ELSEVIER

Chemical Engineering Journal 95 (2003) 37–45

Chemical Engineering Journal
www.elsevier.com/locate/cej

Improvement of catalytic functions of binary V-Sb oxide catalysts for oxidative conversion of isobutane to isobutene

V.P. Vislovskiy[a,d], N.T. Shamilov[a], A.M. Sardarly[a], V.Yu. Bychkov[b], M.Yu. Sinev[b], P. Ruiz[c], R.X. Valenzuela[d], V. Cortés Corberán[d,*]

[a] *Institute of Inorganic and Physical Chemistry, Azerbaijan National Academy of Sciences, 29 H. Javid Avenue, 370143 Baku, Azerbaijan*
[b] *Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin Street, 117334 Moscow, Russia*
[c] *Unité de Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain, Place Croix du Sud, 2/17 B-1348 Louvain-la-Neuve, Belgium*
[d] *Instituto de Catalisis y Petroleoquimica, CSIC, Campus UAM, Cantoblanco, 28049 Madrid, Spain*

Received 18 November 2002; accepted 1 March 2003

Abstract

Dehydrogenation of isobutane in the presence of oxygen—industrially prospective process for isobutene production—has been studied over vanadium-antimony oxide catalysts. Their catalytic behaviour was compared with the sample characterisation data by specific surface area (SSA), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Substantial improvement of the catalytic performance has been achieved as a result of proper spreading of active V-containing component onto an appropriate support. Optimisation of the composition and loading of the active component, the chemical nature and morphology of support material, as well as the preparation procedure allowed to further improve the yield of isobutene. Microspheric γ-alumina with moderate SSA and large average pore diameter was found to be the best support for the efficient catalyst. The loading of vanadia corresponding to 1–1.5 formal monolayer coverage and doping with antimony (V-to-Sb atomic ratio 8.8) were found to be optimal.

The use of “citrate” preparation technique showed an advantage in comparison with ordinary impregnation method, giving the catalyst with well dispersed (amorphous) and homogeneously distributed supported V-Sb-O-component. The optimised catalyst demonstrated improved stability, high activity and olefin selectivity (70% at 36% conversion), producing yields of isobutene (up to 26% per pass) among the best reported in the literature.

Keywords: Isobutane; Oxidative dehydrogenation; Isobutene; Vanadium-antimony oxide bulk and supported catalysts; Active component composition; Catalyst preparation methods; Catalyst characterisation; Optimisation; Catalytic stability, activity and selectivity

1. Introduction

The demand of light olefins, and of products made from them, is increasing steadily and the present capacity might become insufficient to meet this demand. This is specially the case for isobutene, which is the most versatile chemical intermediate among all C_4 olefins. Its current industrial uses include those as a monomer for polyisobutene, butyl rubber and polybutene, and as a feedstock for the production of methylacrylate and other chemicals. Although the use of isobutene to produce methyl-*tert*-butyl ether in large amounts for reformulated gasoline is now under question, the use of heavier ethers on the basis of isobutene in the future is possible.

Now isobutene is produced commercially by the isobutane dehydrogenation process over chromia-alumina catalyst [1]. As of late 2000, a total of eight Catofin™ units exist for the production of isobutene (including two converted from older Catadiene™ units) with an aggregate capacity of about 2.8 million metric tons per annum isobutene. During the 1990s, a large-scale fluid-bed isobutane dehydrogenation unit for about 450,000 metric tonnes per annum isobutene was commercialised by Snamprogetti in Saudi Arabia based on the technology from Yarsintez in Russia. The process of dehydrogenation is, however, thermodynamically limited and very energy-consuming.

Oxidative dehydrogenation (ODH) of isobutane attracts an attention as a potential alternative process for isobutene production due to the using of oxygen as an oxidant displaces the dehydrogenation equilibrium thus making the process exothermic. This approach has been used commercially in the catalytic dehydrogenation of ethylbenzene to styrene but

---

* Corresponding author. Tel.: +34-91-585-4783; fax: +34-91-585-4760.
E-mail address: vcortes@icp.csic.es (V. Cortés Corberán).

1385-8947/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1385-8947(03)00081-0

to date has not succeeded in the dehydrogenation of light or heavy paraffins [1].

Although a large number of studies of light alkanes ODH over different types of catalysts is available [1–13], studies of ODH of isobutane to isobutene have only recently been reported, and their number is negligible as compared to other ODH reactions. It is no mere chance that the latest review paper in the field of production of C_4 olefins by the ODH of paraffins [11] limits itself only to the reaction of *n*-butane.

Several types of catalysts have been reported in the literature to be selective in the isobutane ODH. The most intensively studied ones include noble metal-based catalysts [14], metal phosphates [15,16] and those based on reducible transition metal oxides: molybdenum-based catalysts [17,18], heteropolyacids (molybdophosphoric acid, containing vanadium or not, and tungstophosphoric acids with the Wells–Dawson structure) [19,20], and chromia-based catalysts [21–23] including Cr-V-Nb mixed oxides [24].

Vanadium oxide-based catalysts have been much less investigated in the isobutane ODH, and practically all the relevant results on these systems are presented below.

Hoang et al. [25] studied the catalytic performance of supported transition metal oxides in this reaction at low temperatures and isobutane conversions, and have shown that vanadia-alumina catalyst (as well as almost all studied systems) exhibits much lower selectivity to isobutene (15%) in comparison to chromia-alumina (55%). It should be noted that, preparation methods used for these catalysts were substantially different due to the lack of an appropriate vanadium precursor. Vanadium-containing MCM-41 mesoporous catalysts have been investigated for the isobutane partial oxidation reactions [26–28] and olefin selectivity ca. 50% was achieved at isobutane conversions 10–15%. Zhang et al. [28] have shown that selectivity to isobutene strongly depends on the catalyst preparation method. Catalyst synthesised by direct hydrothermal method gave ∼50% selectivity to isobutene plus 20% selectivity to methacrolein, whereas over the sample prepared by template ion-exchange method the corresponding values were lower than 12 and 3%, respectively. Over VZSM-48 catalyst, olefin selectivity was 60% at 28% isobutane conversion [29].

Some particular examples dealing with isobutane were also published in a few papers and patents mainly devoted to the ODH of other light paraffins [2,30–32]. It is noteworthy that lowest selectivity was obtained in the production of isobutene, which has two allylic hydrogen positions susceptible to oxygen insertion, resulting in the formation of co-products such as aldehydes, ketones and acids along with the olefin. These may be precursors for the formation of carbon oxides, especially when relatively severe reaction conditions are needed to activate the paraffin [2]. C–C bond breaking, leading to cracking products, is easier in isobutane than in propane [30].

V-Sb complex oxides (either as bulk or supported catalytic systems with excess of antimony) are well known as highly efficient catalysts for the prospective industrial process of ammoxidation of propane to acrylonitrile [6,33–36], partial oxidation of toluene [37,38] and of H_2S [39], as well as for selective reduction of NO with ammonia [40]. Shishido et al. [41] mention that $V_1Sb_{10}O_x$ mixed oxide is active in ODH of isobutane to isobutene; however, this subject was not studied in more detail as the authors were focused on the methacrolein formation over Mo-V-Sb oxide systems.

The role of antimony and the effect of V/Sb ratio and coverage of the support with V + Sb oxide component have been studied repeatedly, but only in the ammoxidation of propane (including propane ODH occuring in the course this reaction) [33,34,36,42] and the partial oxidation of toluene [38]. V-Sb oxide catalysts with an excess of vanadia are highly active for propane ODH, while the excess of Sb allows these catalysts to be more selective to acrylonitrile at the expense of propene selectivity [33]. In the case of partial oxidation of toluene to benzaldehyde the Sb-containing sites are believed to carry the function of oxygen insertion into the hydrocarbon molecule [38].

Summarising, isobutane ODH in the presence of vanadium oxide-based catalysts has not been studied systematically, likely due to the non-satisfactory olefin selectivity obtained over V-containing oxide catalysts in the conditions previously used.

Recently, we have shown [43] that Sb-promoted vanadium oxide-based systems supported on alumina are rather active and selective in oxidative conversion of isobutane to isobutene. In this paper we describe our attempt to optimise the catalytic functions of supported V-Sb oxide systems in this industrially important reaction, by means of variation of their quantitative composition, selection of the most appropriate catalyst support and using the more effective catalyst preparation method. The relationship between catalytic performance and structural features of systems under study is analysed using the data obtained by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and surface area measurements.

2. Experimental

2.1. Catalyst preparation

2.1.1. Materials

Ammonium metavanadate (Merck) and antimony(III) chloride (Aldrich) were used as starting materials for preparation of V-Sb oxide catalysts. Nine different supports were used. Among them, four types of Aldrich γ-aluminas with different trade marks, say: “acidic” (a) (Aldrich 19,996-6), “weakly acidic” (wa) (Aldrich 26,774-0), “neutral” (n) (Aldrich 19,997-4) and “basic” (b) (Aldrich 19,944-3). They have very similar textural characteristics: specific surface area (SSA) 150–180 m^2/g, pore volume (V_p) 0.23 ml/g, average pore diameter (D_p) 58 Å and particle size 0.1 mm. They are XRD-amorphous and differ only in surface Na content which varied (according to the XPS data) from 0.15 at.% for γ-Al_2O_3 (a) to 0.6 at.% for γ-Al_2O_3 (b). The microspheric alumina (0.3–0.8 mm particle size, SSA = 85 m^2/g, V_p = 0.37 ml/g and D_p = 175 Å) from Katalizator Co. (Novosibirsk, Russia), further denoted as γ-Al_2O_3 (ms), was also found to be almost XRD-amorphous (traces of corundum were found). The corundum, α-Al_2O_3, from Catalyst and Chemical Europe, S.A., had SSA = 35 m^2/g, V_p = 0.22 ml/g and D_p = 190 Å. Silica-alumina (SiO_2/Al_2O_3 = 9.5) (Aldrich 34,335-8) had high SSA = 468 m^2/g and V_p = 0.67 ml/g. Silica gel (Aldrich 24,398-1) had V_p = 1.21 ml/g, D_p = 150 Å and SSA = 290 m^2/g. Both silica-containing supports were XRD-amorphous, whereas magnesium oxide (Jansenn 22,25340) (SSA = 33 m^2/g, V_p = 0.18 ml/g) was a mixture of two crystalline phases—periclase (cubic MgO) and brucite, $Mg(OH)_2$.

2.1.2. *Preparation methods*

"Citrate" (c) [44] and conventional co-precipitation (cp) (for bulk systems), as well as impregnation (i) (for supported oxides) methods have been used for catalyst preparation.

In the former, aqueous solutions of citric acid monohydrate, $C_6H_8O_7\cdot H_2O$ (Merck) were added to each of the transparent aqueous solutions of NH_4VO_3 and $SbCl_3$ (the latter was acidified with the solution of HCl) containing the needed amounts of the cations so as to reach 1.1 equivalent-gram of acid function per valence-gram of the cations. Then these solutions were mixed, evaporated at 40 °C under reduced pressure to form a syrup-like liquid, and dried in a vacuum oven at 80 °C for 24 h. The obtained solid precursor was decomposed at 300 °C for 16 h and calcined at 550 °C for 8 h to form the final bulk catalyst.

For preparation of the supported samples, the corresponding support was impregnated during 2 h at room temperature with the above-mentioned mixed solution; all subsequent operations were the same.

When conventional co-precipitation and impregnation methods have been used, the same starting aqueous salts solutions were obtained without citric acid. All subsequent operations were the same.

2.2. *Catalytic activity tests*

The catalytic tests were performed under atmospheric pressure in a continuous system. A fixed bed, straight down-flow tubular quartz reactor (i.d. 15 mm) was used. Quartz chips were placed above and below the catalyst bed to reduce the reactor void volume and to avoid the homogeneous reactions in free gas space. In the absence of catalyst, the reactor completely filled with quartz chips showed a very small activity when tested under the reaction conditions used in catalytic tests: isobutane conversion reached only ∼1% at 550 °C and ∼3% at 600 °C. Nevertheless, in the presence of catalysts the contribution of heterogeneously-initiated, homogeneous reactions cannot be excluded [45].

The temperature of the catalyst bed (typically 550 °C) was monitored by a thermocouple placed in a coaxial thermo-well in the centre of the bed. The gas mixture (20 vol.% isobutane; 10 vol.% oxygen; balance: nitrogen) was fed into the reactor at a total flow of 1 cm^3/s and contact time (τ) of 4 s. In these conditions, we were able to obtain considerable alkane conversions, high olefin selectivities and acceptable catalyst productivities. Safety requirements, very important for the industrial process, were also taken into account: relatively low initial oxygen concentration and high oxygen conversions produced practically oxygen-free, i.e. explosion safe, outlet reaction mixture. Measurements were made after 1 h on stream once the desired reaction temperature was reached. A typical run lasted for about 4–6 h. On-line GC analysis of the reaction mixture was carried out using packed chromatographic columns (heptadecane-impregnated diatomite to separate CO_2, C_2–C_4 hydrocarbons and molecular sieve NaX for O_2, N_2, CH_4, CO), and TC detector. Conversion of isobutane (X), yield of isobutene (Y) and olefin selectivity (OS) are expressed as mol%.

2.3. *Catalyst characterisation*

Specific surface area measurements were performed on a Micrometrics Flow Sorb II 2300 instrument by adsorption of N_2 at liquid nitrogen temperature on the surface of samples previously outgassed at 150 °C for 1 h.

XRD patterns were obtained with a high resolution X-ray Kristalloflex 805 (Siemens) diffractometer equipped with a Siemens D-5000 detector using Ni-filtered Cu Kα-radiation. The powdered samples were analysed without any pre-treatment after deposition on a quartz single crystal sample holder.

XPS analysis was performed with an SSX-100 model 206 X-ray photoelectron spectrometer from Surface Science Instruments. Monochromatic X-rays produced by an aluminium anode (Al Kα = 1487.6 eV) were focused on an area of around 1.4 mm^2. The pressed powder samples were placed into small troughs. The binding energy (BE) values were referred to the adventitious C 1s peak at 284.8 eV. The intensities were estimated by calculating the integral of each peak after subtraction of the "S-shaped" background. Atomic concentration (AC) ratios were calculated by correcting the intensity ratios with the theoretical sensitivity factors based on Scofield cross-sections.

3. Results and discussion

3.1. *Bulk vanadium-antimony oxides*

The results of catalytic testing of bulk binary V-Sb-O samples of different composition prepared by "citrate" (c) and co-precipitation (cp) methods are given in Table 1.

Table 1
Catalytic properties of bulk V-Sb-O systems prepared by citrate (c) and co-precipitation (cp) methods in the ODH of isobutane

Catalyst V/(V + Sb) ratio (at.%)	SSA (m^2/g)	iC_4H_{10} conversion, X (%)	Selectivity (%)			iC_4H_8 yield, Y (%)
			iC_4H_8	C_1–C_3	Co_x	
44 (cp)	8.1	11.5	11.6	6.6	81.8	1.3
50 (cp)	4.2	12.6	11.7	5.6	82.7	1.5
50 (c)	16.9	14.3	12.0	7.2	80.8	1.7
90 (cp)	1.3	12.9	12.0	5.4	82.6	1.5
90 (c)	7.0	12.7	11.0	6.1	82.9	1.4

Reaction conditions: 550 °C, $P^0_{iC_4H_{10}} = 20\,kPa$, $P^0_{O_2} = 10\,kPa$, $\tau = 4\,s$, time-on-stream 2.5 h.

Irrespectively of their composition, SSA and preparation method, all studied binary V-Sb oxide systems have very poor efficiency in target reaction: isobutene yield (Y) does not exceed 1.7% with olefin selectivity (OS) around 12%. In spite of the higher SSA obtained, the samples prepared by the "citrate" method showed similar performances that their co-precipitated homologues, which implies them to show a lower area-specific rate. From this point of view, the most active catalyst was the one prepared by co-precipitation with an atomic ratio V/Sb = 8.8.

According to our XRD data [43], the main phase of the fresh catalyst with V/Sb = 1 is the mixed vanadium-antimony oxide $V_{1.1}Sb_{0.9}O_4$; the phase V_2O_5 (shcherbinaite) is present in this sample in lesser amount. In the V-rich V-Sb-O fresh sample (V/Sb = 8.8), V_2O_5 is the predominant phase and $V_{1.1}Sb_{0.9}O_4$ is the minor one. XRD patterns and laser Raman spectra [43] show that bulk V-Sb oxides retain their crystallinity after catalytic tests.

XPS measurements indicate that Sb $3d_{3/2}$ BE value remains almost the same after catalytic runs (540.1 for fresh and 539.9 eV for used samples—see Table 2). This means that antimony is present on the surface of the fresh V-Sb oxide sample in the high oxidation state which does not change significantly after catalysis [46]. On the contrary, in comparison with 517.2–517.6 eV for reference V^{5+}compounds [46,47], BE value for V $2p_{3/2}$ (516.7 eV) shows that vanadium is partially reduced already in the fresh sample and it undergoes a further considerable reduction under reaction conditions: the apparent BE value of V $2p_{3/2}$ XPS peak shifts to 516.1 eV and its full width at half maximum (FWHM) increases. The XPS measured surface vanadium-to-antimony atomic ratios (calculated as V $2p_{3/2}$ AC/Sb $3d_{3/2}$ AC) are four times lower (V/Sb $\sim$ 2.2 for both fresh and used catalysts) than the nominal ratio (V/Sb = 8.8, as prepared). It means that the surface of bulk binary V-Sb-O systems is strongly enriched with antimony.

3.2. Supported V and V-Sb oxide systems

3.2.1. Optimisation of V-loading

On the preliminary stage of the study we have found that increasing of the V-loading in VO_x/Al_2O_3 systems in the range of 0–15 wt.% formal V_2O_5 (Fig. 1) increases the formation of isobutene. Relatively high V_2O_5 content (between 9 and 17.7 wt.%) is favourable for the achievement of high hydrocarbon conversion (X) and olefin selectivity (OS). This loading is equivalent to 0.8–1.7 formal monolayer coverage estimated according to [48]. Both X and OS decrease slightly with V_2O_5-loadings beyond 17.7 wt.%. It is necessary to mention that the activity of VO_x/Al_2O_3 systems decreased considerably with time-on-stream during the catalytic tests. This was due to coke formation, as evidenced

Table 2
Surface and catalytic properties in isobutane ODH of fresh (f) and used (u) bulk and alumina-supported V-Sb-O catalysts (nominal atomic ratio V/Sb = 8.8) prepared by citrate (c) and impregnation (i) methods

Catalyst	SSA (m^2/g)	Binding energy (eV)		XPS V/Sb ratio	iC_4H_{10} conversion, X (%)	Selectivity (%)			iC_4H_8 yield, Y (%)
		V $2p_{3/2}$	Sb $3d_{3/2}$			iC_4H_8	C_1–C_3	CO_x	
Bulk (*c*)									
f	7.0	516.7	540.1	2.2	12.7	11.0	6.1	82.9	1.4
u	13.4	516.1	539.9	2.2	–	–	–	–	–
Supported (*i*)									
f	84.7	517.3	540.3	4.1	29.0	64.8	2.7	32.5	18.8
u	81.1	517.0	540.2	4.7	–	–	–	–	–
Supported (*c*)									
f	69.2	517.2	540.1	8.4	36.5	70.2	6.2	23.6	25.6
u	65.0	517.3	540.1	8.8	–	–	–	–	–

Reaction conditions: 550 °C, $P^0_{iC_4H_{10}} = 20\,kPa$, $P^0_{O_2} = 10\,kPa$, $\tau = 4\,s$, time-on-stream 2.5 h.

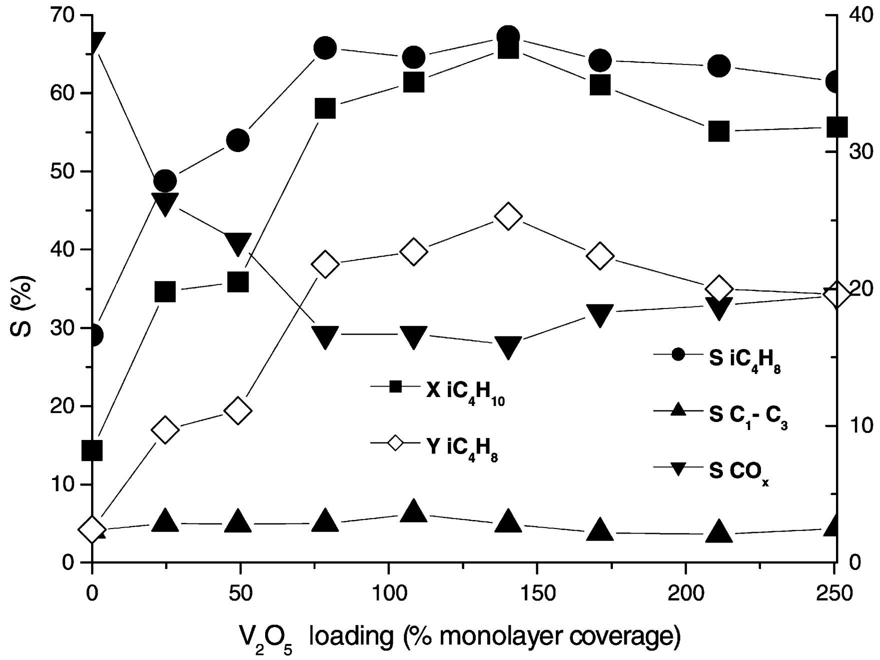

Fig. 1. Effect of alumina surface coverage with vanadia on conversion of isobutane (*X*), yield of isobutene (*Y*) and selectivities to products (*S*) in the ODH of isobutane. Reaction conditions: 550 °C, $P^0_{iC_4H_{10}} = 20$ kPa, $P^0_{O_2} = 10$ kPa, $\tau = 4$ s, time-on-stream 1 h.

by the intense CO_x evolution during catalyst reoxidation by air pulses at 550 °C [43]. So, despite of relatively high efficiency in the initial period (typically, OS ~ 64–66% at $X \sim$ 35–37% after 1 h on stream), these catalysts require a substantial further improvement.

3.2.2. Optimisation of active component composition and catalyst preparation method

A preliminary screening of a large number of alumina-supported V-containing catalysts with different oxide additives [49] revealed that the presence of antimony oxide stabilises their catalytic performances for at least 10–15 h and kept the OS practically unchanged (Fig. 2) [43]. This reduction of the activity loss is due to the efficient hampering of coke formation: much lower amounts of CO_x evolved in reoxidation experiments with spent Sb-modified catalyst than with unmodified catalyst. For this reason, we concentrated on the optimisation of the supported V-Sb-O catalytic systems.

The effect of the variation of the relative vanadium content (V/(V + Sb)) in the binary V-Sb oxide system (including the single Sb and V oxides) supported on γ-Al_2O_3

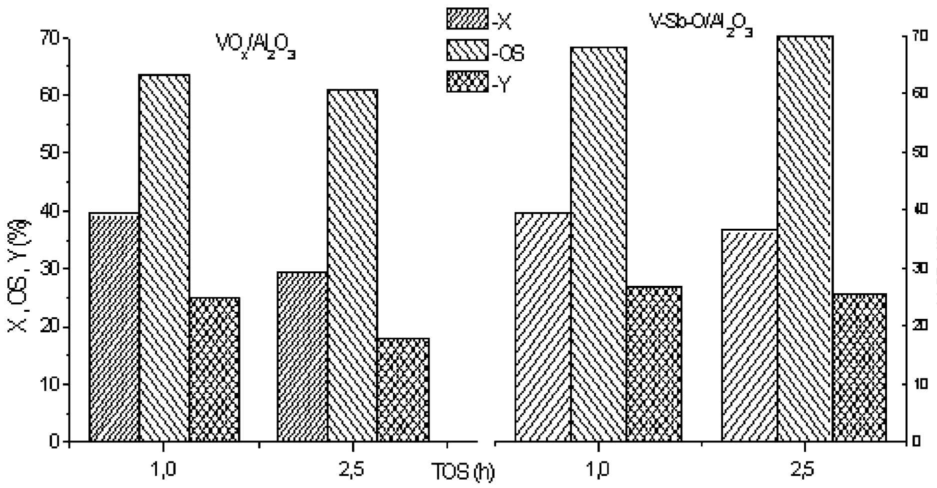

Fig. 2. Catalytic performance of alumina-supported VO_x (15 wt.% formal V_2O_5) and V-Sb-O (15 wt.% formal V_2O_5+2.7 wt.% formal Sb_2O_3; V/Sb = 8.8) in the oxidative conversion of isobutane. Reaction conditions: 550 °C, $P^0_{iC_4H_{10}} = 20$ kPa, $P^0_{O_2} = 10$ kPa, $\tau = 4$ s.

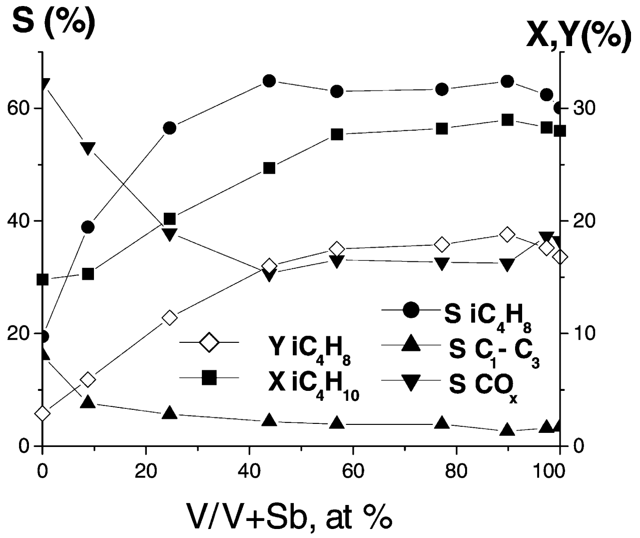

Fig. 3. Effect of V/(V+Sb) atomic ratio in alumina-supported V-Sb oxides on conversion of isobutane (*X*), yield of isobutene (*Y*) and selectivity to products (*S*) in the ODH of isobutane. Reaction conditions: 550 °C, $P^0_{iC_4H_{10}} = 20\,\text{kPa}$, $P^0_{O_2} = 10\,\text{kPa}$, $\tau = 4\,\text{s}$, time-on-stream 4 h.

(ms) was investigated. Catalysts were prepared by impregnation method. Their SSA values (60–105 m^2/g) differ slightly from those for the starting support (85 m^2/g). Since almost all studied V-Sb-O/γ-Al_2O_3 (ms) catalysts exhibit stable activity and selectivity, the catalytic data measured after 4 h on stream are presented in Fig. 3, excepting for the non-stable Sb-free and 2.6 at.% Sb-containing samples, which results correspond to 2.5 h on stream.

Both SbO_x/Al_2O_3 and Sb-rich catalysts are not efficient for olefin formation. The highest yield of isobutene ($Y \sim 18.8\%$) and high OS (~65%) at stable activity were achieved over the supported V-Sb oxide with optimal composition $V/(V + Sb) \sim 0.90$ (V/Sb = 8.8 at.). Evidently, the main ODH activity is associated with V-containing species (see also Section 3.2.1), but their modification with Sb addition results in the further improvement of their performance.

Fresh and used samples of this best performing supported catalyst are XRD-amorphous and the active oxidic species can be reliably detected only using laser Raman spectroscopy, which is very sensitive to the presence of VO_x species [50]. Raman spectrum of the fresh catalyst showed a high background and only the bands corresponding to V_2O_5 phase with very low intensity [51]. However, after the catalytic test, no such a band was detected in the spectrum of the used sample. This indicates that during the catalytic run, vanadia phase looses its crystallinity and the oxide becomes spread onto the surface as an amorphous vanadium oxide. So, one may conclude that VO_x active component is well dispersed on the support surface.

Based on the XPS BE values of V $2p_{3/2}$ (517.3 eV) and Sb $3d_{3/2}$ (540.3 eV) in Table 2, it can be concluded that both elements exist in high oxidation states in the surface of the fresh catalyst. Under catalytic conditions antimony was not reduced (BE and FWHM of Sb $3d_{3/2}$ peak retain their values without any change), whereas vanadium was reduced to a certain (but not big) extent after catalysis: BE and FWHM values of V $2p_{3/2}$ peak change only slightly.

The surface of the catalyst is significantly enriched with antimony (XPS surface atomic ratio V/Sb is 4.1–4.7, whereas bulk V/Sb = 8.8), but the extent of this enrichment is considerably lower than in the unsupported bulk sample. In the latter case, surface V/Sb ratio was 2.2. The increase of the surface V/Sb ratio after catalytic test agrees with the spreading of the vanadium oxide species observed by Raman.

The effect of the preparation method has been studied for the catalyst optimised atomic ratio V/Sb = 8.8. The catalytic results obtained with the homologous supported catalysts, prepared by impregnation and “citrate” method, respectively, are compared in Table 2, together with their surface characteristics. Noteworthingly, catalytic testing of the “citrate” sample reveals a substantial improvement in both isobutane conversion (*X*) and OS in comparison with the impregnated sample. This trend, opposite to the observed one for the bulk samples, may be explained by the surface composition of the active oxides. XPS analysis shows that, at a variance of impregnation, the “citrate” method produces a very homogeneous cationic distribution in the deposited oxides. The XPS measured surface composition of the “citrate” sample (V/Sb ~ 8.8) was equal to its nominal composition. This was not the case for the bulk “citrate” sample, for which an important surface enrichment (V/Sb = 2.2) is measured by XPS. Therefore, it seems that the better performance of the “citrate” supported catalyst is related with the actual surface atomic ratio, thus indicating the importance of high homogeneity of distribution of elements in the supported component.

3.2.3. *Optimisation of the catalyst support*

To check the influence of the support nature, a series of V-Sb oxide catalysts (V/Sb = 8.8, V_2O_5-loading corresponding to one theoretical monolayer [48]) supported on various supports have been prepared by “citrate” method, characterised and tested in the target reaction. Catalytic properties of these V-Sb oxide systems are presented in Table 3 together with their SSA values. All supported V-Sb oxides demonstrate much higher efficiency in the target reaction than that of any bulk binary oxide. It is interesting to stand out that all the catalysts supported on γ-Al_2O_3 display the best results.

The catalytic performance in the isobutane ODH strongly depends on the chemical nature of oxide carriers and decreases in a series:

$$\gamma\text{-}Al_2O_3 > \alpha\text{-}A1_2O_3 > SiO_2\text{-}Al_2O_3 > SiO_2 \approx MgO > \text{unsupported}$$

Among those supported on γ-Al_2O_3, the most efficient catalyst is the one prepared on microspheric γ-Al_2O_3 (ms),

Table 3
Oxidative conversion of isobutane on bulk and supported V-Sb-O systems (V/Sb = 8.8 at.) with 1 theoretical monolayer coverage

Catalyst support	SSA (m^2/g)	iC_4H_{10} conversion, X (%)	Selectivity (%)			iC_4H_8 yield, Y (%)
			iC_4H_8	C_1–C_3	CO_x	
No (bulk)	7.0	12.7	11.0	6.1	82.9	1.4
γ-Al_2O_3 (a)	131	28.4	64.0	3.9	32.1	18.2
γ-Al_2O_3 (wa)	125	34.5	65.0	4.1	30.9	22.4
γ-Al_2O_3 (n)	131	34.4	64.3	5.0	30.7	22.1
γ-Al_2O_3 (b)	114	34.3	65.9	4.0	28.9	22.6
γ-Al_2O_3 (ms)	69	36.5	70.2	6.2	23.6	25.6
α-Al_2O_3	32	20.7	52.0	4.2	43.8	10.8
Si-Al-O	232	19.4	44.6	4.8	50.6	8.6
Silica gel	183	16.3	35.8	5.0	59.3	5.8
MgO	30	15.0	36.7	9.6	53.7	5.5

Reaction conditions: 550 °C, $P^0_{iC_4H_{10}} = 20\,kPa$, $P^0_{O_2} = 10\,kPa$, $\tau = 4\,s$, time-on-stream 2.5 h.

Table 4
Summary of the improvements reached in the optimisation process[a]

Step	Result	X_{st} (%)	OS (%)	Y (%)
Bulk V-Sb-O systems				
Variation of the quantitative composition and preparation methods	Similar poor performance	11–14	11–12	<2
Supported VO_x-based systems				
Use of support and variation of VO_x-loading	1.4 ML VO_x/Al_2O_3 (ms): high activity, but unstable	37 (initial), 21 (at 4 h on stream)	62	23 (13)
Screening of co-components to VO_x/Al_2O_3	SbO_x stabilises activity of VO_x/Al_2O_3	–	–	–
Variation of V/(V + Sb) ratio in V-Sb-O/Al_2O_3	1.7 ML $V_{0.9}Sb_{0.1}O_x/Al_2O_3$ (ms): stable activity	29	65	19
Selection of preparation method	1.7 ML $V_{0.9}Sb_{0.1}O_x/Al_2O_3$ (ms) “citrate”	37	70	26

[a] X_{st}: stable conversion of isobutane; OS: isobutene selectivity, Y: yield of isobutene; ML: theoretical monolayer coverage.

a support with moderate surface area and large average pore diameter. The catalyst SSA and pore structure have some effect on the catalytic performance; however, these should be considered as minor (or secondary) factors as compared with the chemical nature of the support. The acid–base properties (or, more precisely, the Na content) of the starting γ-aluminas have no effect on catalytic properties of resulting supported oxide catalysts.

It is worth noting that the most efficient (γ-Al_2O_3-supported) catalysts are amorphous to XRD, whereas samples supported on silica or silica-alumina showing poor catalytic efficiency display XRD detectable V_2O_5-crystallites.

4. Concluding remarks

Summarising the main improvements reached during each step of the optimisation (Table 4), it can be concluded that, despite of the poor efficiency of bulk vanadium-containing oxides in the ODH of isobutane, their catalytic performance can be dramatically improved by depositing them on various oxide supports. In addition to the chemical composition of the active component, the second most critical parameter is the chemical nature of the oxide support: γ-alumina was found to be the best one, due to a proper spreading of the active component on its surface. The ODH efficiency and catalyst stability can be improved by appropriate doping of active vanadium oxide component with antimony (optimal V-to-Sb atomic ratio is 8.8). A further optimisation consists in the preparation of the catalysts containing ∼1.7 formal monolayer of mixed V-Sb oxide by the “citrate” method.

Characterisation data shortly described above (further detailed publications dealing with the characterisation of supported V-Sb oxide catalytic systems are in preparation [51]) indicate that active component of this alumina-supported catalyst is amorphous, with vanadium and antimony in the high oxidation state. Catalytic performance for selective oxidation on vanadium oxide catalysts is related with the redox properties of vanadium species [7–9,51–55]. This has been evidenced by differential scanning calorimetry, showing that the process occurs via a stepwise redox mechanism with the participation of lattice oxygen from the catalyst [56]. When the supported VO_x component is modified with antimony, the amount of reactive oxygen is increased and reduction–reoxidation cycles of vanadium ion proceed more rapidly and smoothly. Similar effects have been described for Sb-promoted molybdenum oxide [57]. Simultaneously, the addition of antimony decreases the rate of coke formation [43,56,57], which explains the observed improvement in catalytic stability. The parallel improvement of redox properties brought by antimony in supported V-Sb-O systems

[56] lead us to think that this is the main reason for lower rates of coke formation.

Application of "citrate" synthesis route, known to be a powerful method for preparation of homogeneous mixed oxides, gave us an opportunity to synthesise the catalyst whose amorphous supported components are well dispersed and homogeneously distributed on the support surface. This optimised γ-alumina-supported V-Sb oxide catalyst demonstrates the highest activity, selectivity and stability in the ODH of isobutane to isobutene, giving rise to a yield (close to 26%) among the highest ones ever reported for this reaction.

Acknowledgements

This study was partly funded by the European Community under the INCO-Copernicus Programme (contract ERBIC-15-CT-0725, CALIPSO project). VPV thanks the Spanish Ministry of Education, Culture and Sport for the sabbatical research grant (SAB2000-0028). The authors thank Mr. M. Genet for his help in the XPS analysis and Dr. V. Sheinin for his help in catalytic tests.

References

[1] M.M. Bhasin, J.H. McCain, B.V. Vora, T. Imai, P.R. Pujadó, Dehydrogenation and oxidehydrogenation of paraffins to olefins, Appl. Catal. A 221 (2001) 397–419.

[2] H.H. Kung, Oxidative dehydrogenation of light (C_2–C_4) alkanes, Adv. Catal. 40 (1994) 1–38, and references therein.

[3] E.A. Mamedov, V. Cortés Corberán, Oxidative dehydrogenation of lower alkanes on vanadium oxide-based catalysts. The present state of art and outlooks, Appl. Catal. A 127 (1995) 1–40, and references therein.

[4] S. Albonetti, F. Cavani, F. Trifirò, Key aspects of catalyst design for the selective oxidation of paraffins, Catal. Rev.-Sci. Eng. 38 (1996) 413–438, and references therein.

[5] B. Delmon, P. Ruiz, S.R.G. Carrazan, S. Korili, M.A. Vicente Rodriguez, Z. Sobalik, Control of catalyst performance in selective oxidation of light hydrocarbons: catalyst design and operational conditions, Stud. Surf. Sci. Catal. 100 (1996) 1–25, and references therein.

[6] R.K. Grasselli, Advances and future trends in selective oxidation and ammoxidation catalysis, Catal. Today 49 (1999) 141–153.

[7] J. Haber, Oxidation of hydrocarbons, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 5, VCH, Weinheim, 1997, pp. 2253–2274.

[8] T.M. Blasco, J.M. López Nieto, Oxidative dehydrogenation of short chain alkanes on supported vanadium oxide catalysts, Appl. Catal. A 157 (1997) 117–142, and references therein.

[9] B. Grzybowska-Swierkosz, Active centres of vanadia-based catalysts for selective oxidation of hydrocarbons, Appl. Catal. A 157 (1997) 409–420, and references therein.

[10] M. Bañares, Supported metal oxide and other catalysts for ethane conversion: a review, Catal. Today 51 (1999) 319–348, and references therein.

[11] L.M. Madeira, M.F. Portela, Catalytic oxidative dehydrogenation of *n*-butane, Catal. Rev.-Sci. Eng. 44 (2002) 247–286, and references therein.

[12] C. Tellez, M. Abon, J.A. Dalmon, C. Mirodatos, J. Santamaria, Oxidative dehydrogenation of butane over V-Mg-O catalysts, J. Catal. 195 (2000) 113–124.

[13] H.H. Kung, M.C. Kung, Oxidative dehydrogenation of alkanes over vanadium-magnesium-oxides, Appl. Catal. A 157 (1997) 105–116.

[14] L.S. Liebmann, L.D. Schmidt, Oxidative dehydrogenation of isobutane at short contact times, Appl. Catal. A 179 (1999) 93–106.

[15] Y. Takita, K. Sano, K. Kurosaki, N. Kawata, H. Nishiguchi, M. Ito, T. Ishihara, Oxidative dehydrogenation of isobutane to isobutene. I. Metal phosphate catalysts, Appl. Catal. A 167 (1998) 49–56.

[16] Y. Takita, K. Sano, T. Muraya, H. Nishiguchi, N. Kawata, M. Ito, T. Akbay, T. Ishihara, Oxidative dehydrogenation of isobutane to isobutene. II. Rare earth phosphate catalysts, Appl. Catal. A 170 (1998) 23–31.

[17] E. Tempesti, A. Kaddouri, C. Mazzocchia, Sol–gel processing of silica supported Ni and Co molybdate catalysts used for *iso*-C_4 alkane oxidative dehydrogenation, Appl. Catal. A 166 (1998) L259–L261.

[18] R. Zavoianu, C.R. Dias, M.F. Portela, Stabilization of β-$NiMoO_4$ in TiO_2-supported catalysts, Catal. Commun. 2 (2001) 37–42.

[19] F. Cavani, C. Comuzzi, G. Dolcetti, E. Etienne, R.G. Finke, G. Selleri, F. Trifiro, A. Trovarelli, Oxidative dehydrogenation of isobutane to isobutene: Dawson-type heteropolyoxoanions as stable and selective heterogeneous catalysts, J. Catal. 160 (1996) 317–321.

[20] C. Comuzzi, A. Primavera, A. Trovarelli, G. Bini, F. Cavani, Thermal stability and catalytic properties of the Wells–Dawson $K_6P_2W_{18}O_{62}\cdot 10H_2O$ heteropoly compound in the oxidative dehydrogenation of isobutane to isobutene, Top. Catal. 9 (1999) 251–262.

[21] R. Grabowski, B. Grzybowska, J. Sloczynski, K. Wcislo, Oxidative dehydrogenation of isobutane on supported chromia catalysts, Appl. Catal. A 144 (1996) 335–341.

[22] B. Grzybowska, J. Sloczynski, R. Grabowski, K. Wcislo, A. Kozlowska, J. Stoch, J. Zielinski, Chromium oxide/alumina catalysts in oxidative dehydrogenation of isobutane, J. Catal. 178 (1998) 687–700.

[23] M. Hoang, J.F. Mathews, K.C. Pratt, Oxidative dehydrogenation of isobutane over supported chromium oxide on lanthanum carbonate, J. Catal. 171 (1997) 320–324.

[24] G. Karamullaoglu, S. Onen, T. Timur, Oxidative dehydrogenation of ethane and isobutane with chromium-vanadium-niobium mixed oxide catalysts, Chem. Eng. & Process. 41 (2002) 337–347.

[25] M. Hoang, J.F. Mathews, K.C. Pratt, Oxidative dehydrogenation of isobutane to isobutylene over supported transition metal oxide catalysts, React. Kinet. Catal. Lett. 61 (1997) 21–26.

[26] H. Jablonska, E. Włoch, Z. Olejniczak, B. Sulikowski, ^{51}V NMR and catalytic studies of vanadium-containing MCM-41 mesoporous molecular sieves, Mol. Phys. Rep. 29 (2000) 19–24; Chem. Abstr. 134:106406 (2001).

[27] B. Sulikowski, Z. Olejniczak, E. Włoch, J. Rakoczy, R.X. Valenzuela, V. Cortés Corberán, Oxidative dehydrogenation of isobutane on MCM-41 mesoporous molecular sieves, Appl. Catal. A 232 (2002) 189–202.

[28] Q. Zhang, Y. Wang, Y. Ohishi, T. Shishido, K. Takehira, Vanadium-containing MCM-41 for partial oxidation of lower alkanes, J. Catal. 202 (2001) 308–318.

[29] G. Li, C.-L. Zhang, T.-H. Wu, Synthesis and catalytic properties of TiZSM-48, VZSM-48 and ZrZSM-48, Shiyou Huagong 28 (1999) 286–289 (in Chinese); Chem. Abstr. 131: 75875 (1999).

[30] M. Chen, W. Weng, H. Wan, Mechanism of propane and isobutane oxidative dehydrogenation on V-Mg-O catalyst, Wuli Huaxue Xuebao 15 (1999) 938–942 (in Chinese); Chem. Abstr. 131: 324767 (1999).

[31] A.A. Adesina, N.W. Cant, A. Saberi-Moghaddam, C.H.L. Szeto, D.L. Trimm, Structural effects in oxidative dehydrogenation of hydrocarbons over a vanadia-molybdena-niobia catalyst, J. Chem. Technol. Biotechnol. 72 (1998) 19–22.

[32] N. Kishimoto, E. Matsunami, Vanadium-containing oxidation, oxidative dehydrogenation, ammoxidation catalysts and manufacture

and uses thereof, PCT Int. Appl. WO 9641678 (1996); Chem. Abstr. 126:132881 (1997).

[33] G. Centi, S. Perathoner, F. Trifirò, V-Sb oxide catalysts for the ammoxidation of propane, Appl. Catal. A 157 (1997) 143–172, and references therein.

[34] H.-B. Chiang, M.-D. Lee, Characterization and catalytic behaviours of vanadium-antimony oxide catalysts in propane ammoxidation, Appl. Catal. A154 (1997) 55–74.

[35] R. Nilsson, T. Lindblad, A. Andersson, Ammoxidation of propane over antimony-vanadium-oxide catalysts, J. Catal. 148 (1994) 501–513.

[36] J. Nilsson, A.R. Landa-Cánovas, S. Hansen, A. Andersson, The Al-Sb-V-oxide system for propane ammoxidation: a study of regions of phase formation and catalytic role of Al, Sb, and V, J. Catal. 160 (1996) 244–260.

[37] A. Barbaro, S. Larrondo, S. Duhalde, N. Amadeo, Effect of titanium-doping on the properties of vanadium antimonate catalysts, Appl. Catal. A 193 (2000) 277–283.

[38] S. Larrondo, M. Matranga, G. Baronetti, B. Irigoyen, N. Amadeo, Vanadium antimonate as a partial oxidation catalyst, in: M.A. Bañares, I.E. Wachs, R.M. Martin-Aranda (Eds.), Proceedings of the 4th International Symposium on Group Five Compounds, “Bicentennial Meeting”, Toledo, Spain, 2002; Book of Abstracts, UNED, Madrid, 2002, pp. 179–180.

[39] D.-W. Park, B.-K. Park, D.-K. Park, H.-C. Woo, Vanadium-antimony mixed oxide catalysts for the selective oxidation of H_2S-containing excess water and ammonia, Appl. Catal. A 223 (2002) 215–224.

[40] J.F. Brazdil, A.M. Ebner, F.A.P. Cavalcanti, Rutile vanadium antimonates: a new class of catalysts for selective reduction of NO with ammonia, Appl. Catal. A 165 (1997) 51–55.

[41] T. Shishido, A. Inoue, T. Konishi, I. Matsuura, K. Takehira, Oxidation of isobutane over Mo-V-Sb mixed oxide catalyst, Catal. Lett. 68 (2000) 215–221.

[42] M.O. Guerrero-Pérez, J.L.G. Fierro, M.A. Vicente, M.A. Bañares, Effect of Sb/V ratio and of Sb + V coverage on the molecular structure and activity of alumina supported Sb-V-O catalysts for the ammoxidation of propane into acrilonitrile, J. Catal. 206 (2002) 339–348.

[43] V.P. Vislovskiy, V.Yu. Bychkov, M.Yu. Sinev, N.T. Shamilov, P. Ruiz, Z. Schay, Physico-chemical properties of V-Sb oxide systems and their catalytic behaviour in oxidative dehydrogenation of light paraffins, Catal. Today 61 (2000) 325–331.

[44] Ph. Courthy, H. Ajot, Ch. Marcilly, B. Delmon, Oxydes mixtes ou en solution solide sous forme trés divisée obtenus par décomposition thermique de précurseurs amorphes, Powder Technol. 7 (1973) 21–38.

[45] V.P. Vislovskiy, T.E. Suleimanov, M.Yu. Sinev, Yu.P. Tulenin, L.Ya. Margolis, V. Cortés Corberán, On the role of heterogeneous and homogeneous processes in oxidative dehydrogenation of C_3–C_4 alkanes, Catal. Today 61 (2000) 287–293.

[46] J.F. Moulder, et al., Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer, Eden Praine.

[47] S.R.J. Carrazan, C. Peres, J.P. Bernard, M. Ruwet, P. Ruiz, B. Delmon, Catalytic synergy in the oxidative dehydrogenation of propane over Mg-V-O catalysts, J. Catal. 158 (1996) 452–476.

[48] A.J. van Hegstum, J.G. van Ommen, H. Bosch, P.J. Gelllings, Preparation of supported vanadium and molybdenum oxide catalysts using methylacetonate complexes, Appl. Catal. 5 (1983) 207–217.

[49] Final Report of Project “Catalytic Activation of Light Paraffins by Selective Oxidation (CALIPSO)”, E.C. INCO-Copernicus Programme, Contract ERBIC-15-CT-96-0725, 2000.

[50] I.E. Wachs, B.M. Weckhuysen, Structure and reactivity of surface vanadium oxide species on oxide supports, Appl. Catal. A 157 (1997) 67–90.

[51] V.P. Vislovskiy, N.T. Shamilov, V.Yu. Bychkov, M.Yu. Sinev, P. Ruiz, V. Cortés Corberán, Effect of support on physico-chemical properties and catalytic performance of V-Sb oxides in oxidative dehydrogenation of isobutane, Appl. Catal. A, to be submitted for publication.

[52] E.A. Mamedov, R.M. Talyshinskii, R.G. Rizayev, J.L.G. Fierro, V. Cortés Corberán, Mixed M-V-Sb oxides as oxidehydrogenation catalysts, Catal. Today 32 (1996) 177–183.

[53] T. Blasco, A. Galli, J.M. López Nieto, F. Trifirò, Oxidative dehydrogenation of ethane and *n*-butane on VO_x/Al_2O_3 catalysts, J. Catal. 169 (1997) 203–211.

[54] J.M. López Nieto, J. Soler, P. Concepción, J. Herguido, M. Menendéz, J. Santamaria, Oxidative dehydrogenation of alkanes over V-based catalysts: influence of redox properties on catalytic performance, J. Catal. 185 (1999) 324–332.

[55] J. Le Bars, A. Auroux, M. Forrissier, J.C. Védrine, Active sites of V_2O_5/γ-Al_2O_3 catalysts in the oxidative dehydrogenation of ethane, J. Catal. 162 (1996) 250–259.

[56] V.Yu. Bychkov, M.Yu. Sinev, V.P. Vislovskii, Thermochemistry and reactivity of lattice oxygen in V-Sb oxide catalysts for the oxidative dehydrogenation of light paraffins, Kinet. Catal. 42 (2001) 574–581.

[57] E.M. Gaigneaux, H.M. Abdel Dayem, E. Godard, P. Ruiz, Dynamic phenomena and catalytic reactivities of oxide surfaces, Appl. Catal. A: Gen. 202 (2000) 265–283.