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Mixed-oxide catalysts involving V, Nb and Si obtained by a non-hydrolytic sol–gel route: preparation and catalytic behaviour in oxydative dehydrogenation of propane

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Abstract

One-step non-hydrolytic condensation reactions, starting from $VO(O^iPr)_3$ and $NbCl_5$, have been used for the first time to prepare Nb-V oxide catalysts. Different materials containing the $NbVO_5$ phase at different purity levels have been obtained, after thermal treatments, depending on the experimental conditions. The synthetic procedure has also been applied to prepare ternary Nb-V-Si oxide systems. From preliminary catalytic reaction studies it appears that the catalysts so prepared are promising with respect to their interesting performances in the oxidative dehydrogenation (ODH) of propane. It has also been found that α-Sb_2O_4, physically blended with the Nb-V oxide materials, could act as an appropriate promoter to improve the catalytic performances of these systems. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Vanadium niobium mixed oxide; Non-hydrolytic condensation; Oxidative dehydrogenation of propane

1. Introduction

Niobia-based systems are active in the oxidative dehydrogenation (ODH) of light alkanes, particularly in the conversion of propane to propene. More particularly, pure niobium pentoxide is a very selective catalyst for the ODH of propane, but its activity appears rather low [1]. In recent years, it has been shown that promoting niobium pentoxide with elements such as vanadium, chromium and molybdenum could significantly improve the catalytic activity while maintaining a satisfactory selectivity [2]. Among the three elements mentioned, vanadium was found to be the optimal promoter [2], the method of addition of vanadium to niobia exerting a strong influence on the performance of the resulting system [3]. For the catalysts prepared by co-precipitation and containing variable amounts of vanadium (0.3–18 mol%) a model was proposed in which vanadium partially replaces niobium in the T-niobia structure [4,5]. More recently, it has been found that variations in the chemical environment of vanadium do not cause significant changes in activity, whereas selectivity to propene strongly depends on the nature of the catalyst

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because readsorption and interaction of propene with the acid sites leads to total oxidation [6]. Furthermore, in a titania-supported vanadium-niobium oxide catalyst, vanadium sites appear as the active sites, whereas niobium acts as an additive favouring the selectivity to propene [7]. On the other hand, vanadium oxides are known to contain the adequate functionality to convert paraffins into oxygenates, particularly when V is associated with Mg, P or Sb [8–10].

Therefore, the key point to reach high catalytic performance appears to be the ability to tune the catalyst architecture, by controlling the nature and interdispersion of the oxide phases present in these catalysts. This can be accomplished by implementing adequate preparative procedures such as the sol–gel methods, which have been found to be particularly powerful to control the intimacy of molecular scale mixing in mixed oxides [11].

Sol–gel chemistry is based on inorganic polymerization reactions, for which metal alkoxides are generally used as starting materials, obtaining a macromolecular network via hydrolysis and hydroxyl condensation. Transition metal alkoxides with a d^0 configuration, such as Ti(IV) or Nb(V), are very reactive towards hydrolysis, addition of water causing formation of precipitates that do not display the textural properties of a genuine gel. Therefore, unlike silicon systems, the sols must be stabilized in order to prevent precipitation; this can be achieved by using nucleophilic chemical additives such as carboxylic acids or other chelating agents, which control the reaction rates by modifying the reactivity of the precursors, allowing sequential formation of sols and gels [12]. Recently, we have employed the hydrolytic sol–gel method to prepare niobia and silica-niobia systems by using $Nb(OEt)_5$ and $Si(OMe)_4$ as precursors, obtaining high surface areas mixed-oxide materials in a wide composition range, displaying variable acidities [13].

Alternately, non-hydrolytic sol–gel routes (more properly 'non-hydrolytic condensations') to prepare mono- or bi-component oxides are available, in which precursors, solvent, experimental conditions, catalysts and reaction mechanisms are changed [14]. An attractive method of this type is provided by the condensation reaction between metal chlorides and metal alkoxides, releasing alkyl chlorides as co-products, according to the following equation:

$$\mathrm{M{-}X + M'{-}OR \rightarrow M{-}O{-}M' + RX}$$

In particular, non-hydrolytic methods lead to improved control over the molecular level homogeneity and stoichiometry of multicomponent oxides.

The present work deals with the first application of this synthetic route to the production of mixed Nb-V and Nb-V-Si oxide catalysts, with their characterization and with the preliminary tests in propane ODH, also in the presence of a potential promoter such as Sb_2O_4.

2. Experimental

2.1. Reagents and equipments

Organic solvents and reagents were dried and distilled under inert atmosphere (N_2) according to the standard procedure. V_2O_5, $NbCl_5$, $Si(OEt)_4$ and $SiCl_4$ were pure commercial products (Aldrich) and were used as received. $VO(O^iPr)_3$ was prepared according to a published procedure [15]. All the preparations, prior to the thermal treatments, were carried out under inert atmosphere using a suitable glove-box and Schlenk glassware.

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 mm Hg. DSC profiles were obtained by a Perkin-Elmer DSC7 equipment. FTIR spectra (KBr discs) were recorded on a Nicolet 5PC spectrometer. Electrophoretic mobilities were measured by a Zeta Meter 500 instrument. XRD data were obtained, using the Cu Kα radiation, by a Philips PW 1050 instrument at the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. (Parma). SEM images and energy dispersive X-ray microanalyses were performed with the SEM equipment Philips XL30, equipped with an EDAX spectrometer, at the LAMEL Institute (CNR, Bologna, Italy).

2.2. Preparations of the catalysts

2.2.1. Preparation of the V-Nb oxide systems

To 3.30 g (12 mmol) of $NbCl_5$ in a Schlenk tube, 4.68 ml (20 mmol, V:Nb 5:3) or 2.90 ml (12 mmol, V:Nb 1:1) of $VO(O^iPr)_3$ were added under vigorous stirring at room temperature. An exothermic reaction took place leading to an orange solution. The temperature was raised to 100°C with an oil bath resulting in the formation of a gelled, deep-green solid. Heating was suspended after 2 h and the product was dried in vacuo. In order to improve the homogeneity of the starting mixture, a few milliliters of hexane was added in different preparations, obtaining suspensions of the niobium chloride before the addition of the vanadyl alkoxide. This avoided the possible formation of unreacted crusts of $NbCl_5$ on the walls of the reaction vessel. The four materials V:Nb 1:1, V:Nb 5:3 (without hexane), V:Nb 1:1 H and V:Nb 5:3 H (with hexane) were heated at 550°C for 5 h in the air, giving pale orange powders.

For comparative purposes, a 1:1 $V_2O_5+Nb_2O_5$ mechanical mixture was prepared by dispersing the two oxides in heptane, drying in vacuum and calcining at 550°C.

Derived catalysts were prepared by adding Sb_2O_4 to the materials described above: equal amounts (1:1 in weight) of the tetroxide and of the V-Nb mixed oxides were suspended in heptane and stirred for 1 h; the solvent was then removed in vacuo and the resulting solids (V:Nb 1:1 /Sb, V:Nb 5:3 /Sb, V:Nb 1:1 H/Sb, V:Nb 5:3 H/Sb and Mix. 1:1 /Sb) dried in an oven at 100°C.

2.2.2. *Preparation of the V-Nb-Si oxide systems*

To $NbCl_5$ (0.50 g, 1.85 mmol) suspended in hexane by stirring, $VO(O^iPr)_3$ (0.42 ml, 1.85 mmol), $Si(OEt)_4$ (4.13 ml, 18.5 mmol) and $SiCl_4$ (2.12 ml, 18.5 mmol) were added dropwise, in this order, at room temperature. A white solid separated from a pale orange solution was obtained. By raising the temperature to 100°C a limpid, orange solution was obtained, giving, after ca 5 h, a green gel. This material was dried and heated as those described in Section 2.2.1, affording a pale grey powder (V:Nb:Si 1:1:20).

2.3. *Catalytic tests*

Propane oxidation experiments were carried out at 450 and 500°C using a glass, U-shaped, tubular reactor with an internal diameter of 8 mm; the feed composition was 8% C_3H_8, 18% O_2 and 74% N_2 at atmospheric pressure (catalyst mass 1 g, total flow 37 ml/min). The reaction effluent was analysed by gas-chromatography.

3. Results and discussion

3.1. *Characterizations*

A non-hydrolytic condensation procedure involving $VO(O^iPr)_3$ and $NbCl_5$ was attempted to produce V-Nb mixed oxides. In the early stage of this investigation, the V:Nb 5:3 molar ratio was chosen in order to favour an equimolar condensation between chlorines and alkoxy groups. Furthermore, having realized that the main final product, after the thermal treatment, was $NbVO_5$, the preparations were performed with the V:Nb 1:1 molar ratio. Some preparations were carried out in the presence of hexane in order to favour homogeneous mixing of the reagents. Also a ternary V-Nb-Si (1:1:20) oxide system was prepared by this procedure, the reaction being slower. All the obtained xerogels are amorphous solids, characterized by very *broad* IR bands in the region 1000–600 cm^{-1} (Fig. 1a). The SEM-EDX spectra of these materials evidence in all cases the presence of chlorine suggesting that the condensation reactions are not complete, even in the case V:Nb 5:3.

Calcination at 550°C (as suggested by a differential calorimetric scan at 10°C min^{-1}) of the 1:1 or 5:3 V:Nb binary xerogels leads to the formation of crystalline $NbVO_5$, recognized by its XRD pattern. Fig. 2a shows the XRD pattern of the 1:1 material (after the thermal treatment and catalytic runs), which matches exactly the JCPDS files of $NbVO_5$, no other phase being *detectable*. This compound, absent in the phase diagram of the V_2O_5–Nb_2O_5 system [16], appears to be accessible only by sol–gel procedures. It was obtained for the first time by a stepwise hydrolytic method, under strict control of the reaction conditions [17,18]. SEM-EDX investigations on all the heated binary samples showed the complete disappearance of residual chlorines and displayed a rather uniform distribution of $NbVO_5$ prismatic crystallites of about 1 μm in size, as shown in Fig. 3. In the case of the 5:3 system, besides small amounts of V_2O_5, other mixed-oxide phases (such as VNb_9O_{25} and $V_4Nb_{18}O_{55}$) were sometimes detected in traces by XRD.

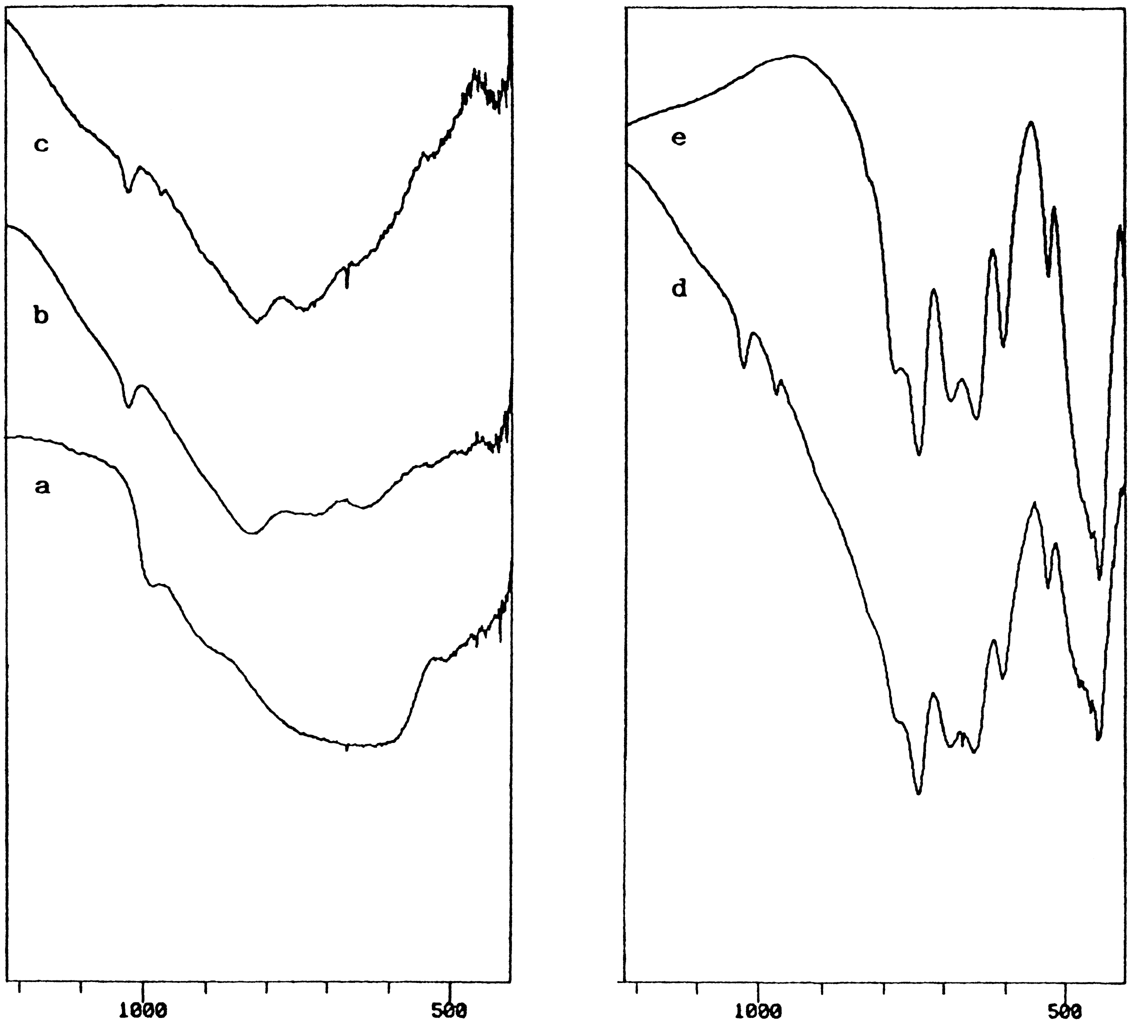

Fig. 1. IR spectra of: (a) the fresh, amorphous Nb:V 1:1 gel; (b) the same material after thermal treatment at 555°C [broad maxima at 1024 (V=O), 814, 720, 636 (M–O) cm^{-1}], containing the practically pure $NbVO_5$ crystalline phase; (c) after catalytic runs; (d) after addition of Sb_2O_4 and catalytic runs; (e) pure Sb_2O_4.

In the case of the ternary system V-Nb-Si the thermal treatment did not lead to any detectable crystalline phase. Regarding the mechanical mixture of the two oxides (Mix. 1:1), the final XRD spectrum showed the patterns of the two separated phases.

Further evidence for the formation of the $NbVO_5$ phase came also from the electrophoretic measurements, which showed that the isoelectric point of these samples was systematically higher than those of the pure oxides or mechanical mixtures. Observed BET surface areas were rather low (1–3 m^2/g) for all the samples.

The IR spectrum of the 1:1 V-Nb fresh gel (Fig. 1a) displays a very broad band centered at about 650 cm^{-1} due to ν(M–O) vibrations in the polymeric xerogel. The spectrum of the heated 1:1 V-Nb system (Fig. 1b) is in substantial agreement with that previously reported for $NbVO_5$ prepared by hydrolytic sol–gel procedures [17] showing in addition a weak band (1024 cm^{-1}) possibly due to ν(V=O) in V_2O_5

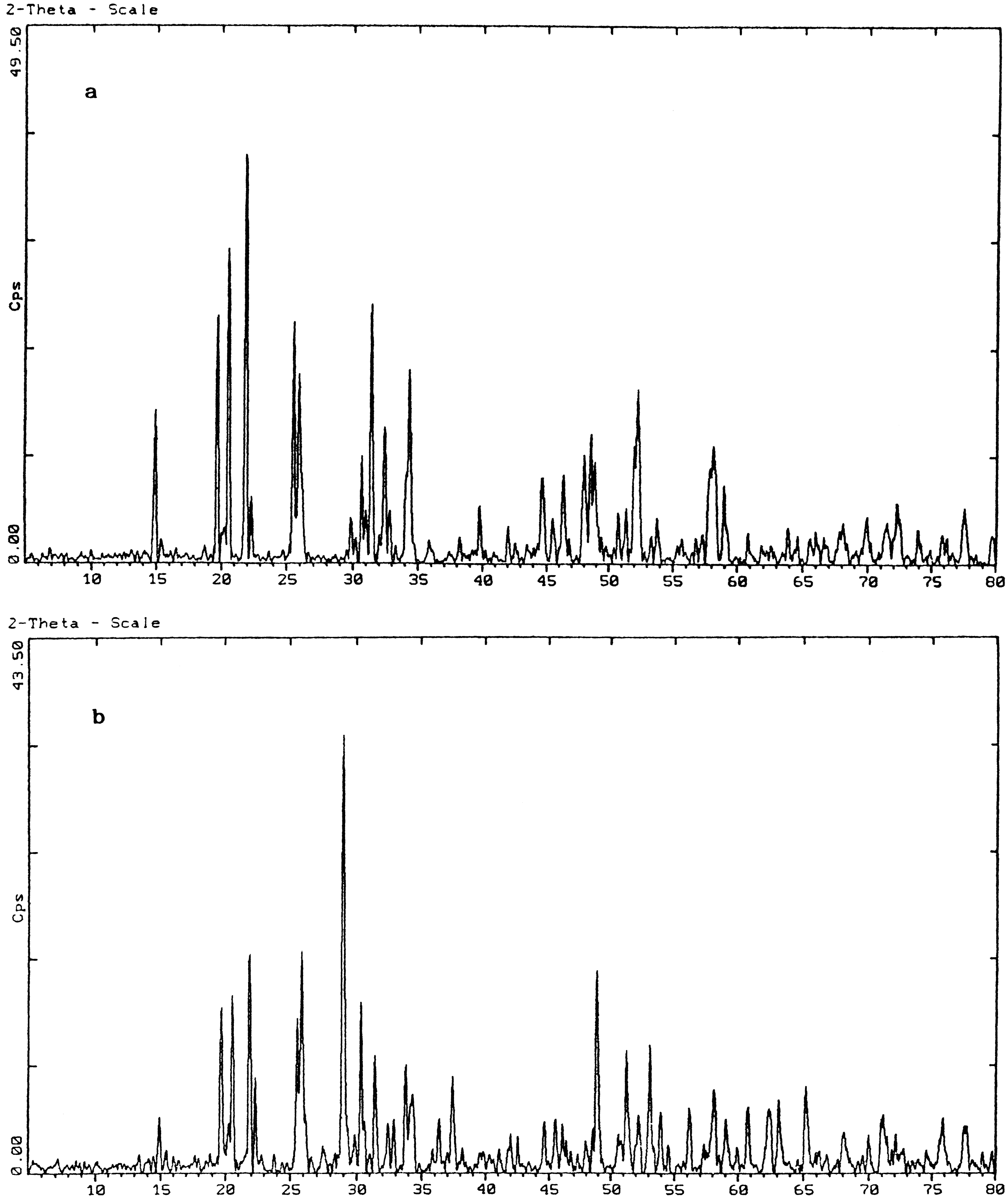

Fig. 2. XRD patterns of: (a) Nb:V 1:1 after the catalytic reactions containing the practically pure $NbVO_5$ phase (file 46–0046 of the JCPDS Powder Diffraction File, International Center for Diffraction Data, Swarthmore, PA, 1989); (b) Nb:V 1:1 /Sb containing $NbVO_5$ and Sb_2O_4 (cervantite, file 32–0042).

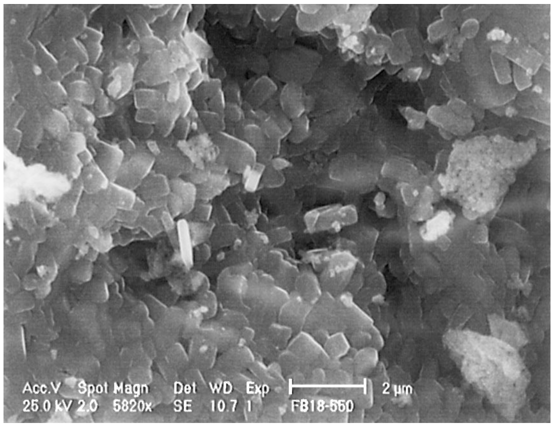

Fig. 3. SEM image of the Nb:V 1:1 catalyst after the thermal treatment, evidencing a rather uniform distribution of micrometer sized crystallites of the $NbVO_5$ phase.

present in trace amounts (undetected by XRD). No substantial differences were observed between the IR patterns of the heated samples and those of catalysts used in the propane ODH, if we exclude the appearance of a very weak band at 970 cm^{-1} (Fig. 1c).

Addition of Sb_2O_4 (1:1 in weight) to the binary materials described above did not result in the formation of detectable amounts of new phases. This is indicated by the XRD profile of the V:Nb 1:1 /Sb sample after the catalytic performance (Fig. 2b), which exhibits the unmodified patterns of $NbVO_5$ and Sb_2O_4 (cervantite), and by the IR spectrum of the same material (Fig. 1d), which appears as the superimposition of the spectrum of pure Sb_2O_4 (Fig. 1e) and that of $NbVO_5$ (Fig. 1c).

3.2. Catalytic activity in propane ODH

Catalytic performance data are reported in Tables 1 and 2. Pure V-Nb catalysts exhibit in general lower conversions (between 4.3 and 6.4%) compared with metal vanadate catalysts (1.7 — about 36%), under experimental conditions which are, however, different [1–4]. In particular, reaction temperatures are usually higher (540–570°C) than in the present work (450–500°C). Propene selectivities in V-Nb catalysts are also lower (13.7–42% compared with 42–68.5% in metal vanadate catalysts). However, at low reaction temperature (450°C), the V-Nb system displays selectivities as high as 60%. It is important to underline that the present V-Nb catalysts show higher catalytic performance than alumina-supported niobia catalysts reported in the literature (very low conversion (1.2%) with a selectivity of 41–64%) [5–7].

The Si catalysts appear to be poorly active but exhibit quite a high selectivity. The addition of hexane during the preparation of sol–gel V-Nb catalysts seems to promote mainly selectivity. The conversion and yield obtained with pure V-Nb catalysts are lower than those obtained with a mechanical mixture of V_2O_5 and Nb_2O_5; nevertheless, the V-Nb catalysts appear to be more selective than the latter.

As indicated in Table 2, whereas pure α-Sb_2O_4 is definitely not active in propane ODH, the addition of α-Sb_2O_4 to V-Nb catalysts resulted in a general improvement in conversion and selectivity [a fourfold increase being observed in the case of the catalyst V:Nb 5:3 (Hex.)]. Considering into account that in all cases the amount of catalyst introduced in the reactor is 1 g, the effect related to the addition of antimony oxide is really impressive. The addition of α-Sb_2O_4 also improves the yield in propene. If the catalyst V:Nb 1:1 (dry) is considered, the yield, at about the same conversion, shows a threefold increase when mixed with α-Sb_2O_4 (2.6 instead of 0.9). As the amount of V-Nb catalysts in the mechanical mixture is half of that present in the mixture, this effect appears still more spectacular. The important fact is

Table 1
Oxidative dehydrogenation of propane to propene. Temperature 500°C. Amount of catalyst: 1 g

Catalysts	Conversion (%)	Yield in propene (%)	Selectivity in propene (%)
V:Nb 1:1 (dry)	6.4	0.9	13.7
V:Nb 1:1 (Hex.)	5.4	1.6	30.4
V:Nb 5:3 (dry)	5.0	1.5	30.0
V:Nb 5:3 (Hex.)	4.3	1.8	42.0
V:Nb:Si 1:1:20	0.5	0.53	ca 100
V_2O_5:Nb_2O_5 (Mech. mixt. 1:1)	21.1	4.5	21.3

Table 2
Oxidative dehydrogenation of propane to propene. Temperature 500°C. Amount of catalyst: 1 g

Catalysts	Conversion (%)	Yield in propene (%)	Selectivity in propene (%)
V:Nb 1:1 (dry)+α-Sb_2O_4	7.4	2.6	35.0
V:Nb 5:3 (dry)+α-Sb_2O_4	4.9	1.5	31.1
V:Nb 5:3 (Hex.)+α-Sb_2O_4	16.1	2.8	17.3
V_2O_5:Nb_2O_5 (Mech. mixt. 1:1)+α-Sb_2O_4	32.5	5.2	16.1

that for the mechanical mixture of $V_2O_5+Nb_2O_5$ and α-Sb_2O_4, the conversion increases by about 50%, the yield in propene by some 25%, while selectivity decreases weakly. Considering that in the mixture with α-Sb_2O_4, the amount of $V_2O_5+Nb_2O_5$ is only 0.5 g, this influence is quite significant.

A further information comes from the analysis of the reaction products. In all cases in which α-Sb_2O_4 is present, a still unidentified product was detected. Preliminary chromatographic analysis indicated that this new peak could not be assigned to *n*-propanol, *iso*-propanol or acrolein. Further studies aimed at identifying this product are in progress.

At this stage of our investigation, a rationale for the catalytic behaviour of our V-Nb catalysts cannot be really proposed. Regarding the sol–gel materials, it appears that the $NbVO_5$ oxide phase, generated by thermal treatment, is essentially responsible for the catalytic activity, which should then depend on the purity and dispersion of this ternary phase. However, the fact that a simple mechanical mixture of $V_2O_5+Nb_2O_5$ presents an acceptable activity complicates the scenario by pointing out another important factor relevant to catalytic performance, i.e. the degree of interdispersion between the two oxide phases (from rough physical mixtures to blending at atomic level as in $NbVO_5$).

Another point concerns the addition of α-Sb_2O_4. The mere presence of this oxide in physical contact with Nb-V catalysts improves significantly the catalytic performance. To propose an explanation of this synergetic effect in the light of the present results would be by far too speculative. At this stage, it can be only suggested that the reason for this synergy is, either a chemical contamination with formation of new more active oxide phases (V-Sb, Nb-Sb or V-Nb-Sb, for instance), or a co-operation between separate phases as it has been proposed previously [8,19]. The fact that mechanical mixtures of V_2O_5 and Nb_2O_5 show a good catalytic performance seems to indicate that the presence of separated oxide phases would be important in V-Nb catalysts. However, at the present stage, pertinent arguments are missing to comment further on the point. Obviously, more experimental work is required to correlate the solid state properties with the catalytic performance.

4. Conclusions

The results obtained demonstrate the feasibility of the non-hydrolytic sol–gel route to prepare V-Nb mixed oxide catalysts. Furthermore, some experimental parameters characterizing the preparation procedure appear as being really critical to determine the properties of the final catalysts and have to be investigated more deeply in order to optimise the preparation method. It seems that interesting catalysts for the ODH of propane could be obtained by refining these parameters and using suitable promoters. In addition, an adequate adjustment of the reaction conditions (contact time, temperature, etc. as in the case of V-Nb-Si catalysts) could most probably open valuable perspectives in the application of such and related catalysts in alkane activation.

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