ELSEVIER

Catalysis Today 61 (2000) 325–331

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Physico-chemical properties of V-Sb-oxide systems and their catalytic behaviour in oxidative dehydrogenation of light paraffins

V.P. Vislovskiy [a,1], V.Yu. Bychkov [b,2], M.Yu. Sinev [b,*], N.T. Shamilov [a], P. Ruiz [c,3], Z. Schay [d,4]

[a] *Institute of Inorganic and Physical Chemistry, Azerbaijan Academy of Sciences, 29 H. Javid ave., 370143 Baku, Azerbaijan*
[b] *Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin str., 117334 Moscow, Russia*
[c] *Université Catholique de Louvain, Unité de Catalyse et Chimie des Matériaux Divisés,*
Croix du Sud 2/17, B-1348 Louvain-la Neuve, Belgium
[d] *Institute of Isotope and Surface Chemistry, Hungarian Academy of Sciences, H-1525 PO Box, Hungary*

Abstract

Catalysts prepared as bulk $VSb_{0.1}O_x$ and supported V_2O_5/Al_2O_3, V_2O_5-Sb_2O_3/Al_2O_3 and Sb_2O_3/Al_2O_3 (containing 0.5, 1 or 2 theoretical monolayers of V_2O_5 or Sb_2O_3) were tested in the oxidative dehydrogenation of iso-butane at 550°C in i-C_4H_{10}:O_2:He=20:10:70 gas mixture. Fresh and used catalysts were characterised by BET, XRD and XPS. Reactivity and thermochemistry of active oxygen taking part in the redox cycle with ethane and hydrogene were studied using in situ differential scanning calorimetry. Temperature-programmed desorption of O_2 in He flow was also investigated and in situ DRIFT was applied to investigate surface species of the catalysts in flows of i-C_4H_{10}, O_2 and i-C_4H_{10}/O_2 mixture. Supported VSb_yO_x catalysts are more active and selective than bulk one. V-only supported catalysts display a high efficiency due to the high reactivity of VOX-species. In bulk catalyst, the surface is enriched with antimony. In supported samples, the surfaces V/Sb are close to the calculated ones. In the presence of antimony, the amount of active oxygen species and their reactivity in redox transformation is improved. The rates of vanadium reduction and reoxidation are also higher. Compared to V-only catalysts, supported V-Sb-catalysts display a lower coking activity and higher on-stream stability. © 2000 Published by Elsevier Science B.V.

Keywords: V-Sb-oxide systems; Oxidative dehydrogenation; Diffuse reflectance infrared Fourier transform spectroscopy; Light paraffins

1. Introduction

Complex V-Sb oxides are known to be very efficient as catalysts for oxidative dehydrogenation (ODH) of C_2–C_4 paraffins [1]. Few fundamental studies have been presented in the literature to explain the role of each component and the reasons why supported catalysts are more efficient than unsupported ones. From Ref. [2], there is no doubt about a redox nature of catalytic action of V-containing oxides in hydrocarbon oxidation processes, but existing information about factors controlling redox behaviour and catalytic performance of these systems is still scarce. In particular, although it is known that binding energy of active oxygen species can determine both activity and selectivity of oxide catalysts [3], no systematic studies on the relationships between composition, reactivity and

---

[*] Corresponding author. Fax: +7-095-938-2156.
E-mail addresses: vislovski@usa.net (V.P. Vislovskiy), bychkov@center.chph.ras.ru (V.Yu. Bychkov), sinev@center.chph.ras.ru (M.Yu. Sinev), ruiz@cata.ucl.ac.be (P. Ruiz), schay@sunsenv.kfki.hu (Z. Schay).
[1] Fax: +994-12-977-456.
[2] Fax: +7-095-938-2156.
[3] Fax: +32-10-473649.
[4] Fax: +361-395-9001.

0920-5861/00/$ – see front matter
PII: S0920-5861(00)00392-8

thermochemistry of V-containing ODH catalysts have been carried out yet.

On the other hand, the nature of catalytic action is strongly related to the mechanism of reactant activation. Despite numerous spectroscopic investigations of surface intermediates formed during an interaction of hydrocarbons with oxide catalysts [4], the structure of surface intermediates and their role in certain reaction pathways (ODH, total oxidation, coking) is still under discussion.

The objective of this study is to trace how appropriate supports and dopants affect the state of V-based systems, their reactivity in redox transformations and catalytic performance. We have chosen alumina as a support material and antimony as a dopant which substantially increase the efficiency of vanadia in ODH of C_2–C_4 paraffins.

In order to reach this objective, several methods were used for a physico-chemical characterization of systems under study. XRD and XPS were used to characterise phase and surface compositions correspondingly. Taking into account the principal role of active oxygen species in the efficiency of V-containing ODH catalysts, we focused our attention on their characterization using a set of complementary techniques. Relatively weakly bonded oxygen species were identified using oxygen TPD in an inert gas flow. In situ differential scanning calorimetry (DSC) was employed to measure heats of catalyst reduction by paraffin and reoxidation by oxygen, to calculate binding energies of active oxygen species and to correlate them with sample reactivity and ODH selectivity. Since the V=O bond is known to vary during redox transformations of vanadia [5], we applied in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to measure the V=O band intensity under different treatments. DRIFTS could also provide an information about carbon-containing species on working catalysts [4].

2. Experimental

Samples used in this study are further denoted as indicated in parentheses. Bulk catalyst of 84.6% V_2O_5-15.4% Sb_2O_3 (wt.%) ($VSb_{0.1}O_x$) composition was prepared by mixing NH_4VO_3 and $SbCl_3$ solutions with further evaporation and calcination. Similar mixed solutions were used for impregnation of alumina. Weakly acidic Aldrich amorphous alumina (A1) (S=165 m^2/g, grain size ∼0.1 mm) and γ-Al_2O_3 (A2) (S=85 m^2/g, grain size 0.3–0.8 mm) supplied by the Katalizator company (Novosibirsk, Russia) were used to prepare the following supported samples: 19.3% V_2O_5/Al_2O_3 (A1) (V19/A1), 9.02% V_2O_5-1.64% Sb_2O_3/Al_2O_3 (A1) (V9Sb1.6/A1), 16.3% V_2O_5-2.97% Sb_2O_3/Al_2O_3 (A1) (V16Sb3/A1), 27.34% V_2O_5-4.97% Sb_2O_3/Al_2O_3 (A1) (V27Sb5/A1), 5.83% V_2O_5/Al_2O_3 (A2) (V5.8/A2), 15% V_2O_5/Al_2O_3 (A2) (V15/A2), 11.9% Sb_2O_3/Al_2O_3 (Sb12/A2), 5.83% V_2O_5-11.9% Sb_2O_3/Al_2O_3 (V5.8Sb12/A2), 15% V_2O_5-2.73% Sb_2O_3/Al_2O_3 (V15Sb2.7/A2). Calcined samples had the same granulation as initial alumina. Assuming monolayer spreading of V_2O_5 and Sb_2O_3 on the support, the number of theoretical monolayers (ML) was calculated as 0.5ML for V9Sb1.6/A1, 1ML for V19/A1 and V16Sb3/A1 and 2ML for V27Sb5/A1 samples.

ODH of iso-butane was studied in a fixed-bed quartz reactor equipped with a thermocouple placed inside the catalyst bed and operated at 550°C; initial gas feed had i-C_4H_{10}:O_2:He=20:10:70 and HGSV=900 h^{-1}.

BET surface areas were measured with a Micrometrics Flow Sorb II instrument by one-point N_2 adsorption at liquid nitrogen temperature after outgassing for 1 h at 150°C.

X-ray diffraction studies were performed using a Kristalloflex 805 (Siemens) diffractometer equipped with a Siemens D-500 detector using the Cu Kα radiation.

The XPS analysis was performed at room temperature using an SSX-100 model 206 SSI photoelectron spectrometer. A monochromated Al anode, powered at 10 keV and 20 mA, was used for X-ray production. The binding energies (BEs) were calculated with respect to the C 1s peak set at 284.8 eV. The intensities were estimated by calculating the integral of each peak after subtraction of the “S-shaped” background. Atomic concentration ratios were calculated by correcting the intensity ratios with theoretical sensitivity factors based on Scoffield cross-sections. Deconvolution of peaks was performed using a fitting routine of the SSI instrument using literature BE data [6].

DRIFTS spectra were recorded by an IFS 88 Bruker Fourier Transform spectrophotometer (resolution 4 cm^{-1}). In situ DRIFTS cell consisted of a cup-shaped ceramic oven with porous bottom and thermocouple, a water-cooled shell with ZnSe windows, gas inlet and outlet tubes. Samples as rough powders ($d\sim0.1$ mm) were placed into the cell, heated for 30 min in air flow at 550°C for standard pretreatment and cooled down to the temperature of investigation. DRIFTS spectra were recorded in flows of i-C_4H_{10}, O_2, or i-C_4H_{10}/O_2 mixtures in a 20–550°C range. In order to study the effect of adsorbed water, instead of treatment at 550°C in air, samples were treated in a dry He flow at room temperature for 30 min before measurements.

Heats of reduction (Q_{red}) and reoxidation (Q_{ox}) were measured using a Setaram DSC-111 differential scanning calorimeter with on-line GC analysis. In order to simplify the analysis of carbon-containing products and to increase the accuracy of thermochemical calculations, we used C_2H_6 and H_2 as reducing agents instead of iso-butane. A flow quartz cell containing 100–200 mg of material under study (0.5–1 mm grain size is preferable for this set-up) was placed into the channel of the calorimetric block. Samples were pretreated for 30 min at 550°C in 30 ml/min air flow. Pulses (0.5 ml) of reducing gas mixtures (30% C_2H_6–He, 10% H_2–He) or air were injected into a pure helium flow (30 ml/min) at 550°C with 5 min interval. A GC analysis of reaction mixture was performed on two columns packed with 5 Å molecular sieves (H_2, O_2, CO) and Porapak N (C_2H_6, C_2H_4, CO_2) using TC detectors. More details about this procedure are given elsewhere [7].

Heat balance in each pulse was calculated in accordance with the following brutto-equations:

$$\begin{array}{ll}
C_2H_6+/O/_s\rightarrow//_s+aC_2H_4+bCO_2+cCO+dH_2O & +Q_{red}\ (\mathrm{kJ/mol}\ C_2H_6)\\
H_2+/O/_s\rightarrow//_s+H_2O & +Q_{red}\ (\mathrm{kJ/mol}\ H_2)\\
O_2+//_s\rightarrow 2/O/_s & +Q_{ox}\ (\mathrm{kJ/mol}\ O_2)
\end{array}$$

Q_{red} values were recalculated to Q_{ox} values, using the scheme:

$$\begin{array}{ll}
2/O/_s\rightarrow 2//_s+O_2 & -Q_{ox}\ (\mathrm{kJ/mol}\ O_2)\\
2C_2H_6+5O_2\rightarrow 4CO+6H_2O & +430.8\ \mathrm{kJ/mol}\ CO\\
2C_2H_6+7O_2\rightarrow 4CO_2+6H_2O & +713.8\ \mathrm{kJ/mol}\ CO_2\\
2C_2H_6+O_2\rightarrow 2C_2H_4+2H_2O & +101.8\ \mathrm{kJ/mol}\ C_2H_4
\end{array}$$

$$Q_{ox}=\frac{430.8n_{CO}+713.8n_{CO_2}+101.8n_{C_2H_4}-Q_{red}}{1.25n_{CO}+1.75n_{CO_2}+0.5n_{C_2H_4}}$$

where n_i is an amount (mol) of (i)-compound. Binding energy of reacted oxygen with oxide lattice E_O (kJ/g-at O) is a linear function of Q_{ox} value and can be calculated as $E_O=\frac{1}{2}(Q_{ox}-E_{O_2})$, where E_{O_2} is the energy of O_2 molecule dissociation. Enthalpy changes ΔH were calculated by a conventional procedure using standard formation enthalpies ΔH_f^o for metal oxides.

Oxygen TPD studies were performed in the same DSC set-up. Samples (100–200 mg) were treated in air flow at 700°C, cooled to 50°C in air and then heated to 650–700°C in a helium flow at heating rate 10°C/min with GC analysis of gas flow after calorimetric cell.

3. Results and discussion

3.1. Catalytic testing

The results of catalytic testing of bulk and supported samples are given in Table 1. Conversion of i-C_4H_{10} in the same reactor filled with quartz was very low, so the effect of noncatalytic transformation can be neglected. Activity and selectivity of the bulk V-Sb-oxide is poor. Sb12/A2 sample displays slightly higher parameters. V15/A2 demonstrates a good initial ODH activity, which declines after 2.5 h on stream. V15Sb2.7/A2 sample provides the initial yield of i-C_4H_8 close to that observed over V15/A2, but this value only slightly decreases after 2.5 h. These observations indicate that catalytic properties mostly determined by vanadium oxide are stabilized by antimony in a binary supported system.

3.2. Phase and surface composition

XRD of fresh $VSb_{0.1}O_x$ sample shows the presence of V_2O_5-type phase and of a mixed phase, close to $V_{1.1}Sb_{0.9}O_4$. The latter was identified by 3.2577, 2.5054, 1.6970 reflexes which are close to 3.2328, 2.5144, 1.7010 values given for $V_{1.1}Sb_{0.9}O_4$

Table 1
Catalytic properties of selected samples in ODH of i-C_4H_{10} (550°C, $P_{iC_4H_{10}}$=20 kPa, P_{O_2}=10 kPa, τ (contact time)=4 s)

Catalyst	i-C_4H_{10} conversion (%)	ODH selectivity (%)	i-C_4H_{10} yield (%)	S (m^2/g)
$VSb_{0.1}O_x$	12.7	11.0	1.4	7.0
V15/A2				
After 1 h	39.5	63.6	25.1	61.3
After 2.5 h	29.5	61.1	18.1	
Sb12/A2	14.8	19.5	2.9	
V15Sb2.7/A2				
After 1 h	39.6	68	26.9	84.7
After 2.5 h	36.5	70.2	25.6	

(37-1075) in JCPDS database. After catalytic testing, the V_2O_5-type phase transforms into a V_2O_3-type one.

Pure Al_2O_3 (A1) is X-ray amorphous. In V9Sb1.6/A1 only traces of the V_2O_5-type phase were observed. In V16Sb3/A1 and V27Sb5/A1 samples reflexes of V_2O_5-type phase become more intense and $V_{1.1}Sb_{0.9}O_4$ phase appears. After catalytic testing, V_2O_5 also transforms into V_2O_3.

Parameters of photoelectron spectra (binding energies, BEs, peak half widths, PWs, and atomic concentrations, ACs) are presented in Table 2 along with V/Sb atomic ratios calculated from XPS data as AC($V2p_3$)/AC($Sb3d_3$) (*) and from formal bulk compositions (**). For the V16Sb3/A1 sample, the analysis of the only $V2p_3$ peak shows that the $V2p_3$ BE decreases and the PW increases after catalytic runs indicating the reduction of vanadium. The $V2p_3$ peak of “used” samples can be fitted, for V(5+), V(4+) and V(3+) components (Table 2). However, there were some complications in the analysis of the XPS spectra of V. The part of XPS spectra with $V2p_3$ peak is overlapped with O1s and $Sb3d_5$ peaks. The background profile should take into account all overlapping peaks, in particular the influence of the biggest O1s peak. In this last case, the resulting baseline is lower compared to that of only $V2p_3$ peak and the reduced species are overestimated. However, even in this last case, reduced vanadium (V^{+4}) is observed after reaction.

An increase of carbon concentration in “used” samples demonstrates the formation of carbonaceous species (coke) on the catalyst surfaces.

For the unsupported $VSb_{0.1}O_x$ sample, the measured surface V/Sb atomic ratio is four times less than that calculated from its formal bulk composition, i.e. the surface of mixed oxide enriched with antimony. In the case of supported samples, measured V/Sb ratios are close to the calculated ones. So, V and Sb are represented on alumina surface in the ratio which corresponds to the chemical composition of the supported component.

3.3. Oxygen TPD

V5.8/A2 releases only 0.9 μmol O_2/g while heating to 670°C. Oxygen desorption from Sb12/A2 starts at 580°C (28 μmol O_2/g). During O_2 TPD from V5.8Sb12/A2 which starts at 510°C, 52 μmol O_2/g were detected. This clearly shows a synergy between components and suggests the formation of new active oxygen species in V-Sb system which are not present in individual supported oxides.

3.4. DSC measurements

Interaction of C_2H_6 or C_2H_6–O_2 pulses with V5.8/A2, Sb12/A2, V5.8Sb12/A2 catalysts at 550°C leads to the formation of C_2H_4, CO_2, CO, H_2O and to the reduction of supported oxides. C_2H_6 conversion decreases and C_2H_4 selectivity increases (Fig. 1a) with the amount of oxygen removed from the oxide by the reduction. Total amounts of removed lattice oxygen by 30% C_2H_6 pulses increases in a series: Sb12/A2<V5.8/A2<V5.8Sb12/A2.

At the first stage of V5.8Sb12/A2 reduction (<200 μg-at O removed, Fig. 1a, curve B) mostly carbon oxides are produced ($S_{C_2H_4}<30\%$). During this stage, $Q_{ox}<320$ kJ/mol O_2 (see Fig. 1b, curve A). The second stage of reduction proceeds at nearly constant ODH selectivity (∼45%) and $320<Q_{ox}<360$ kJ/mol O_2 (Fig. 1a and b). Values of $S_{C_2H_4}$ vs. degree of reduction curves are very similar for the experiments with C_2H_6 and C_2H_6–O_2 pulses supplied on the sam-

Table 2
XPS analysis of samples: binding energy (BE), half width (PW), atomic concentration (AC) data and V/Sb ratios

Sample	$V2p_3$			$Sb3d_3$			Al2p			O1s			C1s			V(5+)			V(4+)			V(3+)			V/Sb atomic ratios calculated from	
	BE (eV)a	PW (eV)	AC (%)	BE (eV)	PW (eV)	AC (%)	BE (eV)	PW (eV)	AC (%)	BE (eV)	PW (eV)	AC (%)	BE (eV)	PW (eV)	AC (%)	BE (eV)	PW (eV)	AC (%)	BE (eV)	PW (eV)	AC (%)	BE (eV)	PW (eV)	AC (%)	XPS data as AC($V2p_3$)/ AC($Sb3d_3$)	Formal bulk compositions
$VSb_{0.1}O_x$																										
Fresh	516.7		14.29	540.1		6.51				530.4		47.8			31.4										2.2	8.8
Used	516.1		13.39	539.7		6.13				530.3		43.65			36.83										2.18	8.8
V16Sb3/A1																										
Fresh	517.2	2.50	3.85	539.8	2.50	0.50	74.3	2.35	25.03	531.0	2.97	54.05			16.56										7.7	8.8
Used	516.7	3.19	3.67	540.1	2.41	0.46	74.0	2.52	27.62	531.4	3.08	48.84			19.41	517.2	2.47	2.14	516	2.47	0.91	515	2.65	0.62	8.0	8.8

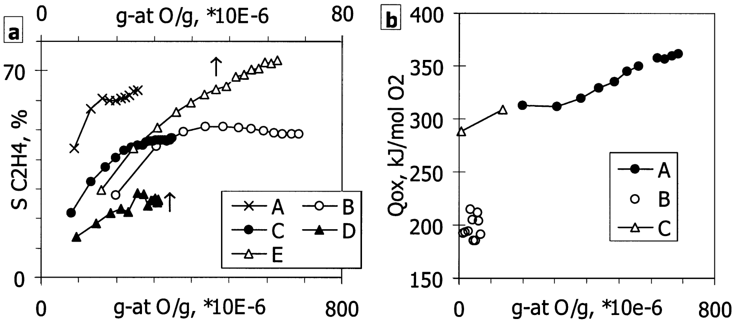

Fig. 1. (a) C_2H_4 selectivity (S) as a function of lattice oxygen removed at 550°C due to interaction of V5.8/A2 (A), V5.8Sb12/A2 (B, C), Sb12/A2 (D, E) with pulses of 30% C_2H_6–He (A, B, E) and 15% C_2H_6–5% O_2–He (C, D) mixtures. (b) Q_{ox} as a function of the amount of lattice oxygen removed at 550°C due to interaction of V5.8Sb12/A2 (A) with C_2H_6 pulses; Sb12/A2 (B) with H_2 pulses; V5.8/A2 (C) with air pulses.

ple (see Fig. 1a, curves B and C). This suggests that in both cases C_2H_4 and carbon oxides are produced at the expense of the reaction of C_2H_6 with catalyst lattice oxygen, and gaseous oxygen takes part only in the reoxidation of reduced catalyst.

Over V5.8/A2 C_2H_4, selectivity in the first ethane pulse was higher (43%, see Fig. 1a, curve A) than for V5.8Sb12/A2. Based on oxygen TPD data, one may assume that higher C_2H_4 selectivity is caused by a lower content of weakly bonded oxygen in this sample. Unfortunately, a precise measurement of Q_{ox} over this sample during the reduction with C_2H_6 is not feasible due to intense coke formation that was proved by intense CO_x evolution during catalyst reoxidation by air pulses at 550°C. Reoxidation of V5.8Sb12/A2 sample is accompanied by an evolution of small amounts of CO_x, so in the case of V5.8Sb12/A2 coke formation is efficiently hampered in comparison with V-only system.

The content of oxygen which can be removed from Sb12/A2 is far lower than in V-containing samples (Fig. 1a, curve D) and only oxygen that desorbs during TPD (31 μmol O_2/g) reacts with ethane. ΔH values for $Sb_2O_5 \rightarrow Sb_2O_4 + \frac{1}{2}O_2$ and $Sb_2O_4 \rightarrow Sb_2O_3 + \frac{1}{2}O_2$ reactions are 171 and 383 kJ/mol O_2 correspondingly. Measured values $Q_{ox} \sim 200$ kJ/mol O_2 are close to the ΔH value of $Sb_2O_5 \rightarrow Sb_2O_4$ transformation. The sample reduced by C_2H_6 pulses (Fig. 1a, curve D) does not undergo efficient reoxidation at 500–600°C. In this case, relatively low Q_{ox} value (and low binding energy of lattice oxygen, see Section 2) does not lead to intense total oxidation, likely due to low content of reactive oxygen.

Fig. 1a (curve D) demonstrates that when Sb12/A2 sample interacts with C_2H_6–O_2 pulses, the $S_{C_2H_4}$ values are two times lower than in the case of C_2H_6 pulses (curve E). This indicates that during catalytic ODH over Sb12/A2, the formation of products is likely affected by adsorbed oxygen species existing in equilibrium with gaseous O_2.

3.5. In situ DRIFTS investigation

In DRIFTS spectra of V-containing samples, the band at 2000 cm^{-1} is attributed to the overtone of ν(V=O) vibration of vanadium oxide. Unfortunately, the main band at 1000 cm^{-1} overlaps with that of the alumina support, so we used 2000 cm^{-1} band for the characterization of vanadium oxide. Fresh samples contain adsorbed water which decreases intensities of this band. Intensities of the band in wet samples measured at 20°C are equal to 0, 20 and 44% (for V9Sb1.6/A1, V16Sb3/A1, V27Sb5/A1, respectively) of intensities observed on the samples calcined in DRIFTS cell at 550°C and cooled to 20°C for measurements. This could indicate that in V9Sb1.6/A1 (0.5 theoretical monolayer), the supported component forms small clusters in which all V=O bonds are accessible for adsorbed water. In V16Sb3/A1 and V27Sb5/A1 samples (1 and 2 theoretical monolayers), some V atoms do not interact with water. This could be due to the formation of bulky crystallites.

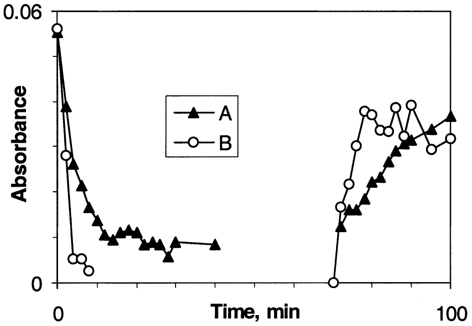

Fig. 2. Drift results. Variations of 2000 cm^{-1} band of V16Sb3/A1 and V19/A1 samples in iso-butane (0–40 min), helium (40–70 min), air (70–100 min) flows.

V16Sb3/A1 demonstrates higher rates of vanadium reduction and reoxidation than V19/A1 (Fig. 2). Since the band at 2000 cm^{-1} disappeared when vanadium ions are reduced approximately to V(3+) state [5], the intensity of this band allows to estimate the reduction degree of vanadium component. It was shown that both in iso-butane and in i-C_4H_{10}/O_2 mixture, vanadium undergoes a reduction at 450°C. The degree of reduction increases with increasing V-Sb-component loading.

Interaction of iso-butane flow with V16Sb3/A1 at 20°C leads to the formation of some adsorbed species. Appearance of the bands ν(O–H) (3500–3600 cm^{-1}), δ(O–H) (1630 cm^{-1}), ν(C–H) (2955–2875 cm^{-1}), δ(C–H) (1475, 1370 cm^{-1}), ν(C=O) (1577 cm^{-1}) is observed with simultaneous decrease of the 2000 cm^{-1} band intensity.

Interaction of iso-butane with V16Sb3/A1 at 250–450°C leads to the formation of other species. At these temperatures, no ν(C–H) bands were detected, but 1560, 1460 cm^{-1} bands were observed by DRIFTS. Similar spectra are usually attributed to “carboxylates”, which are intermediates in the formation of coke, or to some part of the coke formed [8]. At 450°C, the intensity of 1560 cm^{-1} band observed over V16Sb3/A1 is more than twice lower than that observed over V19/A1. This fact is in a good agreement with the conclusion regarding the lower coking activity of Sb-containing samples made above; it also can explain a higher stability of Sb-doped catalysts in steady-state conditions.

On Al_2O_3(A1), carboxylates are stable in He flow and undergo slow oxidation in O_2 at 450°C. Over $VSb_{0.1}O_x$/A1, corresponding bands slowly disappear from the spectrum even in He flow. This process sharply accelerates in O_2-containing atmosphere.

4. Conclusions

Alumina-supported V-containing oxides are more active and selective than bulk ones. V-only supported catalysts display high efficiency in ODH of light alkanes due to the high reactivity of VO_x-species under reduction–reoxidation treatments which mimic the catalytic redox cycle. The amount of active oxygen species and their reactivity in redox transformation further improve in antimony-doped systems. Compared to V-only catalysts, supported V-Sb-catalysts display lower coking activity and higher on-stream stability.

Acknowledgements

This study was funded by the Europeanπ Community under the INCO-Copernicus Programme (contract ERBIC15-CT-96-0725). The authors thank Dr. V. Sheinin for the help in catalytic measurements.

References

[1] R. Juarez Lopez, N.S. Godjayeva, V. Cortes Corberan, J.L.G. Fierro, E.A. Mamedov, Appl. Catal. A 124 (1995) 281.
[2] P. Mars, D.W. van Krevelen, Chem. Eng. Sci. 3 (1954) 41.
[3] A. Bielanski, J. Haber, Oxygen in Catalysis, Marcel Dekker, New York, 1991.
[4] G. Busca, Catal. Today 27 (1996) 457.
[5] D.H. Sullivan, M.P. Harold, W.C. Conner Jr., J. Catal. 178 (1998) 108.
[6] J. Mendialdua, R. Casanova, Y. Barbaux, J. Electr. Spectr. Relat. Phenom. 71 (1995) 249.
[7] M.Yu. Bychkov, M.Yu. Sinev, V.N. Korchak, E.L. Aptekar’, O.V. Krylov, Kinetika i Kataliz 30 (1989) 1137.
[8] J. Datka, Z. Sarbak, R.P. Eischens, J. Catal. 145 (1994) 544.