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New results on the oxidative dehydrogenation of ethane to ethylene Promoting catalytic performance of Mo-V- and Ni-V-oxide by α-Sb_2O_4

T. Osawa[1], P. Ruiz*, B. Delmon

Unité de Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain, Croix du Sud 2/17, 1348 Louvain-la-Neuve, Belgium

Abstract

Synergetic effects were observed in the oxidative dehydrogenation of ethane to ethylene, when Mo-V-O or Ni-V-O catalysts are mechanically mixed with α-Sb_2O_4. Synergy was observed on the conversion, the yield and the selectivity in ethylene. XRD and XPS analyses showed that a chemical reaction between these oxides occurred during the reaction. The role of this contamination was evaluated taking into account results presented in the literature (namely, formation of Mo-Sb-O and $Ni_2Sb_2O_6$) and experimentally, by preparing V-Sb-O and mixing it with Ni-V-O. It is concluded that the formation of a Mo-Sb-O phase is excluded and that contamination induced by V-Sb-O alone cannot explain the synergetic effect observed. The more plausible explanation of the synergy should be the existence of a cooperation between Mo-V-O or Ni-V-O with α-Sb_2O_4. It is proposed that the role of added α-Sb_2O_4 (and $Ni_2Sb_2O_6$, if formed) would be to reoxidize the surface of Mo-V-O and Ni-V-O during the reaction, thanks to a spillover of oxygen.

Keywords: Oxidative dehydrogenation of ethane; Mechanical mixture; Spillover oxygen

1. Introduction

Catalytic oxidative dehydrogenation is believed to become an important industrial technology for the effective utilization of alkanes. Many catalytic systems have been proposed so far ([1–3] and references therein) for oxidative dehydrogenation of ethane to ethylene. These can be classified into two groups, active at temperatures higher or lower than 600°C. The former group consists of basic oxides of alkaline, alkaline earth, and/or rare earth metals. The latter is composed of oxides of the group V and/or VI metals. Most of the relatively effective catalysts of the latter group contain several phases. A representative is a Mo-V-Nb mixed oxide catalyst which can give 37% ethylene yield at 350°C. The effect of adding various metals other than Nb (Sb, Ta, Si, Fe, W, Sn) to the Mo-V system has also been reported [4]. The addition of Nb to Mo-V oxide increases the selectivity to ethylene by about 20%. It was suggested that Nb had two roles, i.e., to eliminate total oxidation sites from MoO_3 or V_2O_5 and to form new mixed phases containing selective sites [5]. The Ni-V-Sb mixed oxide was also reported to be superior to Ni-V-O or Sb-V-O oxides. It was suggested that a cooperation between oxide phases ($Ni_3V_2O_8$, $SbVO_4$, $NiSb_2O_6$) and the absence of NiO and V_2O_5 contributed to the elevation of the selectivity [6]. We have previously demonstrated

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* Corresponding author. Tel.: +32-10-47-3597;
fax: +32-10-47-3649.
E-mail address: ruiz@cata.ucl.ac.be (P. Ruiz).

[1] Present address: Faculty of Science, Toyama University, 3190 Gofuku, Toyama 930-8555, Japan.

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that synergetic effects were due to the concurrence of a remote control mechanism [7–9].

The objective of the present work is to contribute to the understanding of the catalytic performances of the oxide system reported in the literature. More specifically, we investigated the possibility that a co-operation between different phases does operate in the Mo-V-O and Ni-V-Sb catalysts and could explain literature results concerning Mo-V-Sb [4] and Ni-V-Sb [6] catalysts. We applied the following strategies: the starting hypothesis was that the Mo-V-O and Ni-V-O oxides were acceptors of spillover oxygen, and α-Sb_2O_4, a donor. We did not attempt to use pure Mo-V-O or Ni-V-O phases, but we used mixed oxide of the two metals, namely potentially bi- or multiphasic materials. These designated, respectively, Mo-V-O or Ni-V-O, were mixed mechanically with α-Sb_2O_4. The catalytic tests of each individual material and those of the mixtures were carried out in exactly the same conditions. Solid state modifications of the catalysts during the catalytic tests were detected thanks to characterization before and after the test, principally by XRD and XPS. The role of a possible chemical contamination which could occur due to (surface) reaction between the catalyst components in the Ni-V-O+α-Sb_2O_4 mixtures was evaluated by preparing a likely candidate product, namely V-Sb-O, and mixing it with Ni-V-O. We report on the synergetic effects introduced by mechanically mixing α-Sb_2O_4 with Mo-V-O or Ni-V-O catalysts. We propose a plausible explanation of the corresponding phenomena.

2. Experimental

2.1. Catalyst preparation

α-Sb_2O_4 was prepared by calcination of Sb_2O_3 (Aldrich) in air at 500°C for 20 h. Mo-V-O (Mo/V=4.1/1) was prepared by the citric acid method. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Merck, 19.1 g) was dissolved in 150 ml distilled water. After the transparent solution was obtained, 50.2 g of citric acid (Merck) was added. A solution of NH_4VO_3 (UCB, 3.1 g) and citric acid (10.3 g) was prepared in the same manner and was mixed with the first solution. After stirring for 5 h, this solution was evaporated under reduced pressure. The viscous solution was dried at 80°C in a vacuum oven at 80 mmHg for 20 h. The resulting solid was calcined in air at 550°C for 5 h.

Ni-V-O (Ni/V=3/2) was synthesized by an already reported method [6]. A solution of NH_4VO_3 (8.6 g) and tartaric acid (30.5 g) was mixed with a solution of $NiCl_2\cdot 6H_2O$ (UCB, 26.4 g) and tartaric acid (Merck, 18.3 g). The mixed solution was evaporated under reduced pressure to obtain a viscous liquid which was dried at 80°C in a vacuum oven (80 mmHg) for 20 h. The resulting solid was calcined for 2 h each at 200, 400 and 600°C successively. V-Sb-O (V/Sb=1/1) was also prepared by the citric acid method using solutions of (i) NH_4VO_3 (9.3 g) and citric acid (30.8 g) and (ii) $SbCl_3$ (Aldrich, 18.2 g) and citric acid (18.5 g). The mixed solution was evaporated under reduced pressure and dried at 80°C, at 80 mmHg for 20 h. The resulting solid was calcined in air at 550°C for 6 h. Mechanical mixtures of Mo-V-O with α-Sb_2O_4, Ni-V-O with α-Sb_2O_4, and one mixture of Ni-V-O with V-Sb-O (9:1) were prepared by introducing adequate quantities of the powders in *n*-pentane. The suspension was vigorously mixed (200 ml) for 3 min with a mechanical mixer (Ultra Turrax) at room temperature. The solvent was removed under reduced pressure. The composition of the mechanical mixtures is expressed as the mass ratio, R_m=weight A/(weight A+weight B), where A is the supposed acceptor, namely Mo-V-O or Ni-V-O, and B is α-Sb_2O_4.

2.2. Catalytic tests

Oxidative dehydrogenation of ethane to ethylene was carried out in a continuous gas-flow fixed bed reactor (Pyrex, 6 mm diameter) under atmospheric pressure with pure oxides and their mechanical mixtures in exactly the same experimental conditions using the same amount of catalyst (particle size between 0.1 and 0.315 mm, 1.5 or 1.0 g). The vacant space of the reactor was filled with small glass balls to prevent homogeneous reactions. Feed composition was ethane: 25%, O_2: 15%, He: 60%. Total feed rates were 8 ml/min (for experiments using Mo-V-O) or 12 ml/min (for experiments using Ni-V-O). A fresh catalyst was used in each test. Duration of the catalytic test was about 3 h after stabilization of reaction temperature. Catalytic activity was constant on time. Absence of mass transfer limitations was checked by varying the amount of catalysts introduced in the reactor. No conversion was observed in the reactor filled only with glass balls and in the absence of catalysts. Analyses of the products were made on line by gas chromatography (GC) (HP 5890 series II) using Molecular sieve 5A (2 m) and Haysep Q (2 m) (for the analyses of O_2, CO_2, and CO), and WCOT Fused Silica CP-Sil 8 CB (25 m×0.32 mm) (for the analyses of ethane and ethylene). The accuracy of the analysis is estimated to be about 1% of the values measured.

2.3. Synergetic effects

The synergetic effects were evaluated by comparing the conversion, yield, and selectivity with those of the theoretical values (obtained in the absence of synergetic effect). Taken as a first approximation, theoretical values on conversion and yield are calculated on the assumption of a zero order reaction. Under this assumption, conversion and yield are proportional to the amount of catalysts introduced in the reactor. Therefore, the theoretical values of the conversion, yield, and selectivity (C_{th}, Y_{th}, and S_{th}, respectively) were obtained by the following catalyst weight basis:

1. Catalytic tests of the mechanical mixture of Mo-V-O (Ni-V-O) and α-Sb_2O_4

$$C_{\text{th}}\,(\%) = \text{conversion ofethane by Mo-V-O (Ni-V-O)} \times R_{\text{m}} + \text{conversion of ethane by } \alpha\text{-Sb}_2\text{O}_4 \times (1 - R_{\text{m}})$$

$$Y_{\text{th}}\,(\%) = \text{yield of ethylene by Mo-V-O(Ni-V-O)} \times R_{\text{m}} + \text{yield of ethane by } \alpha\text{-Sb}_2\text{O}_4 \times (1 - R_{\text{m}})$$

$$S_{\text{th}}\,(\%) = \frac{100 \times Y_{\text{th}}}{C_{\text{th}}}$$

2. Catalytic tests of the mechanical mixture of Ni-V-O and V-Sb-O (9:1)

$$C_{\text{th}}\,(\%) = \text{conversion of ethane by V-Sb-O (0.1 g)} + \text{conversion of ethane by Ni-V-O (1 g)} \times 0.9$$

$$Y_{\text{th}}\,(\%) = \text{yield of ethylene by V-Sb-O (0.1 g)} + \text{yield of ethane by Ni-V-O (1 g)} \times 0.9$$

$$S_{\text{th}}\,(\%) = \frac{100 \times Y_{\text{th}}}{C_{\text{th}}}$$

2.4. Catalyst characterization

Catalysts were characterized before and after the catalytic tests by BET, XRD and XPS. BET surface areas were measured using a Micromeretics ASAP 2000 instrument by adsorption of krypton at 77 K on 200 mg of samples previously degassed at 150°C for 2 h at a pressure of 0.001 mmHg. XRD was performed on a Siemens D5000 diffractometer using the Kα radiation of Cu (λ=1.5418 Å). The 2θ range between 5 and 70° was scanned at a rate of 0.25°/min. Identification of the phases was carried out by using JCPDS data base. XPS analyses were performed with an SSX model 206 X-ray photoelectron spectrometer. The sample were pressed into small stainless steel troughs of 4 mm diameter. The surface positive charge was compensated by a floodgun operating at 8 eV using a nickel grid positioned 3 mm above the samples. The binding energy values were calculated using the C_{1s} band as reference (284.8 eV). The recorded spectra were decomposed to Gaussian/Lorentzian (85/15) curves using a least squares fitting routine after subtraction of the non-linear background. Element atomic ratios on the surface were calculated from the relative intensities of the decomposed peaks using the sensitivity factors supplied by the manufacturer. $Mo3d_{3/2}$ and $Mo3d_{5/2}$ bands were used for the calculation of Mo, $V2p_{3/2}$ for V, $Sb3d_{3/2}$ for Sb, and $Ni2p_{3/2}$ for Ni.

3. Results and discussion

3.1. Catalytic tests

3.1.1. Catalytic tests of Mo-V-O and their mixture with α-Sb_2O_4

The results are presented in Table 1. The addition of α-Sb_2O_4 induced a synergetic effect on ethane conversion and ethylene yield. Synergetic effects at the R_{m} values of 0.25 and 0.5 were larger than at R_{m}=0.75. For the latter composition ethylene selectivity decreased at 450°C, but slightly increased at 500°C.

3.1.2. Catalytic tests of Ni-V-O and their mixture with α-Sb_2O_4

Table 2 shows the results obtained with Ni-V-O, α-Sb_2O_4 and their mechanical mixtures. When the

Table 1
Catalytic activity of Mo-V-O, α-Sb_2O_4 and their mechanical mixtures[a]

R_m, Mo-V-O/(Mo-V-O+Sb_2O_4)	450°C			500°C		
	Ethane conversion (%)	Ethylene yield (%)	Ethylene selectivity (%)	Ethane conversion (%)	Ethylene yield (%)	Ethylene selectivity (%)
1.0	6.7	1.7	25.7	11.1	3.4	30.9
0.75	7.5 (5.8)	1.7 (1.5)	22.2 (26.6)	11.6 (9.3)	3.5 (2.6)	30.1 (27.7)
0.5	7.4 (4.9)	1.5 (0.8)	20.0 (17.4)	11.7 (7.6)	3.3 (1.8)	28.1 (23.5)
0.25	4.7 (4.0)	1.2 (0.4)	26.6 (10.8)	9.7 (5.9)	2.8 (1.0)	29.3 (16.9)
0.0	3.2	0.02	0.7	4.2	0.2	3.8

[a] Theoretical value (%) is indicated in parentheses. Amount of catalyst: 1.5 g.

R_m value was 0.75, almost no synergetic or even a negative effect was observed. For values of R_m of 0.5 and 0.25, synergetic effects were observed in the ethane conversion at 500°C. Almost no, or even a negative effect, on ethylene selectivity was observed at 500°C.

3.2. Catalyst characterization

3.2.1. BET

Specific surface areas were Mo-V-O=1.7 (cm^2/g), Ni-V-O=2.5 (cm^2/g), α-Sb_2O_4=1.7 (cm^2/g) and V-Sb-O=10 (cm^2/g). For mechanical mixtures, the BET specific surface area corresponded to the single addition of those of pure oxides. No appreciable change was observed after catalytic test.

3.2.2. XRD: JCPDS data base references are indicated in parenthesis

Mo-V-O was a mixture of MoO_3 (No. 35-0609) and V_2MoO_8 (No. 20-1377). Ni-V-O was a mixture of $Ni_3V_2O_8$ (No. 37-0353) and small amounts of NiO (No. 22-1189).V-Sb-O was composed of V_2O_5 (No. 41-1426) and $V_{0.11}Sb_{0.9}O_4$ (No. 37-1075). Sb_2O_4: synthesized Sb_2O_4 found to be α-Sb_2O_4 (No. 11-0694).

The XRD patterns of the mechanical mixtures corresponded exactly to the superposition of those observed for the individual oxides. No change was observed between the phases before and after the catalytic tests.

3.2.3. XPS

Mo in fresh pure Mo-V-O sample was principally Mo^{6+} (236.0 eV, about 92%) and a small amount of Mo^{5+} (234.6 eV, about 8%) (10). After test, Mo^{6+} and Mo^{5+} are always observed, but in addition Mo is strongly reduced to Mo^{4+} (231.5 eV, about 17%).When α-Sb_2O_4 was added to Mo-V-O, only Mo^{6+} was observed before or after the catalytic tests. The binding energy of $Mo3d_{3/2}$ attributed to Mo^{6+} remained nearly unchanged (236.2–235.9 eV). In all cases the $V2p_{3/2}$ (517.0 eV), $Sb3d_{3/2}$ (540.3 eV)

Table 2
Catalytic activity of Ni-V-O, α-Sb_2O_4 and their mechanical mixtures[a]

R_m, Ni-V-O/(Ni-V-O+Sb_2O_4)	450°C			500°C		
	Ethane conversion (%)	Ethylene yield (%)	Ethylene selectivity (%)	Ethane conversion (%)	Ethylene yield (%)	Ethylene selectivity (%)
1.0	6.6	1.1	17.1	10.6	2.9	26.9
0.75	5.9 (5.4)	0.8 (0.8)	14.2 (15.2)	7.9 (8.5)	2.1 (2.2)	26.3 (25.7)
0.5	5.3 (4.3)	0.8 (0.5)	15.7 (13.0)	8.5 (6.5)	1.8 (1.5)	21.2 (22.9)
0.25	4.2 (3.1)	0.6 (0.3)	13.1 (9.2)	7.1 (4.4)	1.0 (0.8)	13.7 (17.8)
0.0	2.0	0.02	0.9	2.4	0.08	3.2

[a] Theoretical value (%) is indicated in parentheses. Amount of catalyst: 1.0 g.

binding energies did not change after the tests. For pure Ni-V-O and in mixtures with α-Sb_2O_4, the binding energy of $V2p_{3/2}$ (516.7–516.9 eV), $Sb3d_{3/2}$ (539.8–540.1 eV) $Ni2p_{3/2}$ (855.4–855.7 eV) did not change after the tests.

The XPS surface atomic ratio of Mo/V on the surface was much higher (6.1) than that of the bulk (4.1). After the test, this value increased (8.2) substantially when R_m was 1.0 and increased only slightly (5.0) for R_m=0.5. For R_m=0.25 Mo/V decreases slightly (3.5). Sb/Mo and Sb/V decrease after the test (from 0.8 to 0.5 and 3.4 to 2.6 for R_m=0.5 and from 2.9 to 1.4 and 12.8 to 5.0 for R_m=0.25, respectively).

For pure Ni-V-O, the surface Ni/V ratio was a little higher (1.9) than that of the bulk ratio (1.5). This ratio remained almost unmodified after the catalytic test (1.7). In mixtures with α-Sb_2O_4, Ni/V ratio remains unchanged after the test (1.8) for R_m=0.5, and decreases (from 1.9 to 1.6) for R_m=0.25. Sb/Ni decreased (from 1.7 to 1.0) after the test for R_m=0.5, but remains almost unchanged (3.1–3.2) for R_m=0.25. Sb/V decreased after the test (from 3.2 to 1.9 for R_m=0.5 and from 5.8 to 5.2 for R_m=0.25).

3.3. *Role of a V-Sb-O new phase*

Table 3 shows the results of the oxidative dehydrogenation of ethane over Ni-V-O, V-Sb-O, and their mechanical 9:1 mixture. V-Sb-O only acted synergetically with Ni-V-O with respect to ethylene selectivity. This effect decreased when the temperature changed from 450 to 500°C. Ethane conversion and ethylene yield decreased compared with the values observed in the absence of any effect (theoretical values).

4. Discussion

In spite of the ethane conversion and ethylene yield being not excessively high, it is obvious that the catalytic tests showed that the addition of α-Sb_2O_4 to Mo-V-O and Ni-V-O induces a synergetic effect. It is true in almost all experimental conditions in the case of the Mo-V-O system, especially at 500°C. For Ni-V-O, this depends on the temperature and the content of α-Sb_2O_4. It can be recalled that, in a general way, possible explanations of synergetic effects in mixtures of oxides are the following: (i) contamination of the surface of one phase by a small amount of element coming from the other or formation of a new phase due to reaction between two phases, (ii) an alternative dual site (bifunctional) mechanism between two phases, and (iii) creation and regeneration of the active sites on one phase by spillover oxygen emitted by the other (remote control mechanism).

The XRD analyses did not indicate any change “before” and “after” the tests. This means that no new phase detectable by XRD was generated during the catalytic tests. This conclusion can also be supported by the fact that there was no change of the binding energy of $V2p_{3/2}$, $Sb3d_{3/2}$, $Mo3d_{3/2}$, and $Ni2p_{3/2}$ after the test when α-Sb_2O_4 was added. In principle, the formation of new phases (principally $V_xSb_{1-x}O_y$ or $Ni_2Sb_2O_6$) could be expected. On the other hand, XPS Sb/Mo and Sb/V atomic ratios in Mo-V-O+α-Sb_2O_4, and XPS Sb/Ni and Sb/V atomic ratios in Ni-V-O+α-Sb_2O_4 (with R_m=0.5) decreased after the tests. One explanation of these results would be a sintering of α-Sb_2O_4 during the catalytic test. However, this explanation seems contradictory to previous results [11] in which a sintering was observed

Table 3
Catalytic activity of Ni-V-O, V-Sb-O and their mechanical mixture (9:1)[a]

Catalyst	450°C			500°C		
	Ethane conversion (%)	Ethylene yield (%)	Ethylene selectivity (%)	Ethane conversion (%)	Ethylene yield (%)	Ethylene selectivity (%)
Ni-V-O (1 g)	6.6	1.1	17.1	10.6	2.9	26.9
Ni-V-O+V-Sb-O (0.9 g+0.1 g)	10.4 (17.8)	3.0 (3.7)	28.7 (20.8)	16.5 (25.2)	5.3 (6.9)	32.3 (27.4)
V-Sb-O (0.1 g)	11.9	2.7	22.9	15.7	4.3	27.7

[a] Theoretical value (%) is indicated in parentheses.

only after a longer time of calcination and at higher temperature (600°C/24 h) than the maxima attained in the present work. On the other hand, when α-Sb_2O_4 was added to Ni-V-O (R_m=0.25), Sb/Ni did not change and Sb/V changed slightly, which is in contradiction with a sintering of oxides, and hence we have to abandon this explanation. A more plausible explanation is a chemical contamination between the oxide phases produced by a reaction between Sb and Mo-V-O or Sb and Ni-V-O. We have reported previously that MoO_3 was not contaminated by the addition of α-Sb_2O_4. More precisely, the formation of a Mo-Sb-O mixed phase is completely excluded [12,13]. The mixed phases which could be formed are thus $V_xSb_{1-x}O_y$ or $Ni_2Sb_2O_6$. The role of a V-Sb-O mixed phase was studied previously in the oxidative dehydrogenation of propane [14]. It was observed that this phase was extremely active and non-selective and failed to promote any improvement in yield or selectivity to propene when in contact with the same Mo-V-O phase used in this work. In the present study, when V-Sb-O was added to Ni-V-O, the ethylene selectivity increased only slightly, and the ethane conversion and ethylene yield significantly decreased. Therefore, the contamination induced by α-Sb_2O_4 (formation of a new V-Sb-O phase) alone cannot explain the synergetic effect observed in this study.

A classical bifunctional mechanism seems difficult to be accepted, because the intermediate species formed after the first abstraction of hydrogen is larger than oxygen species which would more easily migrate between the phases. Another explanation would be the formation of a monolayer by spreading Sb_2O_4 on the surface. Experimental results are in contradiction with this explanation, in fact in all cases the Sb/Mo, Sb/V or Sb/Ni and Sb/V, decreases after the catalytic reaction. The opposite should be observed in the case of antimony (spreading) monolayer formation.

Concerning the role of $Ni_2Sb_2O_6$, Breiter [15] demonstrated that, under industrial conditions, this phase is inactive in the oxidation of acrolein to acrylic acid. However, this phase considerably increases the performance of an already optimized catalyst of formula $Mo_{12}V_3W_{1.2}Cu_2O_x$. The authors attributed this effect to the oxygen-donor properties of $Ni_2Sb_2O_6$.

Our results indicate that the amount of Mo^{4+} increased after the test when Mo-V-O worked alone, but Mo^{4+} was not observed in the presence of α-Sb_2O_4. This fact suggests that the role of α-Sb_2O_4 is to reoxidize the surface of Mo-V-O during the reaction avoiding deep reduction. In other words, α-Sb_2O_4 maintains Mo in an optimal, less reduced, oxidation state during the reaction. Similar phenomena could occur on the surface of Ni-V-O. The role of spillover in the stabilization of surfaces at a more oxidized level with a parallel diminution of the amount of “shear structures” and reconstruction of surfaces has been discussed previously [7,12,13,16–18]. The existence of spillover has been demonstrated by experiments with ^{18}O, and confirmed by FTIR and Raman spectroscopies [19–21].

Our conclusion is that the more plausible explanation of the synergetic effects observed would be a cooperation between α-Sb_2O_4 and Mo-V-O and Ni-V-O oxide phases via spillover oxygen as the remote control predicts. If $Ni_2Sb_2O_6$ is formed, it certainly contributes to the synergy by its donor role. Both Mo-V-O and Ni-V-O oxide phases are acceptor of oxygen spillover.

The catalytic performances of pure Mo-V-O could also be explained taking into account this type of cooperation. It can be suggested that in this catalyst, MoO_3 plays the role of an acceptor of oxygen spillover and V_2MoO_8 the role of a weak donor as has been shown in the oxidative dehydrogenation of propane in propene [14]. In the Ni-V-O catalyst, an acceptor role could be attributed to $Ni_3V_2O_8$. More studies are necessary to attribute a role to NiO.

In this work it has been showed that α-Sb_2O_4 is important to improve catalytic performances of Mo-V-O and Ni-V-O oxide phases. But, as we have discussed previously, other oxides can potentially be better donors than α-Sb_2O_4 and the synergetic effect should be significantly increased. We have demonstrated that the same mechanism discussed in this work has been observed in other reactions in which oxygen plays an important role: oxidation of isobutene to methacrolein, oxidation of butane to maleic anhydride, oxidative dehydrogenation of methanol in formaldehyde, of ethanol in acetaldehyde, of ethanol to acetic acid, of butene to butadiene, propane or pentane to the corresponding olefins and the dehydration of formamides to nitriles in the presence of oxygen [7–14,16–18], etc. We have proposed a scale of acceptor–donor properties of oxides often used as catalysts in selective oxidation catalysis [12,16,17]. This scale can be useful to select the more adequate donor to optimize cooperative effects via the remote control mechanism.

5. Conclusions

When Mo-V-O and Ni-V-O catalysts were mechanically mixed with α-Sb_2O_4, synergetic effects were observed in the oxidative dehydrogenation of ethane. XPS analyses indicate the possible existence of a contamination between the oxides. The role of this contamination was evaluated following previous studies and by mixing synthesized V-Sb-O with Ni-V-O. The contamination induced by α-Sb_2O_4 alone could not explain the synergetic effect observed in this study. One plausible explanation of the synergy observed in this study would be that added α-Sb_2O_4 could reoxidize the surface of Mo-V-O and Ni-V-O during the reaction, thanks to spillover oxygen, thus increasing the number of selective sites and inhibiting non-selective ones.

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