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Mixed MVSb oxides as oxidehydrogenation catalysts

E.A. Mamedov [a], R.M. Talyshinskii [a], R.G. Rizayev [a], J.L.G. Fierro [b], V. Cortes Corberan [b]

[a] *Institute of Inorganic and Physical Chemistry, 370143 Baku, Azerbaijan Republic*
[b] *Instituto de Catalisis y Petroleoquimica, C.S.I.C., Cantoblanco, 28049 Madrid, Spain*

Abstract

Mixed MVSb (M = Ni, Co, Bi, Sn) oxides supported by alumina were characterized and evaluated for oxidative dehydrogenations of light paraffins, ethylbenzene and ethanol. The most selective NiVSb catalyst was the most easily reduced that was interpreted on the assumption of reaction redox mechanism. The results of kinetic measurements revealed the concentration of gas-phase oxygen to be a key parameter affecting the dehydrogenation selectivity. To maintain it an optimum along the catalyst bed, a distributed oxygen feed was used.

Keywords: MVSb oxides; Oxidehydrogenation catalysts

1. Introduction

Alumina-supported BiVSb oxide system developed by us [1] catalyzes with high activity and selectivity (95–98%) the ammoxidation of alkylbenzenes to the corresponding aromatic nitriles. In the absence of ammonia, the oxidation of toluene and xylenes yields mainly the products of their dealkylation and total oxidation. Such behaviour of the catalyst can be explained by a so-called 'dehydrogenation' mechanism occurring via amine- and imine-like intermediates, which has been evidenced by means of different techniques [2,3]. In as much the alkylbenzene conversion to nitrile occurs along the side chain, one would expect the same catalyst to be active in the oxidative dehydrogenation of alkanes. This idea has been confirmed by recent studies [4,5], which revealed the ability of the BiVSb oxide to catalyze the oxidehydrogenation of C_2–C_5 paraffins. It was shown also that the replacement of bismuth by nickel or cobalt used as components in some dehydrogenation catalysts enhanced the dehydrogenation selectivity. Moreover, these catalytic systems have been found to be effective in oxidative dehydrogenations of ethylbenzene to styrene [6] and of ethanol to acetaldehyde [7] as well.

This paper summarizes the data on catalytic performances of mixed MVSb (M = Ni, Co, Bi, Sn) oxides in the oxidehydrogenation of different hydrocarbons. Here we report also the results of catalyst characterization as well as of kinetic and mechanistic studies carried out with a goal to find the ways for improving their catalytic behaviour.

2. Experimental

Catalysts were prepared by impregnation of γ-alumina spheres (1.8–2.0 mm diameter) with

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solutions of ammonium metavanadate and chlorides or nitrates of other metals in tartaric acid. The alumina had a specific surface area of 200 m^2/g and a pore volume of 0.50 cm^3/g. The samples were dried at 393 K and then calcined in air in three steps at 473, 673 and 1073 K for 2 h at each temperature. The total amount of supported components did not exceed 28 wt%. The quantitative composition of catalysts as well as the detailed preparation procedure were reported elsewhere [1,4–6].

Calcined catalysts were characterized before and after reaction by BET surface area measurements, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR) by hydrogen.

Catalytic activity was tested in a tubular, down-flow quartz reactor with a fixed bed of catalyst. Experiments on catalyst long exploitation were run in a pilot scale installation using a fluidized-bed reactor and a fixed-bed reactor with a distributed oxygen feed. Reaction kinetics was studied in a gradientless flow reactor with a vibro-fluidized bed of catalyst. The absence of diffusion control was checked by varying both the catalyst particle size and linear flow rate. Reactants and products were analyzed on-line with a gas chromatograph. Further details on the analysis are available in [4,5].

3. Results and discussion

3.1. Catalytic activity and characterization results

The results of oxidative dehydrogenation of ethane, *n*-butane and isopentane over supported NiVSb, CoVSb, BiVSb and SnVSb oxide catalysts were reported in detail in previous communications [4,5]. Typical catalytic data for these paraffins together with the corresponding data for ethylbenzene and ethanol conversions to respectively styrene and acetaldehyde are presented in Table 1.

Table 1
Activity and selectivity of MVSb oxides in oxidehydrogenation of different hydrocarbons

Catalyst	Hydrocarbon	Conversion (%)	Selectivity (%)
NiVSb	Ethane [a]	14	46
	Butane [b]	40	72
	Isopentane [c]	23	61
	Ethylbenzene [d]	61	90
CoVSb	Ethane [a]	16	42
	Isopentane [c]	26	68
SnVSb	Ethane [a]	24	43
	Butane [b]	48	67
BiVSb	Ethane [a]	15	40
	Butane [b]	36	65
	Ethanol [e]	100	70

[a] 773 K, $C_2H_6/O_2 = 2.5/1$, $\tau = 0.6$ s.
[b] 923 K, $C_4H_{10}/O_2/H_2O = 1/1/20$, $\tau = 1.0$ s.
[c] 878 K, $C_5H_{12}/O_2/H_2O = 1/1/20$, $\tau = 1.0$ s.
[d] 873 K, $C_8H_{10}/O_2/H_2O = 1/0.5/8.5$, $\tau = 1.2$ s.
[e] 563 K, $C_2H_5OH/O_2/H_2O = 1/1.6/3.5$, $\tau = 1.5$ s.

Catalyst testings carried out under the same reaction conditions showed that the overall activity of ternary oxides decreased in the order SnVSb $\gg$ CoVSb $>$ BiVSb $>$ NiVSb, and the oxidehydrogenation selectivity was like NiVSb $>$ CoVSb $\approx$ SnVSb $\approx$ BiVSb. As was reported elsewhere [5], the most active SnVSb catalyst and its binary SbV counterpart consisted of the antimony vanadate $SbVO_4$ and small amounts of the corresponding individual oxides. Another SnV counterpart was a mixture of SnO_2 and V_2O_5. These catalysts showed similar XPS binding energies for metal cations, indicating that their oxidation states, identified as being Sn^{4+}, V^{5+} and Sb^{5+}, were independent of catalyst composition. By comparing XPS relative proportions of metals to their nominal ratios, it was revealed that the surfaces of SnV, SbV and SnVSb catalysts were strongly enriched in vanadium [5]. Since the binding energies for the $V2p_{3/2}$ for these samples were 0.7–0.8 eV higher than that for pure $SbVO_4$ (516.8 eV) but close to the binding energy for V_2O_5 (517.4 eV), one may suggest that their surfaces were predominantly covered with the vanadium pentoxide known to be a rather active oxidation catalyst. As a consequence, the extent of paraffin conversion reasonably increased with increasing the vanadium proportion at the surface of SnV, SbV and SnVSb oxide catalysts (Fig. 1).

Such a relationship was not observed for the most selective NiVSb catalyst and its NiV and SbV constituents, since both nickel-containing samples did not contain free V_2O_5. The XRD pattern of the NiVSb oxide system showed the presence of the nickel orthovanadate, nickel antimonate and antimony vanadate phases [5]. The NiV catalyst contained, along with the $Ni_3V_2O_8$ phase, small amount of NiO. Neither the phase composition nor the oxidation states of supported metal cations, identified with XPS as being Ni^{2+}, V^{5+} and Sb^{5+}, changed after use in catalytic reaction (Table 2).

Taking into account that NiV and SbV oxides were more active but less selective than the NiVSb oxide, the enhanced selectivity of ternary catalyst could be related to the absence of free vanadium and nickel oxides. 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 [8]. In this respect, it was interesting to study and compare the reducibilities of the NiVSb catalyst and its binary NiV and SbV counterparts.

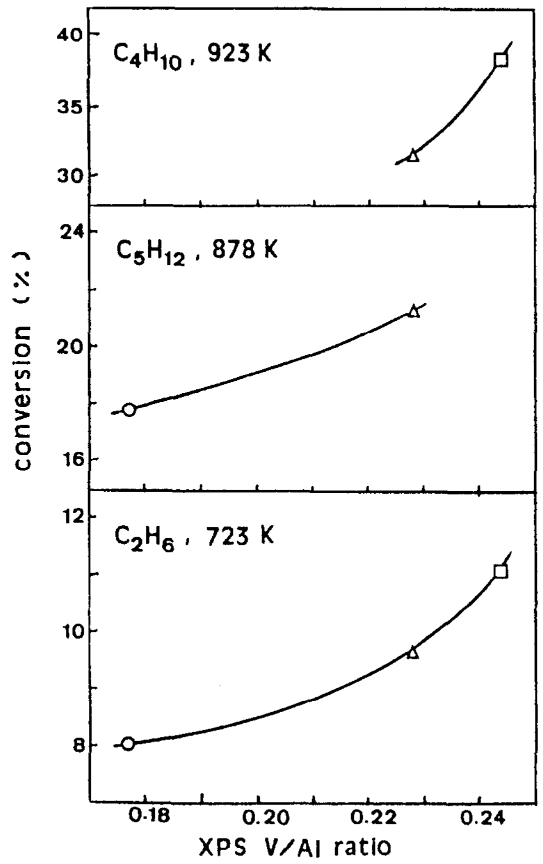

Fig. 1. Paraffin conversion vs. vanadium proportion at the surface of SnV (○), SbV (△) and SnVSb (□) oxide catalysts.

Table 2
XPS characteristics of differently treated mixed NiVSb oxides

Catalyst [a]		Binding energy (eV) [b]			Atomic ratio		
		$V2p_{3/2}$	$Ni2p_{3/2}$	$Sb3d_{3/2}$	V/Al	Ni/Al	Sb/Al
NiV	A	517.6	856.6		0.186	0.105	
	B	517.7	856.7		0.189	0.097	
	C	517.2 (58) 515.7(42)	856.8		0.067	0.111	
	D	516.5	856.8(90) 853.6(10)		0.073	0.059	
SbV	A	517.7		540.1	0.228		0.070
	B	517.6		540.1	0.239		0.078
	C	517.4(55) 515.9(45)		540.7	0.085		0.150
	D	516.2		540.6	0.065		0.132
NiVSb	A	517.7	856.6	540.1	0.214	0.160	0.060
	B	517.4	856.5	540.0	0.226	0.164	0.058
	C	517.1(36) 515.9(64)	856.8(94) 853.7(6)	540.5	0.066	0.100	0.116
	D	516.3	856.7(70) 853.1(30)	540.6(82) 537.8(18)	0.054	0.069	0.121

[a] (A), fresh; (B), after oxidation of ethane; (C), reduced at 673 K; (D), reduced at 773 K.

[b] In parentheses, the percentages of the element different peaks, if any, are given.

3.2. Relationship between catalyst reducibility and selectivity

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, antimony remained unreduced in all samples, and nickel was slightly reduced only in the NiVSb catalyst. V^{5+} was partially reduced to V^{4+} in all samples, and the extent of reduction was higher for the ternary NiVSb catalyst 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. The reduced antimony was detected only in the ternary composition. These results indicate that the surface reducibility of the 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 less selective NiV and SbV oxides.

The catalyst temperature-programmed reduction is shown in Fig. 2. For the SbV oxide, there was one peak with the maximum at ca. 728 K. TPR profiles of nickel-containing oxides displayed two peaks which centered at ca. 613 and 707 K in the case of NiV catalyst, and at ca. 630 and 713 K for NiVSb catalyst. These results imply that under the temperature-programmed conditions, the ease of catalyst bulk reduction by hydrogen was like NiV ≈ NiVSb > SbV.

When comparing the surface reducibilities of the NiV, SbV and oxides with their catalytic properties presented in Table 3, it appears that the most easily reduced catalyst was the most selective. Similar result was reported earlier for VMoNb oxides in the reaction of ethane [9] and for three magnesium vanadate phases in the reaction of propane [10].

The relationship between oxidehydrogenation selectivity and catalyst reducibility can be interpreted assuming that the conversion of paraffin to both olefin and carbon oxides occurred on the catalyst surface. This idea is supported by the linear relation between the ethane conversion and contact time observed over NiVSb oxide

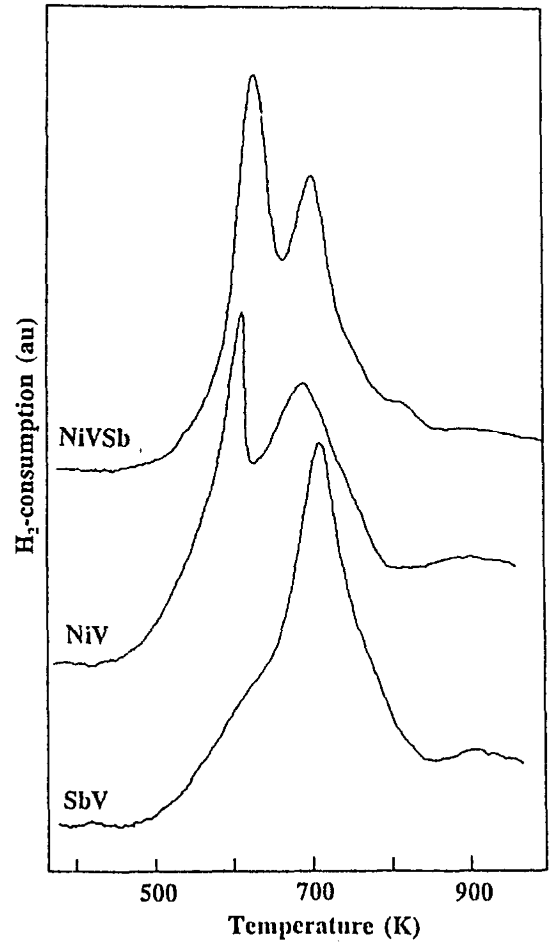

Fig. 2. Temperature-programmed reduction of catalysts (10% H_2 in Ar; heating rate, 10 K/min).

Table 3
Catalytic activity and selectivity of NiVSb oxides in the oxidative dehydrogenation of ethane

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

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

Table 4
Simplified version of the redox mechanism for ethane oxidation

		$N^{(I)}$	$N^{(II)}$
Step 1	$Z + O_2 \overset{k_1}{\Rightarrow} ZO_2$	1	1
Step 2	$ZO_2 + Z \overset{k_2}{\Rightarrow} 2ZO$	1	0
Step 3	$ZO + C_2H_6 \overset{k_3}{\Rightarrow} Z + C_2H_4 + H_2O$	2	0
Step 4a	$ZO_2 + C_2H_6 \overset{k_4}{\Rightarrow} ZC_2H_6O_2$	0	1
Step 4b	$ZC_2H_6O_2 + 2.5O_2 \overset{\text{fast}}{\Rightarrow} Z + 2CO_2 + 3H_2O$	0	1
	$N^{(I)}$: $2C_2H_6 + O_2 = 2C_2H_4 + 2H_2O$ $N^{(II)}$: $C_2H_6 + 3.5O_2 = 2CO_2 + 3H_2O$		

catalyst [5], 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 and this is given in Table 4 (here $N^{(I)}$ and $N^{(II)}$ denote, respectively, different reaction pathways under which the corresponding stoichiometric numbers for each step are written). ZO and Z in Table 4, respectively, represent an oxidized and a reduced site. The oxygen activation is assumed to proceed in two steps: formation of incompletely reduced oxygen species ZO_2 which may be the molecular radical ion O_2^-, and its transformation into the lattice oxygen ZO. The latter is involved in the oxidehydrogenation reaction, whereas 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 [11]. In this case, the oxidehydrogenation selectivity can be expressed as follows:

$$S = \frac{r_3}{r_3 + r_4}$$

By using a steady state approximation regarding reactive oxygen species, it can be transformed into the expression:

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

where P_h is the partial pressure of ethane. In principle, a selectivity close to 100% can be achieved at $k_2[Z] \gg k_4 P_h$. In addition to a high value of k_2, the presence of reduced sites on catalyst surface is needed to obtain a good oxidehydrogenation selectivity. Under the same reaction conditions, more reducible catalyst is expected to be reduced to larger extent and, hence, to exhibit better selectivity than less reducible one. This is consistent with the data reported for alumina-supported vanadia in the oxidative dehydrogenation of butane: more selective isolated VO_x species was more reduced at steady state than less selective two-dimensional vanadia network [12].

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 oxidehydrogenation 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, 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 neighbouring 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 progress.

3.3. Reaction network and kinetics

Ethane, *n*-butane and isopentane oxidations over the studied catalysts yielded olefins, dienes, CO and CO_2; no other oxygenated products were detected. The oxidehydrogenation selectivity decreased with increasing the paraffin conversion, and was much less a function of temperature than of conversion. The apparent activation energies for paraffin oxidehydrogenation and total oxidation are listed in Table 5. Within the error range, the activation energies for these two reactions did not differ strongly, thus explaining a low sensitivity of the dehydrogenation selectivity to temperature.

The effect of contact time on the catalytic performance of the NiVSb oxide indicated that at short residence times olefins and carbon oxides were formed from paraffin via parallel reactions. When extrapolated to zero conversion, the dehydrogenation selectivity was rather high, up to 90%. With increasing the paraffin conversion, the selectivity to CO_2 increased at the expense of the total selectivity to olefins and dienes, implying the existence of consecutive reactions upon these products at longer residence times. Herein, butadiene and isoprene demonstrated much higher reactivity with respect to combustion than the corresponding monoolefins. These results favour a parallel-consecutive reaction network.

The kinetics of oxidative conversion of *n*-butane, isopentane and ethylbenzene over the NiVSb oxide catalyst was described by the same model based on redox mechanism. The rates of oxidehydrogenation and total oxidation reactions obeyed the expressions $r_i = k_i P_h P_o^{0.5}$ and $r_j = k_j P_h P_o$, respectively, in which P_h and P_o are the paraffin (ethylbenzene) and oxygen partial pressures. Since they had exhibited different dependences on the concentration of gas-phase oxygen, this variable appeared to be a key parameter affecting the oxidehydrogenation selectivity.

Table 5
Apparent activation energies for oxidative dehydrogenation and destruction of paraffins over NiVSb oxide catalyst

Paraffin	E (kcal/mol)	
	Dehydrogenation	Destruction
Ethane	23±2	29±4
n-Butane	36±3	33±4
i-Pentane	34±4	44±4

Using the kinetic data, mathematical modelling and optimization of processes were carried out. From a reactor design point of view, two modes of operation were predicted to have a good outlook. These were (i) a cascade of fixed-bed reactors (or catalyst layers) with a distributed oxygen feed, and (ii) a fluidized-bed reactor with a single cofeed of hydrocarbon and oxygen. By carrying out the oxidative dehydrogenation of butane in the three-sectional fixed-bed reactor, it was indeed possible to increase the butadiene yield from 17 to 22–23% per single pass. When using a recycling technology, it rose to 30%. In the one-sectional fluidized-bed reactor, a higher total selectivity to butenes and butadiene at considerably lower C_4H_{10}/H_2O molar ratios was obtained. In this case, however, there were some problems with a mechanical strength of catalyst spheres. As for the stability of catalytic activity, it did not change during a 500 h pilot scale run.

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