ELSEVIER

Catalysis Today 81 (2003) 77–85

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Oxidative dehydrogenation of propane on pure and silica-dispersed multimetallic oxides based on vanadium and niobium prepared via hydrolytic and non-hydrolytic sol–gel methods

Pietro Moggi [a], Michel Devillers [b,*], Patricio Ruiz [c], Giovanni Predieri [d], Daniele Cauzzi [d], Sonia Morselli [a], Omar Ligabue [a]

[a] *Department of Organic and Industrial Chemistry, Parma University, Parco Area delle Scienze 17/A, 43100 Parma, Italy*
[b] *Chemistry of Inorganic and Organic Materials, Chemistry Department, Université Catholique de Louvain, Place Louis Pasteur 1/3, Louvain-la-Neuve B-1348, Belgium*
[c] *Unité de Catalyse et de Chimie des Matériaux Divisés, Université Catholique de Louvain, Place Croix du Sud 2/17, Louvain-la-Neuve B-1348, Belgium*
[d] *Department of General and Inorganic Chemistry, Analytical Chemistry and Physical Chemistry, Parma University, Parco Area delle Scienze 17/A, 43100 Parma, Italy*

Abstract

Pure and silica-dispersed Nb-V, V-Sb and Nb-V-M (M = Sb, Mo) oxide systems were prepared by applying the less conventional sol–gel methods and tested as catalysts in the oxidative dehydrogenation (ODH) of propane. All the prepared systems were active in the propane ODH and selective to propene, particularly the 1:1:5 Nb-V-Si prepared via the non-hydrolytic sol–gel method and the 1:1 Sb-V prepared via the hydrolytic route. Acrolein was detected among the reaction products when working with higher reagents partial pressures and contact time.

Keywords: Niobium-vanadium mixed oxide; Sol–gel methods; Oxidative dehydrogenation; Propane

1. Introduction

The discovery and improvement of heterogeneous catalysts active for the oxidative dehydrogenation (ODH) of light alkanes is a particularly challenging matter in catalysis research. Much work has focused on vanadium oxide-based systems [1,2] and more particularly, on V-Mg-O catalysts [3–7]. The superior performance of vanadium oxide-based systems arises from their specific activity in the C–H bond activation in paraffins, which is the rate-limiting step. Because a worthwhile ODH catalyst must be not only sufficiently active but also selective, the reactivity of lattice oxygen to form C–O bonds with the adsorbed hydrocarbon intermediate must be taken into great consideration in order to avoid complete oxidation of the alkanes to CO_x. It has been suggested that the reactivity of lattice oxygen is related to the strength of the metal–oxygen bond, which can also be viewed in terms of the reducibility of the metal cations in the M–O–V bonds [8]. V_2O_5, which is characterized by easily reducible V–O–V bonds, is

---

[*] Corresponding author. Fax: +32-10-472330.
E-mail addresses: pietro.moggi@unipr.it (P. Moggi), devillers@chim.ucl.ac.be (M. Devillers).

0920-5861/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0920-5861(03)00114-7

active in many reactions of partial oxidation, but the selectivity to the desired product is often low. Since the Nb–O bond is stronger than the V–O bond, niobium oxide was also examined as catalyst in propane ODH to see if it gave any improvement compared to the vanadium compounds [9]. While Nb_2O_5 was found to exhibit low catalytic activity and high selectivity to propene, an increase in the catalytic activity without compromising the high selectivity to propene was obtained by promoting niobium oxide with vanadium [10,11]. It was suggested that the activity increase could be related to the formation of surface V–O–V ensembles containing a more reactive bridging oxygen than V–O–Nb units (the former being easier to reduce than the latter). The high selectivity to propene may probably be related to the presence of these V–O–Nb bonds. Further experiments on niobia-supported vanadium oxide catalysts clearly confirmed that vanadium-containing active sites were definitely necessary to provide a significant catalytic activity in propane ODH, while the selectivity to propene strongly depended on the catalyst nature, in relationship with the optimization of the sorption properties of propene to prevent total oxidation [12]. Multicomponent Nb–V–Mo oxides prepared by different methods were also tried in the selective oxidation of ethane to ethene and acetic acid [13,14]. In particular, temperature-programmed reduction measurements were carried out on several Nb- or V-based catalysts to evaluate their reducibility, which was reported to decrease along the sequence $V_2O_5 > Mo_6V_9O_{40} > MoO_3 = Nb_2Mo_3O_{11} > Nb_2O_5 > NbVO_4$ [14]. The very low reducibility of the only Nb-V oxide reported in this series is related to the fact that this compound is an already partially reduced phase obtained by heat treatment under hydrogen up to 900 °C. Very recently, Chary et al. investigated the influence of MoO_3 on the dispersion of niobia-supported vanadium oxides [15] and concluded that the presence of molybdenum resulted in stabilizing the β-$(Nb,V)_2O_5$ phase, whose formation is considered as being responsible for the decreased reducibility of the catalysts. However, the question whether pure Nb-V phases or phase mixtures are responsible for the catalytic performances in partial oxidation of light alkanes remains unsolved. To improve the understanding of the catalytic role played by these phases, appropriate methods able to provide well-defined and adequately dispersed Nb-V oxide phases are required. In that respect, sol–gel methods are known to be particularly powerful to achieve a molecular scale dispersion in mixed oxides. As far as pure niobia is concerned, an extended sol–gel method based on the hydrolysis of a modified Nb-alkoxide precursor obtained from $Nb(OEt)_5$ and acetylacetone was already reported to be an interesting method to produce nanocrystalline mesoporous films of the T-phase of Nb_2O_5 [16]. The implementation of a classical sol–gel route based on metal alkoxides to prepare Nb-rich ($Nb/V = 6$ or 10) amorphous V-Nb oxides displaying high surface areas was reported recently [17]. Preliminary results dealing with the development of a non-hydrolytic sol–gel route to synthesize Nb-V and Nb-V-Si catalysts were also previously reported by us [18]. These materials were tested in propane ODH, also in the presence of a potential promoter such as Sb_2O_4. The results obtained demonstrated the feasibility of the non-hydrolytic sol–gel route to prepare V-Nb mixed oxide catalysts. Moreover, it seemed that interesting catalysts for the ODH of propane could be obtained by refining the preparation procedure and using suitable promoters.

In the present work, hydrolytic sol–gel procedures were extended to the preparation of a wider series of pure or silica-dispersed Nb-V, V-Sb and Nb-V-Sb systems. In addition, since molybdenum oxide is a fundamental component in catalyst formulations for the oxidation of olefins and in some systems active in the oxidation of paraffins, a Nb-V-Mo system was also prepared.

2. Experimental

2.1. Synthesis of the catalysts

$Nb(OiPr)_5$, $VO(OiPr)_3$, $Sb(OiPr)_3$, $Mo(OiPr)_5$ and $Si(OEt)_4$ were the precursors adopted in the hydrolytic sol–gel preparations. Except $Nb(OiPr)_5$, which was synthesized from $NbCl_5$ (Aldrich), 2-propanol (Aldrich) and triethylamine (Fluka), all reagents were commercial products purchased from Alfa Aesar (isoproxides) or Aldrich (TEOS) and used as received. The hydrolytic syntheses were conducted by adding mixtures of water and 2-propanol to stirred mixtures of the alkoxides in 2-propanol. Each synthesis led to a stable sol, which turned into gel within few days. The metal precursors were mixed in order to obtain the following atomic ratios: 1:1 for the binary systems V-Nb and V-Sb; 1:1:1, 1:2:1 and 1:1:5, respectively, for the ternary systems Nb-V-Mo, Nb-V-Sb and Nb-V-Si. In addition, a binary system Nb-V 1:1 and a ternary system Nb-V-Si 1:1:5 were prepared via the non-hydrolytic sol–gel route. The non-hydrolytic syntheses were conducted by adding dropwise $VO(OiPr)_3$ and/or $SiCl_4$ and $Si(OEt)_4$ to stirred suspensions of $NbCl_5$ in hexane (all reagents purchased from Aldrich). By raising the temperature to 100 °C, limpid solutions were obtained, giving after few hours green gels.

2.2. Catalysts characterization

All the obtained xerogels were activated in air at 550 °C for 5 h. The precursor gels were characterized by thermogravimetry (TGA) and the catalysts by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and surface area determination (BET method). TGA analysis was carried out with a Mettler Toledo TGA/SDTA 851^e analyzer. Raman spectra were recorded on a DILOR-JOBIN YVON-SPEX Olympus DX 40 spectrometer using a He–Ne laser ($\lambda = 632.8$ nm). Powder XRD patterns were measured on a Siemens D-5000 diffractometer using the Cu Kα radiation. SEM images were obtained by a Philips XL30 instrument, at the LAMEL Institute (CNR, Bologna, Italy). BET surface areas were measured with a Micromeritics ASAP 2000 analyzer using nitrogen at 77 K.

2.3. Catalytic tests

Propane oxidation experiments were generally carried out in a glass, tubular reactor at 450–550 °C and atmospheric pressure. The feed composition was changed from 10% C_3H_8, 10% O_2 and 80% He (total flow: 30 ml min^{-1}) to 17% C_3H_8, 17% O_2 and 66% He (total flow: 18 ml min^{-1}). Experiments were usually carried out with 0.5 g catalyst, except in the case of the more finely divided Sb-V and Nb-V-Si (non-hydrolytic) materials, for which 0.3 g only were used. The reaction effluent was analyzed by gas chromatography.

3. Results and discussion

3.1. Physico-chemical characterization of the catalysts

All the obtained xerogels were amorphous solids, characterized by very broad IR bands in the region 1000–600 cm^{-1}. BET surface area measurements are reported for the calcined catalysts in Table 1. Observed BET surface areas are rather low for all the samples, with the only exception of the ternary 1:1:5 Nb-V-Si and binary 1:1 Sb-V systems.

TGA analysis showed two weight losses associated with two endothermal peaks at about 100 °C, due to the elimination of residual water and 2-propanol, and 200 °C, related to the elimination of residual alkoxide ligands for all the prepared xerogels.

The calcination at 550 °C of the 1:1 Nb-V binary system prepared either via the non-hydrolytic method or the hydrolytic one led to the formation of crystalline $NbVO_5$ as evidenced by the XRD pattern. Fig. 1a shows the XRD pattern of the 1:1 Nb-V material after the thermal treatment, which matches exactly the JCPDS file of $NbVO_5$ (46-0046). After the catalytic runs, the $Nb_{18}V_4O_{55}$ phase was recognized in the XRD pattern illustrated in Fig. 1b. It seems worth mentioning that this phase does not result from partial reduction of the metals, both Nb and V remaining in their initial (+V) oxidation state. The decomposition of the $NbVO_5$ phase to the Nb-enriched $Nb_{18}V_4O_{55}$ phase and V_2O_5 was hypothesized from the Raman spectra, in which the characteristic pattern of microcrystalline V_2O_5 (146, 290, 404, 480, 527, 702 and 994 cm^{-1}) was recognized. However, there was no evidence of crystalline V_2O_5 provided by XRD.

Table 1
BET specific surface areas of the catalysts calcined at 550 °C for 5 h

Catalysts	Surface area (m^2 g^{-1})
1:1 Nb-V non-hydrolytic	6.4
1:1 Nb-V hydrolytic	1.3
1:1 Sb-V	31
1:2:1 Nb-V-Sb	7.9
1:1:1 Nb-V-Mo	3.0
1:1:5 Nb-V-Si non-hydrolytic	146
1:1:5 Nb-V-Si hydrolytic	132

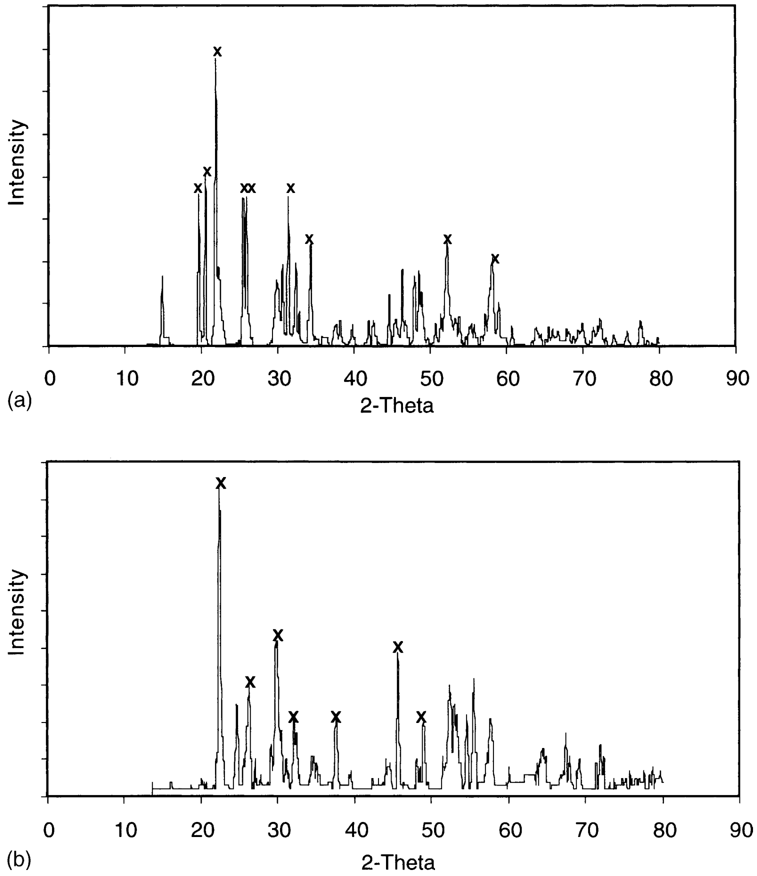


Fig. 1. XRD patterns of 1:1 Nb-V (hydrolytic preparation): (a) after the calcination treatment at 550 °C, containing the practically pure $NbVO_5$ phase and (b) after the catalytic reactions, containing $Nb_{18}V_4O_{55}$.

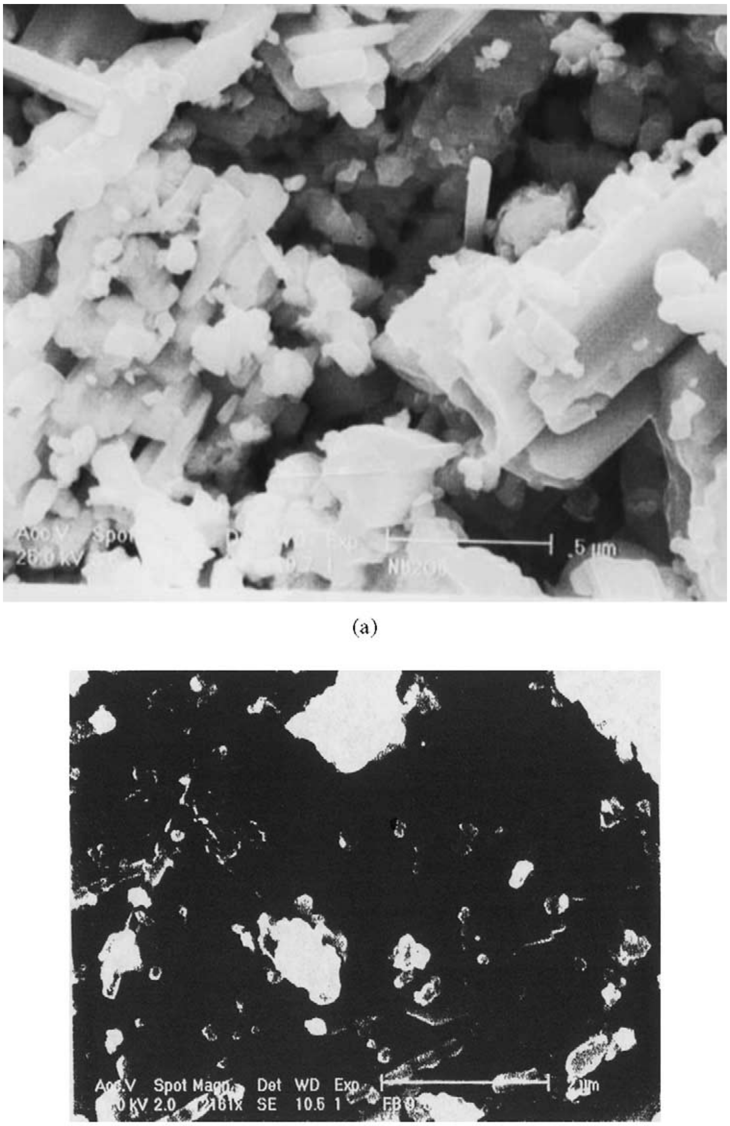
The SEM image of the fresh 1:1 Nb-V catalyst (Fig. 2a, non-hydrolytic preparation) shows the amorphous texture of the sample, from which a rather uniform distribution of micrometer sized crystallites of the $NbVO_5$ phase evolves after the thermal treatment at 550 °C, as evidenced by the SEM image reported in Fig. 2b.

In the case of the binary system 1:1 V-Sb, calcination at 550 °C led to the formation of crystalline $SbVO_4$ as evidenced by the XRD pattern shown in Fig. 3. Unlike the 1:1 Nb-V system, crystalline $SbVO_4$ was maintained even after the catalytic runs.

As far as the ternary system 1:1:1 Nb-V-Mo is concerned, the $Nb_2Mo_3O_{14}$[1] and $(V_{0.07}Mo_{0.93})_5O_{14}$ phases were detected by XRD after the thermal treatment. Once again, the final composition based on the crystalline materials presents a shortage in the overall vanadium content of the fresh catalyst. Similarly to the 1:1 V-Sb material, the XRD pattern of the 1:1:1 Nb-V-Mo system was unchanged after the catalytic runs. In the case of the ternary system 1:2:1

---

[1] The stoichiometry $Nb_2Mo_3O_{11}$ reported in the JCPDS file (18-0840) is based on a paper by Trunov et al. [19], in which there is some confusion. The stoichiometry reported throughout the text is $Nb_2Mo_3O_{14}$ (i.e. "$3MoO_3 \cdot Nb_2O_5$", containing only Mo(VI) and Nb(V)) and only the caption of Table 3 of this paper refers to "$3MoO_2 \cdot Nb_2O_5$" (i.e. $Nb_2Mo_3O_{11}$), which seems therefore to be a wrong formulation. Another more recent paper by Ekström [20] also refers only to the formulation "$3MoO_3 \cdot Nb_2O_5$", i.e. $Nb_2Mo_3O_{14}$. Basically, there is no reason, nor experimental evidence that Mo is fully reduced into Mo(IV) in this phase. We checked this point in the bulk by DR-UV-Vis spectroscopy and at the surface by XPS.



(a)

(b)

Fig. 2. SEM images of 1:1 Nb-V (non-hydrolytic preparation): (a) before and (b) after calcination at 550 °C.

Nb-V-Sb, besides $SbVO_4$, the $Nb_{18}V_4O_{55}$ phase was again evidenced. After the catalytic runs, only traces of $Nb_{18}V_4O_{55}$ were detected besides $SbVO_4$, indicating some structure modifications. Again, although no evidence of crystalline V_2O_5 was given by XRD, the characteristic pattern of V_2O_5 was recognized in the Raman spectrum.

In the case of the ternary system 1:1:5 Nb-V-Si, prepared either via the non-hydrolytic method or the hydrolytic one, the XRD spectra evidence a predominantly amorphous structure, but with the presence of the $NbVO_5$ phase. In Fig. 4, the XRD spectrum of the non-hydrolytic sample after the activation treatment at 550 °C is reported. The characteristic pattern of V_2O_5

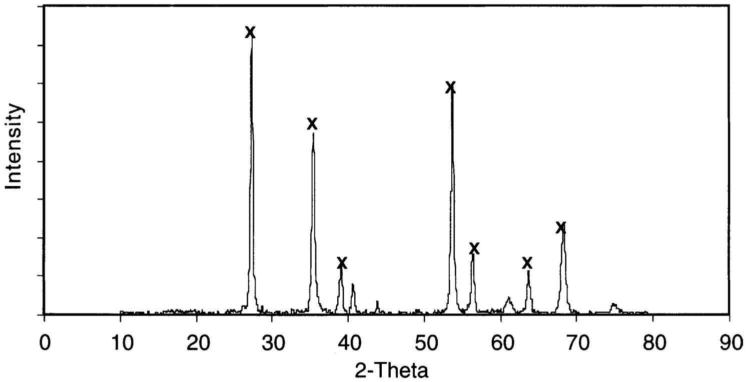


Fig. 3. XRD pattern of 1:1 Sb-V after the calcination treatment at 550 °C containing the practically pure $SbVO_4$ phase (JCPDS file 16-0600).

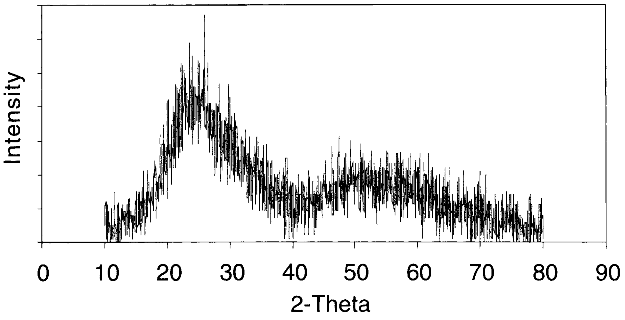


Fig. 4. XRD pattern of the 1:1:5 Nb-V-Si catalyst after calcination at 550 °C (non-hydrolytic preparation).

was recognized in the Raman spectra of both systems after the activation treatment.

3.2. Catalytic results

Catalytic performance data are reported in Tables 2–4. In Table 2, propane conversion ($X_{C_3H_8}$), selectivity to propene ($S_{C_3H_6}$), selectivity to carbon dioxide (S_{CO_2}) and yield in propene ($Y_{C_3H_6}$) are reported. The last column refers to the propene yields normalized with respect to the catalyst amount (expressed as micromoles of propene formed per unit time and unit mass). These catalytic data were collected at the reaction temperature of 500 °C, feed

Table 2
Catalytic results in propane ODH

Catalysts	$X_{C_3H_8}$ (%)	$S_{C_3H_6}$ (%)	S_{CO_2} (%)	$Y_{C_3H_6}$ (%)	$r_{C_3H_6}$ (μmol g^{-1} s^{-1})
1:1 Nb-V non-hydrolytic	33	23	30	7	0.29
1:1 Nb-V hydrolytic	8	37	24	3	0.12
1:1 Sb-V[a]	34	38	39	13	0.89
1:2:1 Nb-V-Sb	33	23	30	7	0.29
1:1:1 Nb-V-Mo	27	25	20	7	0.29
1:1:5 Nb-V-Si non-hydrolytic[a]	39	30	22	11	0.75
1:1:5 Nb-V-Si hydrolytic	31	20	20	6	0.25

Temperature: 500 °C; feed composition: 10% C_3H_8, 10% O_2 and 80% He; amount of catalyst: 0.5 g; total flow: 30 ml min^{-1}.

[a] Catalyst loading: 0.3 g.

Table 3
Catalytic results in propane ODH

Catalysts	$X_{C_3H_8}$ (%)	$S_{C_3H_6}$ (%)	$S_{C_3H_4O}$ (%)	S_{CO_2} (%)	$Y_{C_3H_6}$ (%)	$r_{C_3H_6}$ (μmol g^{-1} s^{-1})
1:1 Nb-V hydrolytic	9	44	6	14	4	0.16
1:1 Sb-V[a]	19	59	5	36	11	0.75
1:2:1 Nb-V-Sb	19	37	0	35	7	0.29
1:1:1 Nb-V-Mo	23	33	6	22	7	0.29
1:1:5 Nb-V-Si non-hydrolytic[a]	25	47	8	23	12	0.82
1:1:5 Nb-V-Si hydrolytic	28	29	0	20	8	0.33

Temperature; 500 °C; feed composition: 17% C_3H_8, 17% O_2 and 66% He; amount of catalyst: 0.5 g; total flow: 18 ml min^{-1}.

[a] Catalyst loading: 0.3 g.

composition: 10% C_3H_8, 10% O_2, 80% He and space velocity of 60 ml min^{-1} g^{-1}. The 1:1 Sb-V and 1:1:5 Nb-V-Si systems only were tested at the different space velocity of 100 ml min^{-1} g^{-1}. The catalysts exhibit about the same conversion level of propane (about 30%) with the only exception of the 1:1 Nb-V catalyst prepared via the hydrolytic method that is characterized by a significantly lower value (8%). Propene selectivity is higher than 20% for all the prepared systems, the 1:1 Nb-V prepared via the hydrolytic method and 1:1 Sb-V catalysts being the more selective ones (almost 40%). The 1:1 Sb-V and 1:1:5 Nb-V-Si prepared via the non-hydrolytic method give the best results in terms of propane conversion and yield in propene. While the higher conversion is in contradiction with the lower amount of catalyst loading, the high yield in propene can be explained by the lower contact time adopted during the catalytic test, which preserves propene from further oxidation to carbon dioxide. Moreover, a minor amount of catalyst favors a better control of the reaction thermal efficiency inside the catalytic bed, reducing phenomena of complete oxidation due to hot spots.

Table 4
Catalytic results in propane ODH: propene productivity normalized with respect to the surface area

Catalysts	$r_{C_3H_6}$[a] (μmol m^{-2} s^{-1})	$r_{C_3H_6}$[b] (μmol m^{-2} s^{-1})
1:1 Nb-V non-hydrolytic	0.045	–
1:1 Nb-V hydrolytic	0.095	0.126
1:1 Sb-V	0.029	0.024
1:2:1 Nb-V-Sb	0.036	0.036
1:1:1 Nb-V-Mo	0.096	0.096

Temperature: 500 °C.

[a] Feed composition: 10% C_3H_8, 10% O_2 and 80% He; total flow: 30 ml min^{-1}.

[b] Feed composition: 17% C_3H_8, 17% O_2 and 66% He; total flow: 18 ml min^{-1}.

The 1:1:5 Nb-V-Si catalyst prepared via the non-hydrolytic method was tested also at the higher temperature of 550 °C. Propane conversion, propene selectivity and yield in propene obtained at 500 and 550 °C are compared in Fig. 5. At 550 °C, propane conversion is slightly lower than at 500 °C; that is probably related to some catalyst deactivation. However, propene selectivity and consequently the yield in propene are significantly higher than at 500 °C. These results achieved with the 1:1:5 Nb-V-Si catalyst at 550 °C are remarkable since they match the best propene productivity data reported in literature for the V-Nb-O catalysts [5] with a value of 0.23 kg of propene per kilogram of catalyst per hour.

A second set of experiments was carried out with increased reagents partial pressures and contact time. Under these conditions, acrolein was detected for almost all the catalysts. In Table 3, propane conversion ($X_{C_3H_8}$), selectivity to propene ($S_{C_3H_6}$), selectivity to acrolein ($S_{C_3H_4O}$), selectivity to carbon dioxide (S_{CO_2}) and yield in propene ($Y_{C_3H_6}$) are reported for those experiments. Catalytic data were collected at the reaction temperature of 500 °C, feed composition: 17% C_3H_8, 17% O_2, 66% He and space velocity of 36 ml min^{-1} g^{-1}. The 1:1 Sb-V and 1:1:5 Nb-V-Si systems only were tested at the different space velocity of 60 ml min^{-1} g^{-1}. The catalysts exhibit a conversion level of propane of about 20%, generally lower than the one of about 30% reported in Table 2. The 1:1 Nb-V catalyst prepared via the hydrolytic method shows again a significantly low conversion value (9%), while the 1:1:5 Nb-V-Si prepared via the hydrolytic method shows the highest

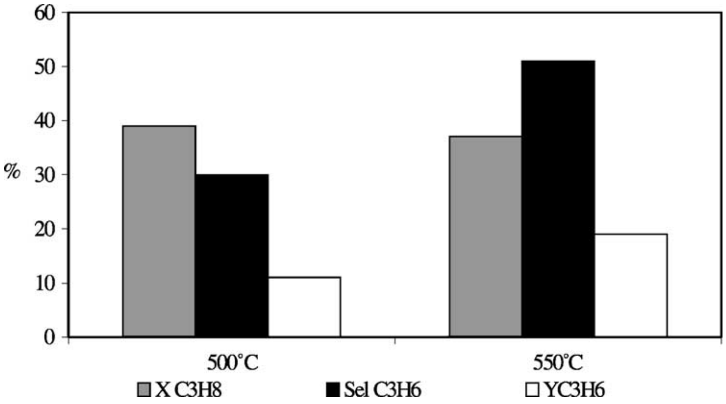


Fig. 5. Catalytic data obtained for the 1:1:5 Nb-V-Si catalyst (non-hydrolytic preparation) at the reaction temperatures of 500 and 550 °C; feed composition: 10% C_3H_8, 10% O_2, 80% He; space velocity: $100\,ml\,min^{-1}\,g^{-1}$.

conversion (28%). In relationship with the higher partial pressures used, propene selectivities are higher than those reported in Table 2, all above 30%, the 1:1:5 Nb-V-Si prepared via the hydrolytic method showing the lowest value of 29%. The 1:1 Sb-V and 1:1:5 Nb-V-Si prepared via the non-hydrolytic method again give the best results with respect to the other catalysts in terms of selectivity and yield in propene because of the minor amount of catalyst adopted during the test and the lower contact time. In these experiments at higher contact time, acrolein was often observed but only in small amounts.

For both sets of experiments, when considering the propene productivity data normalized per unit of catalyst mass, the Sb-V and Nb-V-Si (non-hydrolytic) catalysts tested under conditions of higher space velocity, are found to be the most efficient ones. To take into account the fact that the various catalysts compared in this work are characterized by very different specific surface areas, it is also useful to look at the propene productivity data of the non-silica-dispersed systems normalized per unit surface area (Table 4). The Nb-V (hydrolytic) and Nb-V-Mo systems exhibit clearly the most promising behavior.

4. Conclusions

In this work, mixed oxide systems 1:1 Nb-V, 1:1 Sb-V, 1:2:1 Nb-V-Sb, 1:1:1 Nb-V-Mo and 1:1:5 Nb-V-Si were prepared by applying less conventional preparation methods based on the sol–gel techniques and tested as potential catalysts in the oxidative dehydrogenation of propane. The crystalline, practically pure phases $NbVO_5$ and $SbVO_4$ were identified by XRD in the silica-free 1:1 Nb-V and Sb-V catalysts. Mixtures of mixed oxide phases were detected in the 1:2:1 Nb-V-Sb and 1:1:1 Nb-V-Mo catalysts. The systems containing silica were amorphous and characterized by quite high surface areas. All the prepared systems were active in the propane ODH and selective to propene, particularly the 1:1:5 Nb-V-Si prepared via the non-hydrolytic sol–gel method and the 1:1 Sb-V prepared via the hydrolytic route. Acrolein could also be detected among the reaction products when working with higher reagents partial pressures and contact time.

Acknowledgements

This work was supported by MIUR (Ministero dell'Istruzione, Università e Ricerca, Rome) and the Belgian National Fund for Scientific Research (Brussels). O. Ligabue was recipient of a Socrates-Erasmus grant for a 4-months stay in Louvain-la-Neuve. LAMEL Institute of CNR (Bologna, Italy) is acknowledged for the SEM analyses.

References

[1] F. Cavani, F. Trifirò, Catal. Today 24 (1995) 307.
[2] T. Blasco, J.M. Lopez Nieto, Appl. Catal. 157 (1997) 117.

[3] M.A. Chaar, D. Patel, H.H. Kung, J. Catal. 105 (1988) 463.
[4] A. Corma, J.M. Lopez Nieto, N. Paredes, J. Catal. 144 (1993) 425.
[5] X. Gao, P. Ruiz, Q. Xin, X. Guo, B. Delmon, J. Catal. 148 (1994) 56.
[6] D. Creaser, B. Andersson, Appl. Catal. 141 (1996) 131.
[7] M.C. Kung, H.H. Kung, J. Catal. 134 (1992) 668.
[8] H.H. Kung, Adv. Catal. 40 (1994) 1.
[9] R.H. Smits, K. Seshan, J.R.H. Ross, Stud. Surf. Sci. Catal. 72 (1992) 221.
[10] J.R.H. Ross, R.H.H. Smits, K. Seshan, Catal. Today 16 (1993) 503.
[11] R.H.H. Smits, K. Seshan, H. Leemreize, J.H.R. Ross, Catal. Today 16 (1993) 513.
[12] T.C. Watling, G. Deo, K. Seshan, I.E. Wachs, J.A. Lercher, Catal. Today 28 (1996) 139.
[13] K. Ruth, R. Kieffer, R. Burch, J. Catal. 175 (1998) 16.
[14] K. Ruth, R. Burch, R. Kieffer, J. Catal. 175 (1998) 27.
[15] K.V.R. Chary, C.P. Kumar, K.R. Reddy, T. Bhaskar, T. Rajiah, Catal. Commun. 3 (2002) 7.
[16] F. Lenzmann, V. Shklover, K. Brooks, M. Grätzel, J. Sol–Gel Sci. Technol. 19 (2000) 175.
[17] M. Catauro, C. Pagliuca, L. Lisi, G. Ruoppolo, Thermochim. Acta 381 (2002) 65.
[18] F. Barbieri, D. Cauzzi, F. De Smet, M. Devillers, P. Moggi, G. Predieri, P. Ruiz, Catal. Today 61 (2000) 353.
[19] V.K. Trunov, L.M. Kovba, E.I. Sirotkina, Dokl. Akad. Nauk SSSR (Engl. Transl.) 153 (1963) 1085.
[20] T. Ekström, Acta Chem. Scand. 25 (1971) 2591.