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Synthesis of alkoxide-derived V-Nb catalysts prepared by sol–gel route

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Abstract

Amorphous vanadium-niobium mixed oxides with high surface area have been prepared by sol–gel route starting from metal alkoxides using different H_2O/V ratios. Dried samples have been characterized by XRD, atomic absorption and BET analysis. Calcination of dried materials up to 550 °C in flowing air has been followed with TG–FT-IR spectroscopic analysis. Redox properties of calcined samples have been investigated with TPR technique. Catalytic properties of calcined materials have been tested in the oxidative dehydrogenation of ethane at 550 °C and compared with those of a catalyst prepared by impregnation of Nb_2O_5 with V_2O_5 having the same composition of gel systems. An improvement of the catalytic performances of vanadium for the gel prepared with the higher H_2O/V ratio was found with respect to those of the supported catalyst due to the better interaction between vanadium and niobium. © 2002 Published by Elsevier Science B.V.

Keywords: Sol–gel synthesis; Catalyst

1. Introduction

Vanadium oxide-based catalysts have been widely employed in selective oxidation reactions such as partial oxidation of alkanes [1–3], SCR of NO_x [4], oxidation and ammonoxidation of aromatic hydrocarbons [5] due to the easy mobility of lattice oxygen bound to vanadium which can be involved both in the extraction of hydrogen from hydrocarbons and in the oxidation of the reacting molecule [6]. It is well known that the catalytic behavior of vanadium oxide supported or mixed with other metal oxides depends on the interaction occurring between the two metals [2,3]. Moreover, it has been reported [1,2,7–11] that vanadium functionality is modified by the addition of P, Mg, Mo, or Nb leading to catalysts with better catalytic performances. In particular, the addition of hardly reducible metal, such as Nb, provides an enhanced selectivity in the oxidative dehydrogenation of light alkanes also depending on the preparation method used [2,11]. As a consequence, a good control of the interdispersion of the oxide phases represents an important factor determining the main catalyst features. A great flexibility and control of physical properties of materials can be obtained using the sol–gel processing technology for the preparation of catalysts [12]. The metal oxides synthesized by this method, through hydrolysis and condensation of metal alkoxides, are generally amorphous. In order to avoid the formation of precipitates not showing the textural properties of a genuine xerogel, in the case of

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transition metal alkoxides with a d^0 configuration, such as Ti(IV) or Nb(V), very reactive towards hydrolysis, the sols must be stabilized 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 the sequential formation of sols and gels [13]. Recently [14], the hydrolytic sol–gel method has been employed to prepare niobium silica–niobium systems by using $Nb(EtO)_5$ and $Si(OCH_3)_4$ as precursors, obtaining high surface areas mixed oxide materials in a wide composition range, displaying variable acidities. Alternatively, there are non-hydrolytic sol–gel routes available to prepare mono or bicomponent oxides, in which precursors, solvent, experimental conditions, catalysts and reaction mechanisms are changed [15]. Barbieri et al. [16] have prepared vanadia-niobia gels with different composition starting from $NbCl_5$ and $VO(OPr)_3$ by non-hydrolytic condensation, obtaining different mixed vanadium-niobium oxides in addition to the $NbVO_5$ constituting the main phase.

In this paper bulk vanadium-niobium oxides samples with high surface area have been prepared via sol–gel method. Their physico-chemical properties have been characterized and compared with those of a sample having the same composition but prepared starting from inorganic precursors. These samples have been tested as catalysts for the oxidative dehydrogenation of ethane.

2. Experimental

Three samples containing V_2O_5 and Nb_2O_5 with a V/Nb atomic ratio 1/6 were prepared. One of them was prepared by wet impregnation of the Nb_2O_5, obtained by thermal decomposition of niobium oxide hydrate for 24 h at 120 °C, with an aqueous metavanadate (BDH Laboratory Supplies) solution. The sample was dried overnight at 120 °C. An impregnated sample with a V/Nb ratio 1/10 has also been prepared for comparison. Vanadium-niobium gels were prepared using $Nb(OC_2H_5)_5$ and $VO[(CH_3)_2CHO]_3$ analytical grade reagents as starting materials. Water-free ethanol, obtained by distillation with metallic sodium of commercial anhydrous ethanol was used, since the $VO[(CH_3)_2CHO]_3$ is a very water-sensitive reagent and to allow the control of V/H_2O ratio. Bidistillated water was used for hydrolysis reaction. Due to the high reactivity of niobium pentaethoxide toward moisture, the alcoholic solution was handled inside a glove box at room temperature. A flow-chart indicating the preparation procedure and the composition employed is given in Fig. 1. The two gels differ from each other in the H_2O/V ratio (Table 1). Required amounts of $Nb(OC_2H_5)_5$ were mixed with alcohol and the container was sealed with parafilm and taken out of the glove box. A 37% HCl solution was slowly added dropwise with constant stirring. A clear homogeneous solution resulted. The alcoholic solution of $Nb(OC_2H_5)_5$ was mixed at −20 °C (using liquid N_2) with a water alcoholic solution of $VO[(CH_3)_2CHO]_3$. A clear homogeneous solution resulted. The container was sealed with parafilm and kept at ambient conditions for gelation. Depending upon the amount of the H_2O added, several days were required for a complete gelation. The gelled system was washed for 1 day more at room temperature before drying. The gel was fully dried in air at 50 °C in an electrical oven for 2 days. After these treatments, an amorphous powder was obtained.

Gel samples will be indicated as VNbgel-a and VNbgel-b, respectively, depending on H_2O/V ratio as reported in Table 1. Impregnated samples will be referred to as VNb-6 and VNb-10, respectively, depending on the V/Nb atomic ratio.

The niobium and vanadium content in the dried gel was evaluated by atomic absorption analysis of melted samples obtained by heating at 1200 °C in air about 64 mg of dried gel in a platinum holder for 3 h. The melted gel was air-quenched, weighed, dissolved in concentrated HF and diluted in bidistillated water before the analysis. The amorphous or crystalline nature of the dried and calcined gels, respectively, were ascertained by X-ray diffraction using a Philips diffractometer. Powders of each sample were scanned from $2\Theta = 5$–60° using Cu Kα radiation. All samples have been calcined in flowing air at 550 °C for 3 h before catalytic tests.

A Carlo Erba 1900 Sorpomatic was employed for the BET measurement of surface areas by N_2 adsorption at 77 K. Temperature-programmed reduction (TPR) was carried out using of a Micromeritics TPD/TPR 2900 analyzer equipped with a TCD and coupled with a Hiden HPR 20 mass spectrometer. In the TPR experiments, the sample was reduced by a 2%

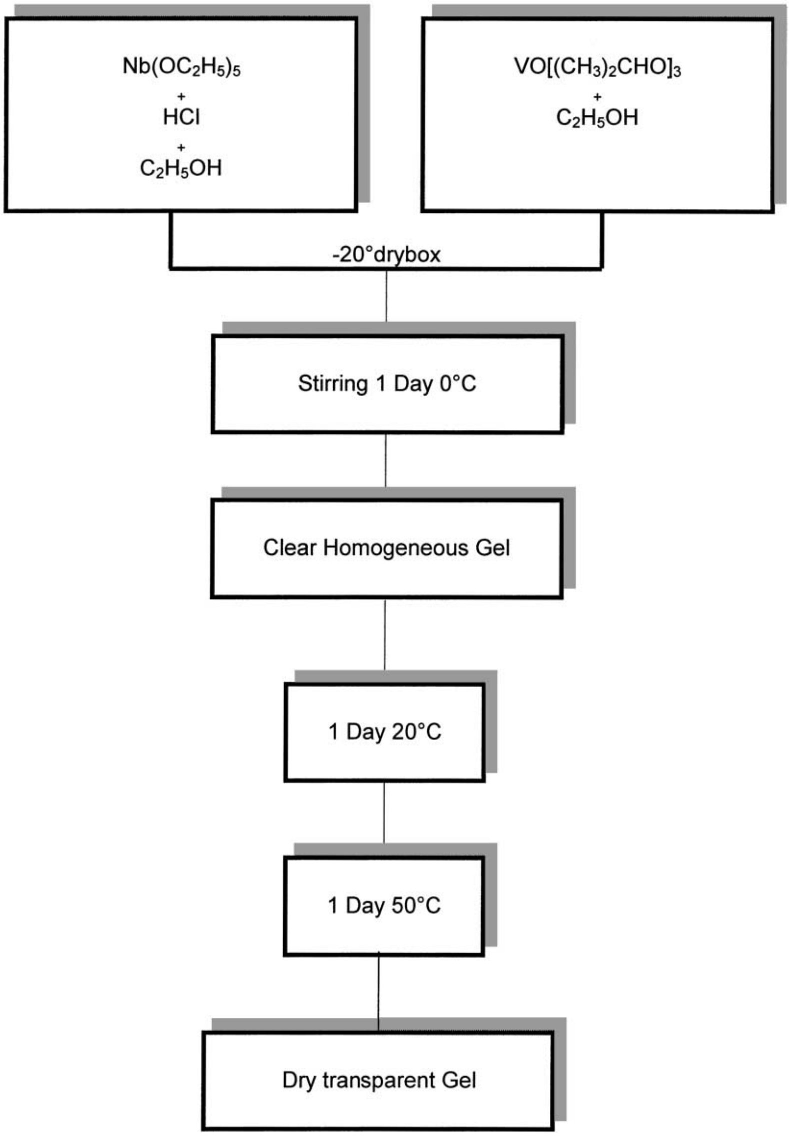

Fig. 1. Flow-chart of gel synthesis.

Table 1
Synthesis parameters, composition and surface area of gel and impregnated materials

Material	Gelation time (days)	H_2O/V molar ratio	V_2O_5/Nb_2O_5 molar ratio	Surface area before thermal treatment ($m^2\ g^{-1}$)	Surface area after thermal treatment ($m^2\ g^{-1}$)
VNbgel-a	5	5	1/6	161	12
VNbgel-b	5	0.050	1/6	84	4
VNb-6			1/6	35	35
VNb-10			1/10	37	37

H_2/Ar mixture (25 $cm^3\ min^{-1}$) by heating 10 °C min^{-1} up to 650 °C. Before the TPR experiments, the sample was treated in flowing air at 550 °C for 2 h. Thermogravimetric analysis was performed with a Perkin-Elmer TGA7 thermo-balance equipped with a high temperature furnace and coupled with a Perkin-Elmer spectrum GX–FT-IR spectrometer for the analysis of the released gases. TG analysis was carried out heating the sample 10 °C min^{-1} in air flow-up to 550 °C holding the final temperature for 3 h as for the calcination treatment.

The catalytic tests were carried out in a fixed bed quartz micro-reactor operating under atmospheric pressure as reported in [11]. The feed composition was 4% C_2H_6 and 2% O_2 in a balance of He. The reaction temperature was 550 °C, the space velocity was 0.13 g s N cm^{-3}. Carbon balance was closed within 3% error in all experiments.

3. Results and discussion

Gelation is the result of hydrolysis and condensation reactions according to the following equations:

Hydrolysis :

$$-\mathrm{Nb-OEt} + \mathrm{H-OH} \Rightarrow -\mathrm{Nb-OH} + \mathrm{H-OEt} \quad (1)$$

Dealcoholation :

$$-\mathrm{Nb-OEt} + \mathrm{HO-Nb}- \Rightarrow -\mathrm{Nb-O-Nb}- + \mathrm{H-OEt} \quad (2)$$

Dehydration :

$$-\mathrm{Nb-OH} + \mathrm{HO-Nb}- \Rightarrow -\mathrm{Nb-O-Nb}- + \mathrm{H-OH} \quad (3)$$

At room temperature, the hydrolysis reaction (Eq. (1)) is much faster than the condensation reactions (Eqs. (2) and (3)), so that the number of Nb–O–Nb bridges formed is insufficient to give gelation and precipitation of hydrated niobium oxide–alkoxide aggregate occurs. Mixing at a lower temperature (−20 °C) allows the control of the hydrolytic reactivity of niobium pentaethoxide, so that soluble polymeric intermediates are obtained, which then undergo further polymerization to form a gel. The reaction mechanisms are not known in every detail, however, it is generally accepted that they proceed through a second order nucleophilic substitution [13]. The interaction between the electrophilic metal, Nb, and the nucleophilic agent (H_2O or $C_2H_5O^-$) gives rise to addition (Eq. (1)). In all cases, the gels were clear, transparent and light yellow in color (Fig. 2). C_2H_5OH acts as the mutual solvent and HCl, as the deflocculating agent. In the absence of HCl, it was not possible to prepare clear sols. Precipitation of colloidal particles was encountered on the addition of any water to $Nb(OC_2H_5)_5$ due to high reactivity of the alkoxide toward water. The HCl concentration appears to have no influence on the gelling time.

Chemical analysis of melted gel showed that good composition control was provided by sol–gel process (Table 2). The analyzed and theoretical value are in fairly good agreement.

3.1. BET measurement

The BET analysis shows that the gels have a very high value of the surface area as it was expected using the sol–gel preparation method [12].

The severe thermal treatment at 550 °C, however, results in a strong reduction of surface area of the gels due to crystallization of amorphous materials in different phases (Fig. 3). Both VNbgel-a and VNb-6 show signals of monoclinic Nb_2O_5 (JCPDS 27-1313) whereas, in addition to these peaks, VNbgel-b shows also signals of n-Nb_2O_5 (JCPDS 27-1311) and of the mixed vanadium-niobium oxide (JCPDS 16-132). This could suggest that the presence of a larger amount of water during the synthesis of gels results in the formation of niobium oxide particles likely covered by a vanadium oxide layer as for the impregnated material whereas, the formation of a mixed compound prevails when water is almost absent. It has been verified that the strong reduction of the surface area already occurs at quite low temperature by evaluating the values of BET area of VNbgel-a sample treated at 250 and 450 °C, respectively, under the same conditions used for the treatment at 550 °C. It should be pointed out, however, that the reduction of surface area of gels prepared in this work is less dramatic than that reported by Barbieri et al. [16] for vanadia-niobia gels that underwent the same thermal treatment. Calcination at 550 °C does not affect the surface area of impregnated sample with the same composition, which, although starting from a lower value as dried

Fig. 2. V-Nb gel dried for 1 day at 50 °C.

sample, maintains a good value of surface area as calcined.

3.2. TG analysis

In Fig. 4, the catalyst weight loss is reported as a function of both time and temperature for gel and impregnated samples in TG experiment reproducing the calcination conditions. All catalysts reach a constant weight after the complete thermal treatment. The total weight loss is 17.8 and 11.4% for the VNbgel-a and the VNbgel-b, respectively, whereas it is 13.0% for the impregnated sample. After a first release of physisorbed water, occurring at low temperature, all

Table 2
Chemical analysis of melted gels

Constituent	Analyzed (wt.%)	H_2O/V molar ratio
V_2O_5	10.20	10.24
Nb_2O_5	89.70	89.76

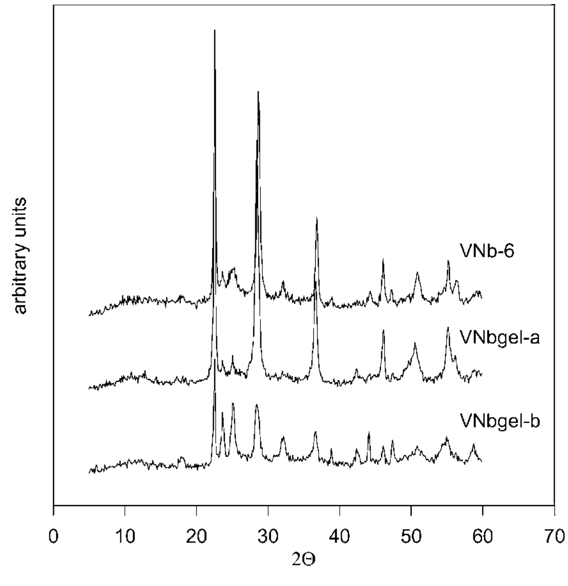

Fig. 3. XRD patterns of gel and impregnated materials.

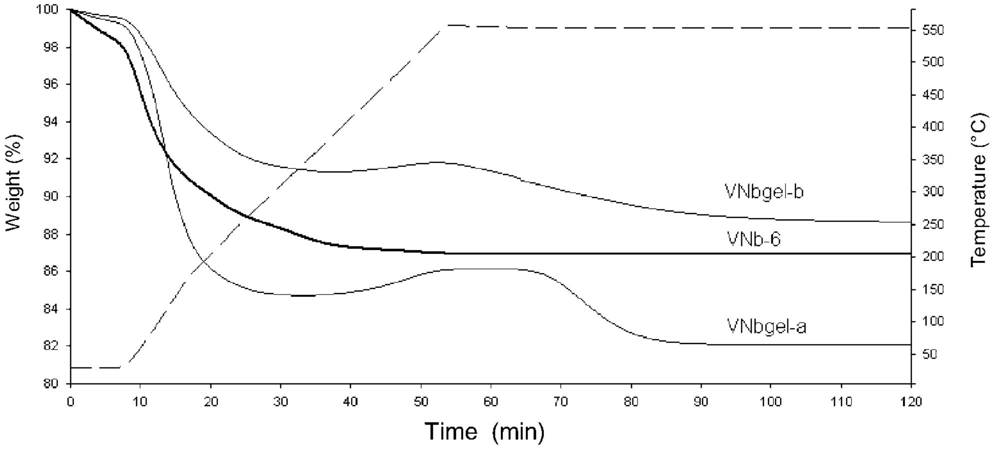

Fig. 4. Weight loss of gel and impregnated materials heating up to 550 °C in air.

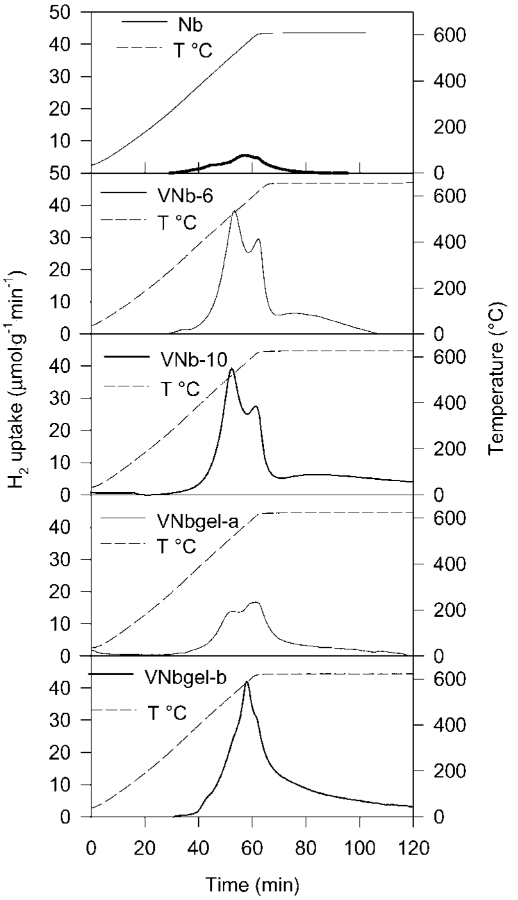

Fig. 5. TPR curves of gel and impreganted materials.

samples lose rapidly weight up to 230–250 °C. After that the impregnated sample slowly reaches a constant weight which does not change during the following 3 h treatment at 550 °C, whereas a weight increase starting at about 400 °C is observed for the two gels. During the isothermal step, the gels start to lose weight again.

Only water is released by the impregnated sample during the whole TG experiment, due to the easy decomposition of the ammonium precursor during the drying step, while a release of CO_2 is associated to the weight loss of the two gels up to 80–90 min run likely related to the oxidation of the organic precursors. On the other hand, the weight increase observed for the two gels is not associated to any IR-detectable species and, therefore, could reasonably be related to the oxidation of vanadium likely partially reduced during the synthesis.

Table 3
H_2 uptake evaluated from TPR experiments

Material	H_2 uptake × 10^4 (mol g^{-1})	H/V (mol mol^{-1})
VNbgel-a	4.5	0.8
VNbgel-b	8.5	1.5
VNb-6	7.2	1.3
VNb-10	8.4	2.6

Table 4
Rate of ethane consumption referred to sample weight ($r_wC_2H_6$) and sample surface area ($r_sC_2H_6$) and rate of ethylene formation (rC_2H_4) evaluated from catalytic tests

Material	$r_wC_2H_6$ (μmol s^{-1} g^{-1})	$r_sC_2H_6$ (μmol s^{-1} m^{-2})	rC_2H_4 (μmol s^{-1} g^{-1})
VNbgel-a	1.55	0.13	0.61
VNbgel-b	0.34	0.085	0.17
VNb-6	1.47	0.042	0.51

3.3. TPR measurements

In Fig. 5 TPR profiles of calcined vanadium-niobium samples and that of pure Nb_2O_5 are reported. The comparison between the intensity of signals of vanadium-containing samples and that of niobium oxide suggests that reduction can be reasonably attributed to vanadium neglecting niobium contribution in the mixed samples. This was further confirmed carrying out a TPR experiment on a impregnated vanadium-niobium sample with a different V/Nb ratio (1/10) which gave rise to a TPR profile having the same proportion among the different contributions of the sample with a V/Nb ratio 1/6. In the TPR curve of all samples, except that of VNbgel-b, two main contributions are evident. The former shows a peak temperature in the range of 515–540 °C, while for the latter the value of the peak temperature corresponds to the change of the heating rate. This could suggest a double step reduction of vanadium or could be associated to differently reducible vanadium species not present in VNbgel-b sample which gives rise to a curve peaked at higher temperature. The different nature of VNbgel-b, already shown by XRD analysis, is therefore confirmed by TPR.

The results of the integration of TPR curves and the peak temperatures are reported in Table 3. The ratio $H/V < 2$ suggests that V^{5+} is not completely reduced to V^{3+} as observed for supported vanadium-niobium mixed oxide [11] or that a fraction of vanadium was in the $+4$ oxidation state before the TPR experiment.

3.4. Catalytic tests

The catalysts have been employed in the oxidative dehydrogenation of ethane in order to compare their performances with those of other vanadium-niobium-based catalysts [11]. The reaction products are ethylene, CO and CO_2. In Table 4 the values of ethane consumption and ethylene formation rate, evaluated under differential conditions, are reported. VNbgel-a and VNb-6 samples show a very similar activity but VNbgel-a is a little more selective. Moreover, if surface area is taken into account, VNbgel-a is also significantly more active than the impregnated sample. A very low activity, also associated to a very poor selectivity, has been shown by VNbgel-b. These results are in very good agreement with those obtained by the physico-chemical characterization of the calcined materials and confirm the different nature of the gel synthesized with a low H_2O/V ratio. The higher activity of VNbgel-a and VNb-6 could be likely associated to a larger surface exposure of vanadium oxide phase. On the contrary, for VNbgel-b it can be hypothesized that vanadium, more involved in the formation of a bulk mixed compound with niobium, is less available for the ODH reaction.

4. Conclusions

Preparation of V-Nb gels through hydrolysis and polycondensation of niobium ethoxide with vanadium oxytriisopropoxide leads to the formation of high surface area, amorphous solids containing residues that are lost during heating. The H_2O/V ratio used during the synthesis strongly influences the main feature of the product obtained after calcination at 550 °C, necessary to use the materials as catalysts for the oxidative dehydrogenation of ethane, leading to niobium oxide particles covered by amorphous vanadium oxide, similar to those obtained by impregnation of Nb_2O_5 with a vanadium precursor, for high H_2O/V ratio and to a V-Nb mixed oxide for low H_2O/V ratio. The former materials exhibit a much higher catalytic activity and selectivity towards ethylene formation.

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