K-promoted vanadium catalysts with high K loading (V5 K5 and V5 K10).

The catalyst color was black when the samples were probed in reaction. The main cause for these catalyst deactivations is the coke formation. All the samples turned inactive after 2 h of reaction.

Figure 3 shows the variation of the selectivity to total olefins with the n-butane conversion at 823 K on different catalysts.

It was observed that the alkali promoter modifies the selectivity to total olefins of these samples. Moreover, it
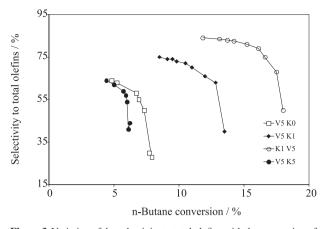
Figure 3. Variation of the selectivity to total olefins with the conversion of n-butane obtained at a reaction temperature of 823 K for all K-promoted supported vanadium alumina catalysts.

Figure 4. TPR profiles of fresh and regenerated V5 K5 catalyst.

must be noted that the selectivity increases at the same time that the conversion to n-butane decreases, for example: in catalyst V5 K1 (Figure 3), the selectivity to total olefins increases from 40.0 to 74.0% while the conversion of n-butane slightly decreases from 13.5 to 9.5%.

On the other hand, the selectivity to total olefins improves with low K loading, for example: in catalyst V5 K1, the selectivity value was 73.0% for a conversion value of 7.7% and for the same conversion value, the selectivity was minor (30.0%) in potassium free supported vanadium alumina catalyst (V5). The selectivity drops for samples with high K content (V5 K5).

The order of aggregation also affects the selectivity. For example, the catalyst K1 V5 displays a selectivity value of 84.0% to total olefins at a conversion level of 11.8%, while the catalyst V5 K1 presents 70.0% for the same conversion.

It is worth noting that the deactivation of K-promoted vanadium catalysts and the coke formation are lower than in non-promoted samples.

Spent catalysts after n-butane dehydrogenation activity evaluation were analyzed for total carbon content. The result is reported in Table 2.

Table 2. Determination of carbon in spent catalysts

Catalyst	C / (mol g^{-1} cat.)
V5 K0	21×10^{-4}
V5 K1	9×10^{-4}
V5 K5	11×10^{-4}
V5 K10	not determined
K1 V5	8×10^{-4}

Then, the spent catalysts V5 and V5 K5 were regenerated and characterized by temperature programmed reduction. Figure 4 shows only the TPR profiles of the V5 K5 catalyst that presents important reducibility changes.
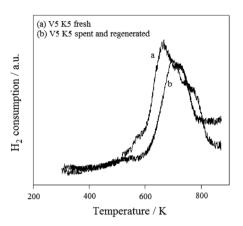
Discussion

It was made a tentative to relate the characterization study of these catalysts to the catalytic properties in order to prove useful information leading to a better understanding of the K action and the effect of promoter order aggregation in the supported vanadium alumina catalysts for the non-oxidative dehydrogenation of n-butane.

In Figure 2, it can be observed that the activity of the V5 catalyst is less than the catalysts with low K amount (K1 V5 and V5 K1). Therefore, it is worth to note that a well vanadium dispersion in these samples is not sufficient to obtain high catalytic activity. The K promoter at low loadings improves the performance of the supported vanadium alumina catalysts for the non-oxidative dehydrogenation of n-butane. The best K loading in these catalysts is 1 wt.%.

In according with Madeira et al.,[21] it was observed that the rate of n-butane conversion decreases with increasing promoter content and besides the lowest values of conversion when the promoter amount was 10 wt.%. In this last case, it is probably the existence of strong interactions between the promoter and VO_x species. The species present in this catalyst (V5 K10) are very difficult to reduce, in according with the TPR results.

Considering our TPR results, it is suggested that different surface vanadium species are responsible for the catalytic activity and the environment of the V-species plays an important role in the catalytic behavior of K-promoted supported vanadium oxide catalysts.

There remains a lack of understanding about the role played by the different surface species that are present on the supported catalysts. McGregor et al.[20] attempt to redress this through characterization of a series set of θ-Al_2O_3 supported VO_x catalysts at all stages during the direct dehydrogenation of n-butane in the absence of

gas-phase oxygen. Through the application of a number of analytical techniques, such as solid-state nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopies, they provided additional insight to the relationship between surface VO_x species and catalytic activity.

Setnička et al.[22] postulated that the highest activity and selectivity to olefins were reached on materials with high content of isolated monomeric VO_x units with tetrahedral coordination, this being generated up to 4-5 wt.% of vanadium. They studied the role of VO_x species supported on hexagonal mesoporous silica (HMS).

The surface of V5 catalysts predominantly contains polyvanadates (dimeric and polymeric chains of VO_4 units). In line with this, McGregor et al.[20] postulated that polyvanadate and crystalline vanadia are predominant on the surface of non-promoted catalysts with vanadium loadings $\geq$ 1 wt.%. Isolated vanadia species show high activity, but very low selectivity due to the undesirable formation of coke. Polymeric VO_x species, however, show a greater selectivity towards the desired C_4 dehydrogenation products.

The catalysts V5 K1 and V5 K5 contain two different vanadium species such as polyvanadates (first peak) and isolated monomeric vanadium oxide species very close to K (tailing on the high temperature side). The peak of the K1 V5 catalyst possibly corresponds to the preferably reduction of isolated monovanadates very close to K.

In V5 K10 catalyst probably contains some other kind of surface vanadium oxide species, perhaps an incipient potassium vanadate phase. Thus, this vanadium compound was well dispersed on the surface of the support with the crystalline size below the limit of detection of XRD (X-ray diffraction) method. This phenomenon was described by Chen et al.[23] as the stabilization of a new phase associating K and V. The strong interaction between V and K atoms results in the formation of mixed compounds rather than a stable surface vanadia monolayer.

Considering these results, it is postulated that the catalytic activity and the nature of surface vanadium oxide species are affected by the presence of potassium. Ramis et al.[24] proposed that potassium may replace surface protons, giving rise to V–O–K and Al–O–K linkages of different types for KA-supported vanadium catalysts. On the other hand, Klisińska et al.[25] postulated that K transfers electrons towards both V and O atoms in the active group, and does not form a definite O-K bond, but is rather "adsorbed" on the cluster.

In addition, Si-Ahmed et al.[26] showed by Raman spectroscopy that the potassium addition strongly changes the environment of V sites and forms alkali vanadates and/or

bronzes on V/TiO_2. Other authors[20,30] reported the formation of amorphous vanadates below monolayer coverage at a higher K/V atomic ratio (1:1), case for the V5 K10 catalyst, the K/V atomic ratio is 2:1.

The color of the catalysts was black when the samples were probed in reaction. In according with McGregor et al.,[20] the dark color of the catalysts is the result from both coke deposition and VO_x reduction.

The coke formation is one of the possible reasons for the catalyst deactivation. It has also been observed that the carbon deposition is the main cause of deactivation in alkane dehydrogenation catalysts. Sahoo et al.[27] proposed that the coke formation is a bi-functional reaction, requiring the dehydrogenating capacity of the metallic function and the condensation-polymerization capacity of the acidic function.

Coke may itself participate in the dehydrogenation of n-butane, as mentioned by McGregor et al.[28] Thus, the presence of coke completely modifies the scenario for the interest reaction and one could expect that the catalytic difference between K1 V5 and V5 K1 was due to a different amount of coke in each case. However, at early reaction times, when coke poisoning could be neglected, the catalytic properties of V5 K1 are different from those of K1 V5. Furthermore, following 1 h of reaction, catalysts K1 V5 and V5 K1 approximately present the same amount of coke (see Table 2). Once again, the activity and selectivity of the samples are completely different. Thus, coke would not be related with the difference in the activity and in the selectivity observed for the catalysts.

The result demonstrated that the non-promoted vanadium alumina catalyst (V5 K0) had the highest amount of carbon. It is postulated that the promoter (K) is related to the structural arrangement of the acid sites, which are the responsible for the coke formation. For this reason, although all the catalysts lose activity during the course of the reaction, this phenomenon is more evident in non-promoted vanadium catalysts and in catalysts with high K loading.

On the other hand, the regenerated catalysts (V5 and V5 K5) were analyzed. The activity of V5 catalyst was recovered, but the K-promoted catalysts show a decrease in activity respect to fresh samples. The decreases were in the order of 3-4% during the first 20 min of reaction.

Then, the TPR study of these samples was carried out. If we compare the regenerated and fresh catalyst for V5 K5 (Figure 4), it can be concluded that it is not possible to attain again the vanadium structural arrangements of the fresh promoted catalysts. In line with this, the catalytic activity of regenerated V5 K5 is lower than the fresh one. This result is in agreement with the conclusion of McGregor et al.,[20]

whom suggested that after regeneration, the catalytic activity of a non-promoted VO_x/Al_2O_3 catalysts cannot be recovered as a result of transformations to both the surface VO_x species and the pure support, with vanadium appearing to catalyze a phase transformation in Al_2O_3 above 823 K.

It can be concluded, by these TPR studies, that the presence of dopant does change the nature of vanadium species in the promoted vanadium catalysts.

Selectivity

The supported vanadium alumina catalysts are active but not selective to dehydrogenation. In the absence of gas phase oxygen, the reaction of n-butanes on calcined vanadium species can proceed through two parallel reactions: combustion of n-butane to CO and CO_2 and water, and oxidative dehydrogenation to butenes and water.

Low values of selectivity to total olefins were observed for V5 catalyst (Figure 3). In addition, the catalyst rapidly deactivates due to fouling by heavy carbonaceous materials. Therefore, the properties of vanadia need to be modified to suppress the formation of by-products and to increase the olefin selectivity.

One explication for these results is that the carbon oxides were the main products formed during the first minute on stream. This is probably due to the reduction of vanadium oxide by n-butane. It is possibly that the reduction of the oxidized surface vanadium species is responsible for the rather low selectivities towards alkenes in the beginning of the dehydrogenation reaction. In addition, Le Bars et al.[29] suggested that the better selectivity seems to be a characteristic of the reduced surface.

It is mentioned in the literature[10,25,30] that K alkali doping can have the effect of increasing selectivity. The selectivity to total olefins improves with the low promoter aggregation: V5 K1 and K1 V5 (Figure 4). Both catalysts, K1 V5 and V5 K1 show relatively high selectivity values, mainly at low conversion values. However, K1 V5 is more selective than V5 K1 if comparisons are performed at the same level of conversion (Figure 3). The origin of the higher selectivity of the former sample should be related to a beneficial distribution of V species due to K presence. This "selective" distribution is attained when V is added to K/Al_2O_3, but not when K is added to VO_x/Al_2O_3. In the context of the present results, it is not possible to further describe this "selective" K-VO_x surface (in K1 V5) and the reason for the fact the sequence of the addition of K and VO_x is of paramount importance for creating the "selective" distribution of species. However, the catalytic results unambiguously indicate that a quite different distribution of V species is present in K1 V5 and in V5 K1.

On the other hand, a diminution of selectivity to total n-olefins occurred with the high promoter content V5 K5 (Figure 3). The best selectivity to total olefins was obtained with the K1 V5 catalyst in which the promoter was first aggregated.

It is not been completely clarified yet how the alkali metal affects the alkene selectivity. However, one could conclude that the differences in dehydrogenation selectivity are related with the different alumina coverage and vanadium environment. It is suggested that the uncovered alumina, along with Brønsted acid groups of the vanadium oxide layer, was involved in the formation of total oxidation products (secondary reactions). Moreover, the formation of oxygen-containing products would be facilitated if the adsorbed alkene could interact with the vanadium ions in two adjacent VO_x units.

It is postulated that the introduction of dopant before vanadium could facilitate the structural changes in the alumina active sites for vanadium chemical anchoring.

It is possible that the promoter changes the distance between vanadium units (VO_x) and diminishes the non-desirable secondary reaction and thus, improves the selectivity to total olefins. This is in according with Grabowski et al.,[30] whom postulated that the alkaline promoters favor the basicity of these catalysts and hence, facilitate the desorption of unsaturated C_4 hydrocarbons from the catalyst surface, preventing them from further oxidation to carbon oxides.

The order of promoter aggregates influences the different selectivity to total olefin values: for example, it was observe for the catalyst K1 V5 a selectivity value of 82.0% for a 13.5% of n-butane conversion and a selectivity of 40.0% for the same conversion value for V5 K1 catalyst.

From a structural point of view, it is postulated that the difference of selectivity between V5 K1 and K1 V5 catalysts can be attributed to the different arrangements of vanadium oxide species.

The selectivity to total olefins in promoted vanadium catalysts strongly depends on the presence of modifiers, and to a lesser extent, the order of promoter aggregation.

It seems that only lower levels of alkali metals, homogeneously distributed on the catalyst surface prior to vanadium loading, giving the better value of olefins selectivity.

Conclusions

The nature of surface vanadium oxide species in alumina supported catalyst is affected by the presence of potassium. This is evident in the reducibility of the catalysts. It was observed a lower reducibility of vanadium species when

the potassium was first aggregated, or when the potassium was anchored at higher loadings after vanadium deposition.

The drop in the non-oxidative dehydrogenation conversion observed at higher potassium loadings could be attributed to the presence of aggregates on the surface of the catalyst. Perhaps, these surface structures correspond to some kind of incipient amorphous potassium vanadate. No crystalline phases of vanadium or potassium can be detected, within the technical sensitiveness.

The results presented herein seem to indicate that the optimum loading of K for these supported vanadium alumina catalysts is 1 wt.%. Thus, a higher dispersion of the vanadium species with this potassium amount was obtained.

This regeneration treatment is not sufficient to recover the catalytic activity in K-promoted catalysts. TPR data of spent and regenerated promoted catalysts indicate irreversible structural changes in the vanadium oxide speciation.

Summarizing, it is postulated that in these promoted vanadium catalysts, the order of potassium aggregates influences the catalytic activity and selectivity to total olefins. The efficiency of the catalyst can be markedly increased by promoting it with small amounts of additive. However, the extent of enhancement depends on the composition of the catalyst and, to a lesser extent, the order of aggregation. The combined effect of these two parameters determines an optimum catalyst for production of olefins.

References

1. Sanfilippo, D.; *Cattech* **2000**, *4*, 56.

2. Bañares, M. A.; *Catal. Today* **1999**, *51*, 319.

3. Bhasin, M. M.; McCain, J. H.; Vora, B. V.; Imai, T.; Pujadó, P. R.; *Appl. Catal., A* **2001**, *221*, 397.

4. Kung, H. H.; Kung, M. C.; *Appl. Catal., A* **1997**, *157*, 105.

5. Cavani, F.; Trifirò, F.; *Catal. Today* **1999**, *51*, 561.

6. Sakurai, Y.; Suzaki, T.; Ikenaga, N.; Suzuki, T.; *Appl. Catal., A* **2000**, *192*, 281.

7. Vislowskiy, V. P.; Chang, J. S.; Park, M. S.; Park, S. E.; *Catal. Commun.* **2002**, *3*, 227.

8. Wachs, I. E.; Weckhuysen, B. M.; *Appl. Catal., A* **1997**, *157*, 67.

9. Watson, R. B.; Ozkan, U. S.; *J. Catal.* **2000**, *191*, 12.

10. Abello, M. C.; Gomez, M. F.; Cadus, I. F.; *Catal. Lett.* **1998**, *53*, 185.

11. Concepción, P.; Kuba, S.; Knözinger, H.; Solsona, B.; López Nieto, J. M.; *Stud. Surf. Sci Catal.* **2000**, *130*, 767.

12. Harlin, M. E.; Nieme, V. M.; Krause, A. O. I.; *J. Catal.* **2000**, *195*, 67.

13. López Nieto, J. M.; Soler, J.; Concepción, P.; Herguido, J.; Menéndez, M.; Santamaría, J.; *J. Catal.* **1999**, *185*, 324.

14. Eberhardt, M. A.; Proctor, A.; Houalla, M.; Hercules, D. M.; *J. Catal.* **1996**, *160*, 27.

15. Clark, D. M.; Tromp, P. J. J.; Arnoldy, P.; US pat. 5,220,092 **1993**.

16. Bond, G. C.; Tahir, S. F.; *Appl. Catal.* **1991**, *71*, 1.

17. Stobbe-Kreemers, A. W.; van Leerdam, G. C.; Jacobs, J. P.; Brongersma, H. H.; Scholten, J. J. F.; *J. Catal.* **1995**, *152*, 130.

18. Blasco, T.; López Nieto, J. M.; Dejoz, A.; Vázquez, M. I.; *J. Catal.* **1995**, *157*, 271.

19. Deo, G.; Wachs, J. E.; *J. Catal.* **1991**, *129*, 307.

20. McGregor, J.; Huang, Z.; Shiko, G.; Gladden, L. F.; Stein, R. S.; Duer, M. J.; Wu, Z.; Stair, P. C.; Rugmini, S.; Jackson, S. D.; *Catal. Today* **2009**, *142*, 143.

21. Madeira, L. M.; Martín-Aranda, R. M.; Maldonado-Hódar, F. J.; Fierro, J. L. G.; Portela, M. F.; *J. Catal.* **1997**, *169*, 469.

22. Setnička, M.; Bulánek, R.; Čapek, L.; Čičmanec, P.; *J. Mol. Catal., A: Chem.* **2011**, *344*, 1.

23. Ching-Shium Chen; Wu-Hsun Cheng; Shou-Shium Lin; *Appl. Catal., A* **2002**, *238*, 55.

24. Ramis, G.; Busca, G.; Bregani, F.; *Catal. Lett.* **1993**, *18*, 229.

25. Klisińska, A.; Haras, A.; Samson, K.; Witko, M.; Grzybowska, B.; *J. Mol. Catal., A: Chem.* **2004**, *210*, 87.

26. Si-Ahmed, H.; Calatayud, M.; Minot, C.; Lozano Diz, E.; Lewandowska, A. E.; Bañares, M. A.; *Catal. Today* **2007**, *126*, 96.

27. Sahoo, S. K.; Rao, P. V. C.; Rajeshwer, D.; Krishnamurthy, K. R.; Singh, I. D.; *Appl. Catal., A* **2003**, *244*, 311.

28. McGregor, J.; Huang, Z.; Parrot, E. P. J.; Zeitler, J. A.; Lien Nguyen, K.; Rawson, J. M.; Carley, A.; Hansen, T. W.; Tessonnier, J. P.; Sheng Su, D.; Teschner, D.; Vass, E. M.; Knop-Gericke, A.; Schlögl, R.; Gladden, L. F.; *J. Catal.* **2010**, *269*, 329.

29. Le Bars, J.; Védrine, J. C.; Auroux, A.; Pommier, B.; Pajonk, G. M.; *J. Phys. Chem.* **1992**, *96*, 2217.

30. Grabowski, R.; Grzybowska, B.; Samson, K.; Sloczyński, J.; Stoch, J.; Wcislo, K.; *Appl. Catal., A* **1995**, *125*, 129.