Ethane oxidehydrogenation selectivity and reducibility of mixed NiVSb oxides

R.X. Valenzuela, J.L.G. Fierro, V. Cortés Corberán [1] and E.A. Mamedov

Instituto de Catálisis y Petroleoquímica, CSIC, Campus UAM – Cantoblanco, 28049 Madrid, Spain

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Alumina-supported NiV, SbV and NiVSb oxides were characterized and tested as catalysts for the oxidehydrogenation of ethane. The results of their surface and bulk reduction by hydrogen revealed that the most easily reduced NiVSb catalyst was the most selective. The relationship between catalyst reducibility and selectivity was interpreted on the assumption that the reaction occurred through a redox mechanism.

Keywords: ethane oxidehydrogenation; mixed oxides; redox mechanism; oxide reducibility; selectivity; vanadium oxide; antimony oxide; nickel oxide

1. Introduction

Alumina-supported mixed VSb oxides are able to catalyze the oxidehydrogenation (OXD) of lower paraffins [1,2]. They exhibit a high overall activity but relatively low dehydrogenation selectivity ranging from 40 to 50%. Such catalytic behavior has been accounted for by a strong oxidizing power of the vanadium pentoxide which predominantly covered their surface. When adding nickel oxide, it reacts with free V_2O_5 producing nickel vanadate. As a result, an essential increase in selectivity has been observed [2]. The enhanced selectivity of the NiVSb oxide can thus be related to the absence of free vanadium and nickel oxides (the latter was present in the less selective NiV catalyst). Both V_2O_5 and NiO are known to be active in the total oxidation of hydrocarbons due to low binding energy of lattice oxygen [3]. In this respect, it was interesting to study and compare oxygen mobilities in the NiVSb catalyst and its binary NiV and VSb counterparts.

The relative ease of removal of lattice oxygen is frequently characterized by the ease of catalyst reduction with hydrogen or hydrocarbon. Using a pulse reduction technique coupled with calorimetric measurements of the heats of reoxidation of the reduced catalysts, Andersen and Kung [4] have found that the selectivity for OXD of butane on alumina-supported vanadia increased as the oxygen was more strongly bound to the catalyst. In another paper of the same research group [5], similar correlation has been reported for different metal vanadates; more selective catalysts showed higher onset reduction temperatures. Contrary relationships between OXD selectivity and catalysts reducibility have been established for VMoNb oxides in the reaction of ethane [6] and for three pure magnesium vanadate phases in the reaction of propane [7]. In both cases, the most easily reduced catalyst was the most selective. These derivations are mostly based on the results of catalyst bulk reduction which may differ from those of the surface reduction. As has been reported in ref. [8], there are metal oxides possessing roughly the same metal–oxygen bond energies in the bulk but showing quite a difference in energies of oxygen binding with the surface. Upon reducing their monolayers, the activation energies have been found [9,10] to increase with the amount of removed oxygen ions in parallel with binding strengths of surface oxygen. This means that the data on catalytic activity/selectivity should be correlated with the parameters of surface reduction rather than with those of bulk reduction.

In the present work we studied the reducibilities of the surface as well as of the bulk of mixed NiVSb oxides. The redox properties of catalysts and related characterization data were compared to their performances in the OXD of ethane.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by simultaneous impregnation of γ-alumina spheres (1.8–2.0 mm o.d., specific surface area: 200 m^2/g, pore volume: 0.50 cm^3/g) with solutions of ammonium metavanadate (NH_4VO_3) and chlorides of other metals. The required amounts of NH_4VO_3, nickel chloride and antimony chloride were separately dissolved in aqueous solution of tartaric acid. After mixing these solutions in a ratio defined by the composition of the catalyst to be prepared, alumina was

[1] To whom correspondence should be addressed.

immersed in the mixed solution, and the solvent was removed under continuous stirring. The solid was dried at 393 K and then calcined in air stream in three steps at 473, 673 and 873 K for 2 h at each temperature. The total amount of supported components did not exceed 28 wt%.

2.2. Catalyst characterization

BET surface areas were measured with a volumetric sorption unit of standard design using nitrogen adsorption at 77 K. The samples were outgassed at 633 K before sorption studies were performed.

Powder X-ray diffraction (XRD) patterns were recorded on a Phillips PW 1730 diffractometer using nickel-filtered Cu Kα radiation. For each sample, Bragg's angles between 5 and 70° were scanned at a rate of 2°/min. JCPDS-ICDD (1990–1991) standard spectra software was used to determine the phases.

X-ray photoelectron spectra (XPS) were acquired with a Fisons Escalab MkII 200R spectrometer equipped with a hemispherical electron analyzer and a Mg Kα 120 W X-ray source. The catalyst reduction by hydrogen was carried out within the pretreatment chamber prior to being moved into the analysis chamber. The detailed procedure is described in ref. [2]. All binding energies (BE) were referred to the Al 2p line at 74.5 eV which gave BE values within an accuracy of 0.2 eV.

Temperature programmed reduction (TPR) experiments were run in a conventional system equipped with a thermal conductivity detector (TCD). The reduction was carried out in flow of H_2 (10%) in Ar (60 ml/min) using a heating rate of 10 K/min. The amount of hydrogen uptake in TPR was estimated from integrated peak areas.

2.3. Catalytic tests

Continuous OXD of ethane was run at temperature 673–773 K with inlet gas mixture containing 41.6 vol% C_2H_6, 16.8 vol% O_2, the rest He with a contact time 0.6 s as detailed in ref. [2]. Under these conditions, no oxidation of ethane in the absence of catalyst was observed. Reactants and products were analyzed on-line by gas chromatography.

3. Results

3.1. Catalyst characterization

The BET surface areas of freshly prepared catalysts listed in table 1 were not found to differ strongly from each other. After reduction, they remained unchanged or slightly (about 15%) decreased.

The results of XRD analysis described in detail elsewhere [2] are summarized in table 1. Besides γ-Al_2O_3, the major phases in supported NiV and SbV oxides were respectively nickel orthovanadate and antimony vanadate with small amounts of the corresponding individual oxides. The latter were not detected in the bulk of ternary NiVSb oxide which consisted of nickel vanadate, nickel antimonate and antimony vanadate phases. After use in ethane oxidation, no remarkable changes were observed in the phase composition of these catalysts.

Table 2 shows binding energies (BE) of the most intense peaks of supported metal cations together with their surface atomic ratios as measured with XPS. For the Sb 3d core level spectra, the less intense Sb $3d_{3/2}$ peak of the Sb 3d doublet was taken for calculating BE owing to the overlapping of the principal Sb $3d_{5/2}$ peak with the much more intense O 1s peak arising from the Al_2O_3 carrier. Fresh catalysts showed practically the same BE's for all metal cations, indicating that their oxidation states, identified as V^{5+}, Ni^{2+} and Sb^{5+}, were independent of catalysts composition. Using the metal-to-aluminium ratios listed in table 2, relative proportions of metals at the surface were calculated and compared to the nominal Ni/V/Sb ratio equaled to 1.0/0.3/0.6. It was found that the surface of all catalysts was enriched in vanadium, whereas, compared to that of nickel, the antimony content was approximately the same as in the bulk of catalysts. After catalytic work, no changes in surface compositions as well as in BE were detected for all catalysts.

3.2. Catalyst surface reduction

Table 2 contains XPS data on reduction of catalysts by hydrogen carried out at 673 and 773 K within the pretreatment chamber of the spectrometer. At 673 K, nickel and antimony remained unreduced, while V^{5+} was partially reduced to V^{4+} and the extent of reduction was

Table 1
Characterization and catalytic activity results

Catalyst	S (m^2/g)	Phase composition	Rate[a] (mmol/(m^2 h))	Selectivity[b] (%)	
				3	10
NiV	99.7	$Ni_3V_2O_8$, NiO	0.13	45.7	41.8
SbV	100.7	$SbVO_4$, Sb_2O_4, V_2O_5	0.12	48.1	46.7
NiVSb	74.8	$Ni_3V_2O_8$, $SbVO_4$, $NiSb_2O_6$	0.09	63.2	50.0

[a] Overall reaction rate at conversion of about 10% and 723 K.
[b] Ethylene selectivities at conversions of 3 and 10%.

Table 2
XPS characteristics of differently treated mixed NiVSb oxides

Catalyst [a]	Binding energy [b] (eV)			Atomic ratio		
	V $2p_{3/2}$	Ni $2p_{3/2}$	Sb $3d_{3/2}$	V/Al	Ni/Al	Sb/Al
NiV						
f	517.6	856.6		0.186	0.105	
u	517.7	856.7		0.189	0.097	
r_1	517.2 (58)	856.8		0.067	0.111	
	515.7 (42)					
r_2	516.5	856.8 (90)		0.073	0.059	
		853.6 (10)				
VSb						
f	517.7		540.1	0.228		0.070
u	517.6		540.1	0.239		0.078
r_1	517.4 (55)		540.7	0.085		0.150
	515.9 (45)					
r_2	516.2		540.6	0.065		0.132
NiVSb						
f	517.7	856.6	540.1	0.214	0.160	0.060
u	517.4	856.5	540.0	0.226	0.164	0.058
r_1	517.1 (36)	856.8 (94)	540.5	0.066	0.100	0.116
	515.9 (64)	853.7 (6)				
r_2	516.3	856.7 (70)	540.6 (82)	0.054	0.069	0.121
		853.1 (30)	537.8 (18)			

[a] f: fresh; u: used; r_1: reduced at 673 K; r_2: reduced at 773 K.
[b] Numbers between parentheses indicate the %contribution of each component.

higher for the ternary NiVSb catalysts in comparison with the binary NiV and SbV catalysts. The reduction at 773 K induced larger differences. At this temperature, vanadium was completely reduced to V^{4+} in all three catalysts. Simultaneously, Ni^{2+} was partially reduced to Ni^0 in the NiV oxide and much more in the NiVSb oxide (fig. 1). The reduction of antimony was more difficult. Nevertheless, as seen from fig. 2, the antimony in the ternary composition showed higher reducibility than that present in the binary SbV oxide. Note also that in the reduced catalyst there was a noticeable decrease in the M/Al ratios probably due to the agglomeration of reduced components.

3.3. Catalyst bulk reduction

The TPR patterns of catalysts are shown in fig. 3. For the SbV oxide catalyst, there was one peak with the maximum at ca. 728 K. TPR profiles of nickel-containing oxides displayed two peaks, centered at ca. 613 and 707 K in the case of the NiV catalyst, and at ca. 630 and 713 K for the NiVSb catalyst. The data on integral consumption of hydrogen during the reduction are shown in table 3, which also includes the theoretical hydrogen consumptions calculated on the assumption of the complete reduction of the oxide to metal. The hydrogen uptake measured for the NiV catalyst was close to the calculated one, indicating that this mixed oxide was completely reduced under the conditions applied. The experimental hydrogen consumptions for SbV and NiVSb oxides were somewhat lower than those theoretically expected for their quantitative reduction to metals. Taking into account the above-presented XPS data on catalyst reduction, one may suggest that the small fraction of the antimony-containing oxide(s) remained unreduced or was partially reduced.

3.4. Catalytic behavior

The results of continuous ethane oxidation over supported NiVSb oxide catalyst and its binary NiV and SbV counterparts have been reported in detail in the previous communication [2]. The reaction products were only C_2H_4, CO and CO_2. The selectivity for dehydrogenation appeared to be little dependent on temperature in the range 673–773 K, being much more a function of the extent of ethane conversion. With increasing ethane conversion, the selectivity to CO_2 increased at the expense of the selectivity to ethylene, implying the existence of consecutive reactions for these products at longer residence times. Typical catalytic data presented in table 1 show that binary oxides are more active but less selective than the ternary composition.

4. Discussion

The TPR study of catalysts showed that the ease of

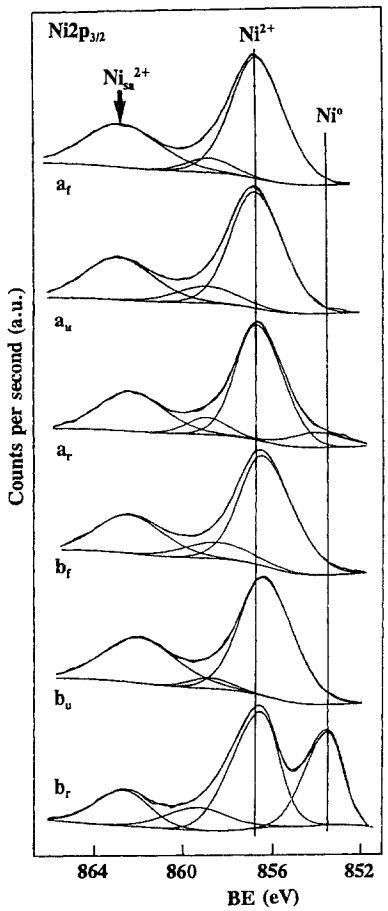

Fig. 1. Ni $2p_{3/2}$ spectra of (a) NiV and (b) NiVSb catalysts: (a_f, b_f) fresh; (a_u, b_u) after reaction; (a_r, b_r) reduced at 773 K.

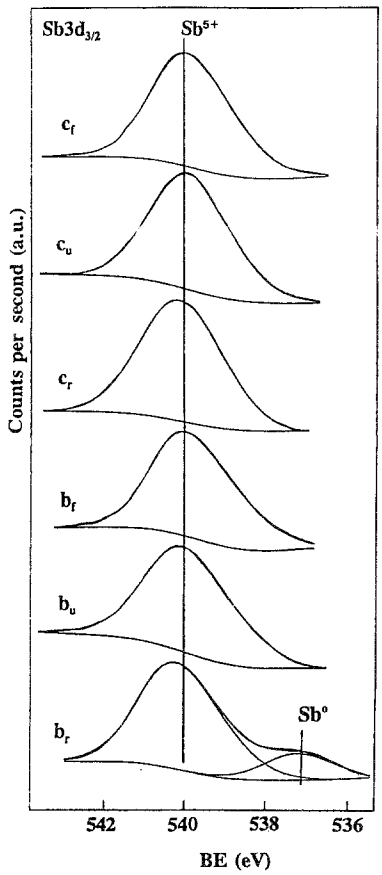

Fig 2. Sb $3d_{3/2}$ spectra of (b) NiVSb and (c) SbV catalysts: (b_f, c_f) fresh; (b_u, c_u) after reaction; (b_r, c_r) reduced at 773 K.

their bulk reduction by hydrogen was NiV > NiVSb > SbV. The results of catalyst surface reduction obtained by XPS technique indicated that the reducibility of catalyst components decreased in the order $V^{5+} > Ni^{2+} > Sb^{5+}$, and that all these cations in the ternary oxide exhibited higher reducibilities than those present in NiV and SbV oxides. For instance, vanadium reducibility decreased as follows: NiVSb > SbV > NiV. So, the results of catalyst bulk reduction differed from those of surface reduction. For the reasons mentioned in the Introduction, the surface reducibility was used for correlations with catalytic activity and selectivity.

The overall activity of catalysts, as it follows from the data presented in table 1, was NiV ≈ SbV > NiVSb, and the selectivity to ethylene decreased in the order NiVSb > SbV > NiV. Note that there is no correlation between the activity and reducibility, while the selectivity to ethylene follows the order similar to that for the surface reducibility, i.e. the most easily reduced catalyst is the most selective. The parallelism in changes of the OXD selectivity and catalyst redox properties was reported also for MoVNb [6] and MgV [7,11] oxides.

The relationship between OXD selectivity and catalyst reducibility can be interpreted assuming that the conversion of paraffin to both olefin and carbon oxides occurred on the catalyst surface. According to Burch

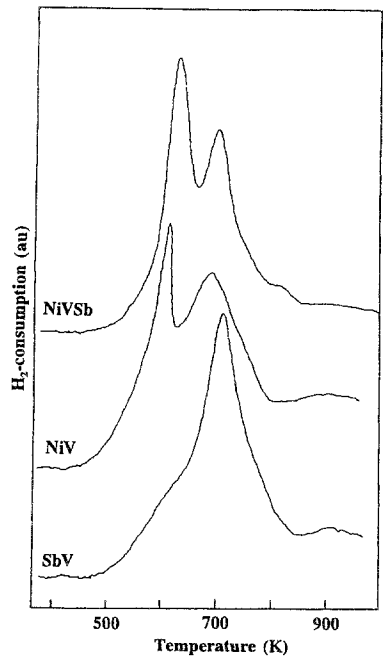

Fig 3. TPR profiles for NiV, SbV and NiVSb oxide catalysts.

Table 3
TPR parameters for binary and ternary oxide catalysts

Catalyst	Nominal content (wt%)			T_{max}	H_2 consumption (cm^3/g)	
	NiO	V_2O_5	Sb_2O_5	(K)	meas.	calc.
SbV	–	6	12	728	53.8	64.9
NiV	10	6	–	613, 707	69.7	67.2
NiVSb	10	6	12	630, 713	78.1	95.2

and Swarnakar [6], the relative contributions from pure heterogeneous and heterogeneous–homogeneous routes to alkene formation depend on the reaction temperature, as well as on the catalyst nature. At high temperatures (> 900 K), one would expect a greater tendency for alkyl species to desorb into the gas phase and form there alkene by reacting with dioxygen; for reducible oxides, particularly those based on transition metal oxides, there may be a greater tendency to produce alkene via surface alkoxide ion. Since our catalyst contained vanadium and nickel reducible oxides and operated at temperatures lower than 750 K, it seems very probable that the oxidation of ethane on the catalysts studied was a pure surface catalyzed reaction. This idea as supported by the linear relation between ethane conversion and contact time observed over NiVSb oxide catalyst [2], which suggests the absence of contributions from the heterogeneous–homogeneous reactions. Based on this assumption, a simplified version of redox mechanism for ethane oxidation can be proposed (here $N^{(I)}$ and $N^{(II)}$ denote the different reaction pathways under which the corresponding stoichiometric numbers for each step are written):

		$N^{(I)}$	$N^{(II)}$
step 1.	$Z + O_2 \xrightarrow{k_1} ZO_2$	1	1
step 2.	$ZO_2 + Z \xrightarrow{k_2} 2ZO$	1	0
step 3.	$ZO + C_2H_6 \xrightarrow{k_3} Z + C_2H_4 + H_2O$	2	0
step 4a.	$ZO_2 + C_2H_6 \xrightarrow{k_4} ZC_2H_6O_2$	0	1
step 4b.	$ZC_2H_6O_2 + 2.5O_2 \xrightarrow{fast} Z + 2CO_2 + 3H_2O$	0	1

$N^{(I)}$: $2C_2H_6 + O_2 \rightleftharpoons 2C_2H_4 + 2H_2O$

$N^{(II)}$: $C_2H_6 + 3.5O_2 \rightleftharpoons 2CO_2 + 3H_2O$

where ZO and Z respectively represent an oxidized and reduced site. The oxygen activation is assumed to proceed in two steps: formation of incompletely reduced oxygen species ZO_2 which can suggestedly be molecular radical O_2^-, and its transformation into the lattice oxygen ZO. The latter is involved in the OXD reaction, wheres the former oxidizes ethane into a surface intermediate of the carbonate–carboxylate type which then rapidly decomposes to CO_2 and H_2O by interaction with gas- phase oxygen [12]. Steps 3 and 4b are not elementary reactions being really more complex. For instance, step 3 comprises the first hydrogen abstraction with formation of an ethyl species, followed by its dehydrogenation to ethylene on the same active site. Similarly, step 4b involves a number of elementary rections of consecutive oxidation of the carboxylate-carbonate species to CO_2 and H_2O. To simplify the kinetic analysis, both steps are written as brutto-reactions. In this case, the OXD selectivity can be expressed as follows:

$$S = \frac{r_3}{r_3 + r_4} = \frac{k_3 P_h [ZO]}{k_3 P_h [ZO] + k_4 P_h [ZO_2]} .$$

In the steady state approximation regarding the reactive oxygen species the balance equations are:

$$[Z] + [ZO] + [ZO_2] = 1 ,$$

$$r_1 = r_2 + r_4 ,$$

$$2r_2 = r_3 .$$

By using them, the following expression for selectivity can easily be obtained:

$$S = \frac{2k_2[Z]}{2k_2[Z] + k_4 P_h} ,$$

where P_h is the partial pressure of ethane. In principle, a selectivity close to 100% can be achieved at $k_2[Z] \gg k_4 P_h$. This means that in addition to fast transformation of adsorbed oxygen species into the lattice oxygen (step 2), the presence of reduced sites on the catalyst surface is needed for obtaining a good OXD selectivity. The importance of both these factors for selective oxidation has been emphasized earlier by Sokolovskii [12]. Under the same reaction conditions, a more reducible catalyst is expected to be reduced to a larger extent and, hence, to exhibit better selectivity than a less reducible one. This is consistent with the data reported for alumina-supported vanadia in the OXD of butane: the more selective isolated VO_x species was more reduced at steady state than the less selective two-dimensional vanadia network [4].

The active sites of the V_2O_5-based catalysts are generally accepted to be vanadium ions, and the reaction mechanism is assumed through a redox cycle between

V^{5+} and V^{4+} [13]. It can consequently be suggested that the easier this cycle occurs, the more effective the catalyst is. This was the case for the NiVSb catalyst which showed both higher vanadium reducibility and OXD selectivity than NiV and SbV oxides did. The absence of free NiO and V_2O_5 in the ternary system can explain its better selectivity but not the increased vanadium reducibility. Compared to binary counterparts, the NiVSb catalyst contained the same $Ni_3V_2O_8$ and $SbVO_4$ phases and, in addition, a new $NiSb_2O_6$ phase which, however, did not comprise vanadium. It appears that there was a cooperation between these phases resulting in the enhancement of the vanadium reducibility. Neither the literature nor our results give a precise indication concerning the exact mechanism of such cooperation. Another explanation is that, when preparing the ternary catalyst, mutual contamination between the oxides containing and not containing vanadium took place. In a contaminated phase or layer, the occurrence of the $V^{5+} \leftrightarrow V^{4+}$ cycle could be assisted by the neighboring metallic ion absent in a pure phase. To elucidate which interpretation is more valid for our catalysts, specially designed experiments on pure and "artificially" contaminated phases as well as on their mixtures are needed. This work is in process.

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