



Surface Characterization of Composite Catalysts Prepared by Sol-Gel Route

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The aim of this work is to synthesize Nb-V oxide catalysts by sol gel route starting from metal alkoxides using different H₂O/V ratios. Dried samples are characterized by X-ray diffraction (XRD), atomic absorption, and Brunauer-Emmett-Teller (BET) analysis. Calcination of dried materials up to 600°C in flowing air has been followed with Thermogravimetry-Fourier-transform infrared spectroscopy (TG-FTIR) spectroscopic analysis. The catalytic properties of calcined materials are tested in the oxidative dehydrogenation of ethane at 600°C. An improvement of the catalytic performances of vanadium for the gel prepared with the higher H₂O/V ratio is found with respect to those of the supported catalyst due to the better interaction between vanadium and niobium.

metal, such as Nb, provides an enhanced selectivity in the ODH of light alkanes also depending on the used preparation method.^[4,5] 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. Topography and surface chemistry are in fact increasingly studied and characterized because they can greatly influence adsorption process and therefore the catalytic activity.^[6–9] The architecture design of the specific catalyst can be accomplished by implementing adequate

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. 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 maintaining a satisfactory selectivity.^[1]

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 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

preparative procedures such as the sol-gel methods, which have been found to be particularly powerful to control the intimacy of molecular scale in mixed oxides.^[10–12] 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 d⁰ configuration, such as Ti(IV) or Nb(V), are very reactive towards hydrolysis, addition of water causing formation of precipitates insoluble hydroxides 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.^[13–16]

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. These samples have been tested as catalysts for the ODH of ethane.

2. Experimental Section

Two samples containing V₂O₅ and Nb₂O₅ with a V/Nb atomic ratio 1/5 were prepared. Vanadium-niobium gels were prepared using Nb(OC₂H₅)₅ and VO[(CH₃)₂CHO]₃ analytical grade (Aldrich) reagents as starting materials. Water-free ethanol, obtained by distillation with metallic sodium of commercial anhydrous ethanol was used. Bidistilled water was used for the hydrolysis reaction. Due to the high reactivity of niobium pentaethoxide toward moisture, the alcoholic solution was handled inside a glove box at room temperature. The two gels differ from each other in the H₂O/V ratio (Table 1). A clear homogeneous solution resulted. The container was sealed with parafilm and kept

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Table 1. Synthesis parameters, composition, and surface area.

Material	Gelation time (day)	H ₂ O/Vmolar ratio	V ₂ O ₅ /Nb ₂ O ₅ Molar ratio	Surface area before thermal treatment (m ² g ⁻¹)	Surface area after thermal treatment (m ² g ⁻¹)
Nb gel-1	6	4	1/5	149	11
Nb gel-2	6	0.04	1/5	70	3

at ambient conditions for gelation. Depending upon the amount of the H₂O 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.

The niobium and vanadium content in the dried gel was evaluated by inductively coupled plasma-emission spectrometer (ICPE-9000 Shimadzu, Tokyo, Japan). Before ICPE analysis, the samples were acidified with HNO₃ solution to pH = 2. 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 2θ 5–60° using Cu Kα radiation. All samples have been calcined in flowing air at 600°C for 3 h. Porosity and specific surface area particles were evaluated by BET (Fisons Instruments) analyses, which were performed at liquid nitrogen temperature and using gaseous N₂ to evaluate the specific surface of powders.

The TG/FTIR measurements were carried out using a SETARAM 92-16.18 TG apparatus equipped with 250 μL alumina crucibles filled with about 100–150 mg of sample at 10°C min⁻¹, under argon flow (40 mL min⁻¹), in the temperature range 25–600°C for the analysis of the released gases. TG analysis was carried out by heating the sample at 10°C min⁻¹, in air flow up to 600°C holding the final temperature for 2h 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 a previous investigation.^[5] The feed composition was 4% C₂H₆ and 2% O₂ in a balance of He. The reaction temperature was 600°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

The gelation is the result of the hydrolysis and condensation reactions. At room temperature, the hydrolysis is much faster than the condensation reactions so that the number of Nb-O-Nb bridges formed is not sufficient to give gelation and precipitation of hydrated niobium oxide-alkoxide aggregate occurs. Mixing at a lower temperature (–10°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. Both the gels were clear, transparent, and light yellow in color. Chemical analysis of melted gel showed that a good composition control was provided by sol-gel process (Table 2). The analyzed and theoretical value are in fairly good agreement. 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]

Table 2. Chemical analysis of gels.

Constituent	Analyzed (wt.%)	H ₂ O/Vmolar ratio
V ₂ O ₃	10.10	10.10
Nb ₂ O ₃	89.80	89.57

The severe thermal treatment at 600°C, however, results in a strong reduction of surface area of the gels due to the crystallization of amorphous materials in different phases VNbgel-1. These results show signals of monoclinic Nb₂O₅ (JCPDS 27–1313) whereas, in addition to these peaks, VNbgel-2 shows also signals of n-Nb₂O₅ (JCPDS 27–1311) and of the mixed vanadium-niobium oxide (JCPDS 16–132). This finding 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, 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-1 sample treated at 200°C and 400°C, respectively, under the same conditions used for the treatment at 600°C. Calcination at 600°C starting from a lower value as dried sample, maintains a good value of surface area as calcined. The TG analysis of the catalyst 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-1 and the VNbgel-2. After a first release of physisorbed water, occurring at low temperature, all 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 600°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. 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. The catalysts have been employed in the ODH of ethane in order to compare their performances with those of other vanadium-niobium-based catalysts.^[13] The reaction products are ethylene, CO, and CO₂. In Table 3, the values of ethane consumption and ethylene formation rate, evaluated under differential conditions, are reported. VNbgel-1 has high more selectivity of VNbgel-2. Moreover, if surface area is taken into account, VNbgel-1 is also significantly more active than the impregnated sample.^[14–17] A very low activity, also associated to a very poor selectivity, has been shown by VNbgel-2. 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

Table 3. Rate of ethane consumption referred to sample weight ($r_w\text{C}_2\text{H}_6$) and sample surface area ($r_s\text{C}_2\text{H}_6$) and rate of ethylene formation ($r\text{C}_2\text{H}_4$) evaluated from catalytic tests.

Material	$r_w\text{C}_2\text{H}_6$ ($\mu\text{mol s}^{-1} \text{g}^{-1}$)	$r_s\text{C}_2\text{H}_6$ ($\mu\text{mol s}^{-1} \text{m}^{-2}$)	$r\text{C}_2\text{H}_4$ ($\mu\text{mol s}^{-1} \text{g}^{-1}$)
VN-b gel-1	1.55	0.13	0.61
VN-b gel-2	0.34	0.085	0.17

with a low $\text{H}_2\text{O}/V$ ratio. The higher activity of VNbgel-1 could be likely associated to a larger surface exposure of vanadium oxide phase. On the contrary, for VNbgel-2 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 $\text{H}_2\text{O}/V$ ratio used during the synthesis strongly influences the main feature of the product obtained after calcination at 600°C , necessary to use the materials as catalysts for the ODH of ethane, leading to niobium oxide particles covered by amorphous vanadium oxide. The former materials exhibit a much higher catalytic activity and selectivity towards ethylene formation.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

catalyst, Sol-gel synthesis

- [1] F. Barbieri, D. Cauzzi, F. De Smet, M. Devillers, P. Moggi, G. Predieri, P. Ruiz, *Catal. Today* **2000**, 61, 353.
- [2] M. Catauro, C. Pagliuca, L. Lisi, G. Ruoppolo, *Therm. Acta* **2002**, 381, 65.
- [3] S. Albonetti, F. Cavani, F. Trifiro, *Catal. Rev. Sci. Eng.* **1996**, 38, 413.
- [4] S. A. Korili, P. Ruiz, B. Delmon, *Catal. Today* **1996**, 32, 229.
- [5] P. Ciambelli, G. Ruoppolo, L. Lisi, G. Russo, J. C. Volta, *Stud. Surf. Sci. Catal.* **1997**, 110, 285.
- [6] G. Raffaini, F. Ganazzoli, *Langmuir* **2013**, 29, 4883.
- [7] G. Raffaini, F. Ganazzoli, *J. Biomed. Mat. Res. A.* **2006**, 76A, 638.
- [8] L. De Nardo, G. Raffaini, E. Ebramzadeh, F. Ganazzoli, *International Journal of Artificial Organs* **2012**, 35, 629.
- [9] G. Raffaini, S. Elli, F. Ganazzoli, *J. Biomed. Mat. Res. A.* **2006**, 77, 618.
- [10] M. Catauro, M. G. Raucchi, A. G. Ausanio, *J. of Mater. Sci.: Mater. in Medicine* **2008**, 19, 531.
- [11] M. Catauro, F. Barrino, G. Dal Poggetto, F. Pacifico, S. Piccolella, S. Pacifico, *Mater. Sci. and Eng. C* **2019**, 100, 837.
- [12] R. Gonzales, T. Lopez, R. Gomez, *Catal. Today* **1997**, 35, 293.
- [13] M. Catauro, E. Tranquillo, G. Dal Poggetto, M. Pasquali, A. Dell'Era, S. Vecchio Cipriotti, *Materials* **2018**, 11, 2364.
- [14] M. Catauro, M. G. Raucchi, F. De Gaetano, A. Marotta, *J. Mater. Sci* **2003**, 38, 3097.
- [15] M. Catauro, F. Barrino, G. Dal Poggetto, G. Crescente, S. Piccolella, S. Pacifico, *Materials* **2019**, 12, 148.
- [16] M. Catauro, *F. Bollino Journal of Applied Biomaterials and Functional Materials* **2013**, 11, 172.
- [17] M. Catauro, R.A. Renella, F. Papale, S. Vecchio Cipriotti, *Mater. Sci. Eng. C* **2016**, 61, 51.