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Synthesis and characterization of V_2O_5 - TiO_2 and V_2O_5 - Al_2O_3 materials application in heterogeneous catalysis.

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ABSTRACT

Synthesis of porous materials offers a new possibility for the creation of catalysts that are effective in many industrial processes. The aim of this work is to prepare 20 wt%. V_2O_5 - Al_2O_3 and 20 wt%. V_2O_5 - TiO_2 mixed oxides by the sol-gel method. The materials are characterized by FTIR and XRD analysis which have shown an amorphous structure of V-Al xerogel and a crystalline structure for V-Ti xerogel with the presence of both TiO_2 rutile and anatase varieties. The surface BET of V_2O_5 - Al_2O_3 is $135\text{ m}^2\text{g}^{-1}$ approximately five times bigger than V_2O_5 - TiO_2 surface area. The sol-gel materials have shown to be efficient catalysts for the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone mixture; an important intermediate for manufacturing of 6,6 nylon. The use of H_2O_2 as oxidant, acetic acid as solvent and 20 wt%. V_2O_5 - Al_2O_3 as catalyst gives the best result; more than 22% conversion with 90.69% selectivity for alcohol product.

Key words: Mixed oxide, inorganic materials, sol-gel method, catalysis.

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INTRODUCTION

The preparation process of inorganic materials is one of the most aspects of material science. Not only the chemical composition of particular metal plays a crucial role of many applications but also its structure. The proper choice of the chemical precursors and the preparation technique to obtain a material with desired chemical and physical properties is a challenge for both material scientists and inorganic chemists.

Sol-gel processes have attracted the attention of many researchers in recent years [1-5]. In fact, the physical and chemical features of the materials obtained by these methods (e.g., particle sizes, surface areas and mechanical properties) can be changed according to the temperature, operating conditions, and to the used precursor. Nowadays, sol-gel methods are well established allowing the preparation of a board variety of supported metals, metal oxides, coating and composite materials with tailored properties. It presents the advantage to use mild chemistry and maintain purity and homogeneity of products. The obtained materials emerging from these processes can be used in selective heterogeneous catalysis, which represents an area of great economical interest.

In this work we wish to report about the sol-gel synthesis of 20 wt. % V_2O_5 - Al_2O_3 and 20 wt.% V_2O_5 - TiO_2 mixed oxides. V-containing mixed metal oxides and supported vanadia have found wide applications as catalysts in several reactions such as: the deshydrogenation of ethane on $V_2O_5/\gamma-Al_2O_3$ [6], the methane oxidation with V_2O_5 - TiO_2 xerogel [7]; the ethylbenzene oxidation into acetophenone with V_2O_5/Al_2O_3 [8]; the oxidation of ethanol by $V_2O_5/\gamma-Al_2O_3$ - TiO_2 [9]; the photodegradation of acetone with $V_2O_5/SmVO_4$ [10]; the oxidation of cyclohexane on V_2O_5/TiO_2 catalyst [11, 12]. In this later reaction, we have chosen to investigate the V_2O_5 - Al_2O_3 and V_2O_5 - TiO_2 sol-gel materials in presence of hydrogen peroxide as oxidant. Cyclohexane oxidation is currently of considerable commercial significance [13- 17].

EXPERIMENTAL

Synthesis of samples

Mixed oxides materials were prepared by an acid-catalyzed sol-gel process [3, 4]. Vanadium pentoxide (Sigma) was dissolved in hydrogen peroxide (Prolabo, 30% in water); the resulting solution was stirred for 30 min and then a mixture containing titanium butoxide (Aldrich; 97%), acetic acid (Prolabo; 100%) and butanol (Aldrich) was added into solution while stirring to obtain V_2O_5 - TiO_2 xerogel. For the synthesis of V_2O_5 - Al_2O_3 , a mixture containing aluminum propoxide (Aldrich; 98%), acetic acid and propanol-2 (Fluka) was added into solution. xerogels were finally dried at 120 °C and then calcined at 300 °C for 6h under an air flow.

Catalysts characterization

The $V_2O_5-Al_2O_3$ and $V_2O_5-TiO_2$ catalysts have been characterized by X-ray powder diffraction (XRD) using a Philips PW 3710 diffractometer with $Cu K\alpha$ radiation ($\lambda=1.54060 \text{ \AA}$) in the range of $2\theta=20^\circ-80^\circ$. BET surface area was determined from N_2 adsorption isotherms at 77K using a Micrometrics Tristar instrument. The mixed oxides have also been investigated by FT-IR spectroscopy using an AVATAR 320 Thermo-Nicolet FT-IR spectrometer.

Catalytic cyclohexane oxidation reactions

Cyclohexane oxidation reactions were carried out in a 250 ml three-necked flask, placed in a temperature equilibrated oil bath and fitted with a reflux condenser. Typically, a mixture containing 66.5 mmol cyclohexane (Prolabo; 98%), 19 mmol initiator (cyclohexanol; Merck-Schuchardt; 99%), 66.5 mmol hydrogen peroxide, 24.8 ml solvent (acetone or acetic acid) and 0.1 g $V_2O_5-Al_2O_3$ or $V_2O_5-TiO_2$ catalyst was magnetically stirred under atmospheric pressure at 343 K for 6 h.

The consumption of H_2O_2 was determined by iodometric titration [18] and the reaction mixture was analyzed by gas chromatography (GC), taking aliquots at different reaction times. A Shimadzu GC-14 B gas chromatograph equipped with an Apiezon L column (10% on Chromosorb P UNDMCS) and a flame ionization detector (FID) was used. To such an end, 0.5 ml of sample was added to 0.04 ml of internal standard 1-pentanol (Prolabo) and 0.3 μ l of this mixture was analyzed.

RESULTS AND DISCUSSIONS

Characterization

The surface area of the 20 wt% $V_2O_5-TiO_2$ mixed oxide material, measured according to the BET method, is $27 \text{ m}^2\text{g}^{-1}$ approximately. It is about $135 \text{ m}^2\text{g}^{-1}$ for 20 wt% $V_2O_5-Al_2O_3$, so five times bigger.

XRD analysis of $V_2O_5-TiO_2$ (figure 1A) shows two well known titanium oxide crystalline phases, namely anatase (diffraction peaks labeled a, ICDD card no. 21-1272) and rutile (peaks b, ICDD card no. 21-1276). The anatase titanium oxide phase is generally obtained in mild acidic conditions and at low temperature. On the contrary, titanium rutile variety of TiO_2 is obtained in highly acidic medium and at high temperature (400 and 1200°C) or in the presence of tetravalent elements with +6 coordination number (V, Sn, Pb). Considering the mild acidic conditions and the temperature at which the $V_2O_5-TiO_2$ has been prepared, we can argue that the appearance of the rutile variety beside the anatase phase would be favoured by the presence of vanadium oxide [19].

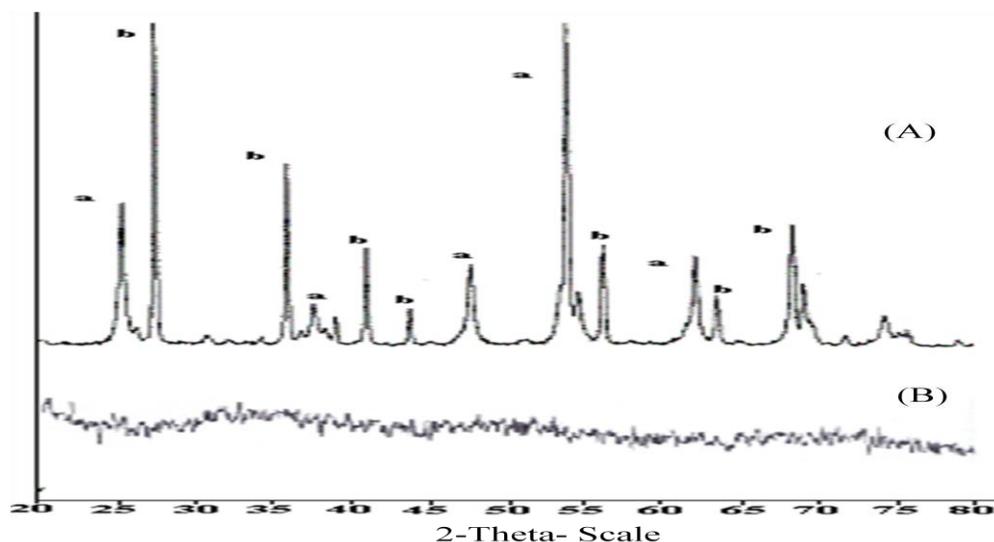


Fig. 1: X-ray diffraction patterns of V_2O_5 - TiO_2 (A) and V_2O_5 - Al_2O_3 (B); a: anatase; b: rutile.

XRD analysis of V_2O_5 - TiO_2 does not present any characteristic diffraction peak of V_2O_5 phase or other vanadium oxide. Therefore, vanadium oxide would be either amorphous or much dispersed on the TiO_2 phase.

XRD pattern of V_2O_5 - Al_2O_3 (figure 1B) shows an amorphous structure. It cannot be possible to identify alumina or vanadia crystalline phases. Generally, Al_2O_3 crystallize at a temperature treatment of samples higher than $300^\circ C$. Such result let us propose that the impossibility to observe V_2O_5 crystalline phase can be mainly due to the large dispersity of this oxide on the alumina surface. Probably nanosized vanadia crystallites supported on alumina were formed [20].

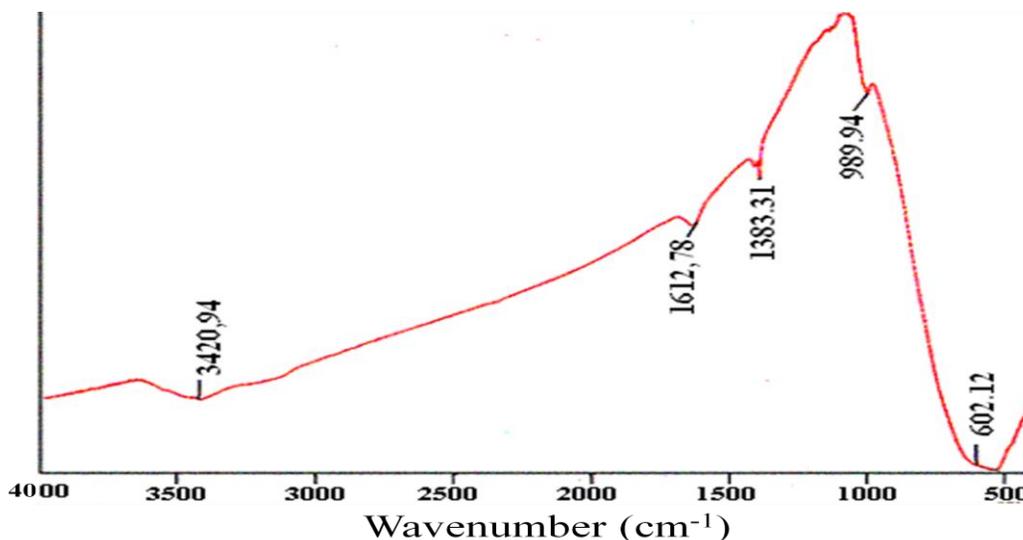


Fig. 2: FT-IR spectrum of V_2O_5 - TiO_2 xerogel.

Figure 2 shows the IR spectrum of V_2O_5 - TiO_2 material. The wide band at 3420 cm^{-1} is attributed to the OH elongation mode of H_2O . The deformation band of H_2O is situated at 1612 cm^{-1} . The band appearing around 1400 - 1390 cm^{-1} is due to the CH_3 group [21]. The peak situated between 1000 and 900 cm^{-1} could be assigned to Ti-O-C bond. Other authors have attributed this band to the coupled vibration between V=O and V-O-V [12]; this has been confirmed in the IR spectrum of V_2O_5 treated at $300\text{ }^\circ\text{C}$ (figure 3) where we found a band at 1020 cm^{-1} corresponding to V=O bond. The main TiO_2 adsorption peak is attributed to the Ti-O bond which appears at 510 - 500 cm^{-1} in figure 2, and which corresponds to the anatase phase. Another peak situated near 550 cm^{-1} is attributed to the presence of rutile phase. Therefore, these results supplement the XRD analysis. The peak at 610 - 600 cm^{-1} corresponds to the band of the V-O bond [4, 22].

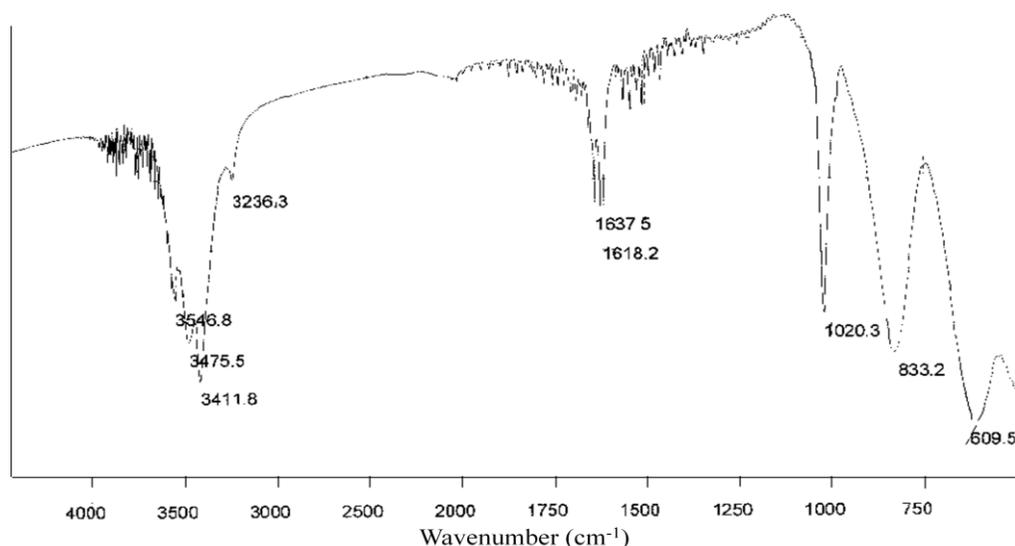


Fig. 3: FT-IR spectrum of V_2O_5 calcined at 300°C for 6 h.

In the IR spectrum of V_2O_5 - Al_2O_3 (figure 4) we found practically the same bands observed in figure 2: the OH elongation mode of H_2O is situated at 3103 cm^{-1} ; the deformation band of H_2O appears at 1547.86 cm^{-1} . The band appearing around 1500 - 1350 cm^{-1} is due to the CH_3 group. Other authors attributed these bands to the carbonate or carboxylate surface compounds formed due to adsorption of atmospheric CO_2 on the mixed oxide surface [8]. The bands corresponding to V=O and V-O bonds are situated around 1000 - 900 cm^{-1} and 700 - 600 cm^{-1} respectively. Figure 4 shows also the Al-OH stretching vibration band at 3653.89 cm^{-1} [23, 24].

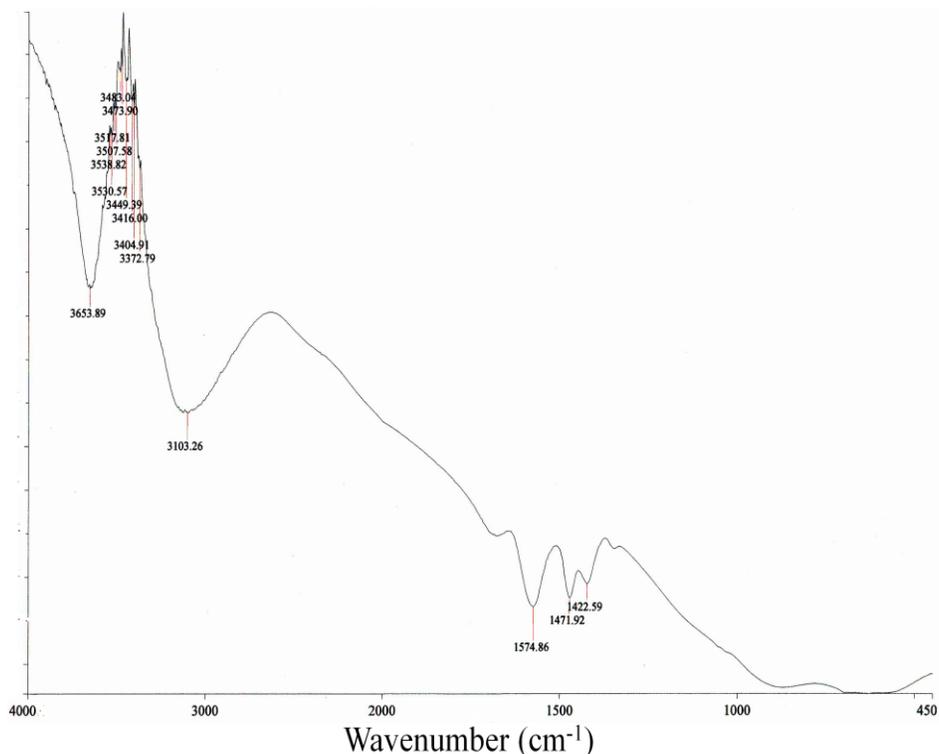


Fig. 4: FT-IR spectrum of V₂O₅-Al₂O₃ xerogel.

Catalytic tests

Cyclohexane oxidation reaction was first carried out in absence of any solvent, but no conversion was noticed for the control reaction after the addition of hydrogen peroxide, in the complete absence of both catalyst and initiator. The sole addition of the catalyst (V₂O₅-Al₂O₃ or V₂O₅-TiO₂) did not produce any change, thus showing that the oxidation of C₆H₁₂ remains a hard reaction at a low temperature (70 °C). However, the addition of cyclohexanol as initiator produced slightly better results.

On the other hand, it has been shown that the presence of a polar solvent in cyclohexane oxidation reaction makes catalyst active [4]. Efficient removal of the oxidation products from the active sites of the catalyst by the polar solvent is assumed to explain this weak activity [25].

Table 1: Oxidation of cyclohexane with hydrogen peroxide in acetic acid as solvent.

| Catalyst | Cyclohexanol (m.mol) | Cyclohexanone (m.mol) | Conversion (%) | H ₂ O ₂ consumption (%) |
|---|----------------------|-----------------------|----------------|---|
| V ₂ O ₅ -TiO ₂ [4] | 0.00 | 1.48 | 2.22 | 90.66 |
| V ₂ O ₅ -Al ₂ O ₃ | 13.74 | 1.41 | 22.81 | 87.99 |

Reaction conditions: 66.5 mmol cyclohexane, 66.5 mmol H₂O₂, 19 mmol cyclohexanol, 24.8 mmol acetic acid, 0.1 g catalyst, T = 343 K, t = 6 h.

Table 2: Oxidation of cyclohexane with hydrogen peroxide in acetone as solvent.

| Catalyst | Cyclohexanol (m.mol) | Cyclohexanone (m.mol) | Conversion (%) | H ₂ O ₂ consumption (%) |
|---|----------------------|-----------------------|----------------|---|
| V ₂ O ₅ -TiO ₂ [4] | 0.42 | 0.56 | 1.47 | 85.75 |
| V ₂ O ₅ -Al ₂ O ₃ | 4.44 | 2.18 | 9.98 | 70.05 |

Reaction conditions: 66.5 mmol cyclohexane, 66.5 mmol H₂O₂, 19 mmol cyclohexanol, 24.8 mmol acetone, 0.1 g catalyst, T = 343 K, t = 6 h.

So, in this work, the catalytic test was carried out in presence of the cyclohexanol as initiator using two different solvents acetic acid (table 1) and acetone (table 2).

The sol-gel materials, especially vanadia-alumina xerogel, have shown to be efficient catalysts for the selective oxidation of cyclohexane, and the best result was obtained for V₂O₅-Al₂O₃/ H₂O₂/ acetic acid system (table 1). In all cases studied, the consumption of H₂O₂ is more than 70% after 6 hours of reaction. This effect may be due to the liberation of uncomplexed V⁵⁺, which are prone to decompose H₂O₂ instead of reacting with cyclohexane [12].

The use of acetic acid as solvent leads to the stabilization of the peroxo bond of H₂O₂ as peracid [13]. A cyclohexane conversion of 22.81% into cyclohexanol and cyclohexanone products was obtained. This conversion is approximately ten times bigger than one obtained with V₂O₅-TiO₂ catalyst, it's may be due to the surface BET of catalysts.

In the case of acetone (table 2), The V₂O₅-Al₂O₃ catalyst showed also a good conversion (9.98%) compared to V₂O₅-TiO₂ results (1.47%). The use of acetone as solvent leads to the formation of the dimethyldioxyrane, which is a powerful oxidizer for organic compounds [26].

CONCLUSION

The 20 wt. % V₂O₅-Al₂O₃ and 20 wt. % V₂O₅-TiO₂ mixed oxides materials were prepared by the sol-gel method. XRD and FTIR analysis showed that V₂O₅-TiO₂ presents a crystalline structure with the presence of both TiO₂ rutile and anatase varieties. The V₂O₅-Al₂O₃ presents an amorphous structure. The surface BET of V₂O₅-Al₂O₃ is 135 m²g⁻¹ approximately five times bigger than V₂O₅-TiO₂ one.

The sol-gel materials have shown to be efficient catalysts for the selective oxidation of cyclohexane. It has been shown that cyclohexane oxidation system catalyzed by the 20 wt. % V₂O₅-Al₂O₃ mixed oxide, in presence of hydrogen peroxide as oxidant and acetic acid as solvent presents more than 22% conversion into cyclohexanol and cyclohexanone product, with 90.69% selectivity for cyclohexanol.



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