



Influence of preparation methods and structure of niobium oxide-based catalysts in the epoxidation reaction



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ABSTRACT

The catalytic activity of niobium oxide-based materials, containing the same amount of Nb₂O₅ (~15 wt%) and prepared by different methods, with that of pure Nb₂O₅ in the epoxidation of methyl oleate with hydrogen peroxide was compared.

The catalytic performances of the catalyst prepared by impregnation do not differ substantially from the ones of Nb₂O₅. The performances of Nb-supported catalysts prepared by sol–gel can be modulated by controlling the process parameters. The high dispersion of the active NbO_x species obtained by this preparation method gives very higher selectivity than in the case of pure Nb₂O₅. Morphologic and structural characterization of the catalysts helped justifying the obtained catalytic results in terms of activity and selectivity.

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1. Introduction

In the last decade, niobium based materials have received an increasing attention in the catalysis field. Niobic acid, niobium pentoxide and niobium containing mixed oxides have been studied as catalysts and supports in many important chemical reactions, especially when high acidity and water tolerance are needed. Among them, dehydration of alcohols and sugars, condensation, oxidation, hydrolysis, esterification and isomerization deserve to be mentioned [1,2].

Niobium pentoxide (also known as niobic acid when fully hydrated) represents the most studied oxide of niobium; for catalytic purposes it can also be supported on different support materials. Different niobium surface species (isolated or bulk) may be formed depending on the nature and properties of the support

material, niobium precursors, niobium content and synthesis method. According to Jehng and Wachs [3] the molecular structure of niobium species on the surface of SiO₂ matrix depends on the niobium content. At low niobium oxide content (about 1 wt%), isolated NbO₄ units prevail, while nano-aggregates of Nb₂O₅ arise with increasing niobium loading. These species are responsible for specific properties and catalytic activity. The presence of both Brønsted and Lewis acid sites was reported in hydrated niobium pentoxide [4] and niobium–silicon mixed oxides [3]. The Lewis acid sites are due to the presence of an excess of effective positive charge in NbO₄ tetrahedra, while the Brønsted ones are related to the presence of an excess of effective negative charge in NbO₆ octahedra. Particularly, in hydrated niobium pentoxide, water-tolerant Lewis acid sites were found even after the formation of NbO₄–H₂O adducts [4]. In niobium–silicon mixed oxides, Brønsted acidity was related to the Nb₂O₅ nano-domains with octahedral structure, the amount of which depends on the Nb₂O₅ loading. Hence, Brønsted acid sites were associated to surface slightly distorted NbO₆ octahedra [5].

Therefore, the catalytic performance of the niobium oxide-based materials can be controlled by modulating the distribution and the

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relative amount of Lewis and Brønsted acid sites, by regulating the structure and in turn, the preparation method.

The aim of this study is to compare the catalytic activity of niobium oxide-based materials, containing the same amount of Nb_2O_5 (≈ 15 wt%) and prepared by different methods, with that of pure Nb_2O_5 in the epoxidation of methyl oleate with hydrogen peroxide.

As a matter of fact, the increasing interest for vegetable oils in the chemical industry is due to their easy accessibility from renewable resources. Epoxidized soybean oil and epoxidized methyl esters derived by oils play an important role as building blocks for the preparation of chemical intermediates, that are the basis for a wide variety of consumer products. For example, they are used as plasticizers and stabilizers for PVC, and as components of lubricants.

On the industrial scale the epoxidation reaction is currently carried out with peroxycarboxylic acids, obtained in situ by using mineral acids as catalysts, according to the Prileshajew method [6]. Use of hydrogen peroxide as oxidant and heterogeneous catalysts could be an interesting answer to more sustainable and green processes.

Recently, some papers have been devoted to the use of niobium-based catalysts in oils epoxidation with hydrogen peroxide [7–9]. Periodic mesoporous organosilicas containing niobium prepared by Novak et al. [7] have shown excellent catalytic activity and selectivity for direct oxidation of vegetable oils. High selectivity to epoxide products in FAME (fatty acids methyl esters) epoxidation with hydrogen peroxide was also found by Guidotti et al. [8], using NbO_x^- dispersed on silica catalysts obtained by grafting bis(cyclopentadienyl)niobium(IV) dichloride on to different pure silica supports. They proved that the higher was the contribution of Nb_2O_5 -like nanoaggregates in the catalyst, the poorer was the catalytic performance in terms of activity. Therefore, the efficiency of the catalysts was related to the presence of well isolated Nb(V) sites in tetrahedral coordination highly dispersed on the silica matrix [8]. Some of us have studied the influence of Nb content on the catalytic performance of Nb_2O_5 - SiO_2 catalysts prepared by sol-gel technique in the epoxidation of soybean oil with hydrogen peroxide [9]. It was found that the distribution of surface acid sites strongly affects the catalyst efficiency: Lewis acid sites promote the epoxidation and strong Brønsted acid sites promote the reaction of ring epoxide opening by hydrolysis forming diols [9].

This study is aimed at obtaining better insights on the influence of the preparation procedure on the structure and distribution of surface acid sites of $\text{Nb}_2\text{O}_5/\text{SiO}_2$ solid catalysts. The impregnation method and two different sol-gel routes will be examined in order to evaluate how the different synthesis parameters affect the efficiency of niobium oxide-based catalysts in the epoxidation of methyl oleate with hydrogen peroxide.

2. Experimental

2.1. Synthesis of catalysts

The $\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalyst obtained by wet impregnation was prepared according to the procedure reported elsewhere [10], using a commercial silica (grinded Silica Degussa Aerolyst 3038 whose morphological characteristics are: BET surface area = $194 \text{ m}^2 \text{ g}^{-1}$; pore volume = $0.96 \text{ cm}^3 \text{ g}^{-1}$; average pore size $\approx 19 \text{ nm}$) and niobium oxalate in oxalic acid solution (0.1 M), as Nb source. The niobium oxalate was obtained from niobium pentoxide according to [10]. After drying, the solid was calcined at 975°C for 6 h. The final sample contained a nominal content of Nb_2O_5 equal to 20 wt%. Hereafter this sample will be indicated as Nb_{imp} .

The $\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalysts obtained by sol-gel were prepared according to two routes: sgl [11] and sgII [12]. In the sgl route,

niobium(V) ethoxide, $\text{Nb}(\text{OCH}_2\text{CH}_3)_5$ (99.95%, Sigma–Aldrich), and tetraethoxysilane, $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) (98%, Fluka), were used as starting materials. Niobium ethoxide (handled under nitrogen flow) was added under vigorous stirring to an ethanolic (EtOH) solution of TEOS hydrolyzed with concentrated hydrochloric acid (0.1 M) at room temperature for ca. 60 min. The $[\text{TEOS} + \text{EtOH}]/\text{HCl}$ and EtOH/TEOS volume ratios were kept equal to 58 and 3.8, respectively. Then, the addition of a defined amount of tetrapropylammonium hydroxide ($(\text{C}_3\text{H}_7)_4\text{NOH}$, TPAOH, 20 wt% in water) led to gelation. For a complete and fast gelation, the TPAOH/(Nb + Si) molar ratio was kept equal to 0.30. The unripe solid was aged at room temperature for 24 h, dried under vacuum at 40°C for 2 h, and then calcined at 550°C for 8 h. The final sample contained a nominal amount of Nb_2O_5 equal to 14.9 wt%. Hereafter this sample will be indicated as Nb_{sgI} .

On the other hand, in the sgII route, niobium chloride, NbCl_5 (99%, Gelest), and TEOS (99%, Gelest) were used as starting materials. A solution of NbCl_5 in anhydrous ethanol having a molar ratio $\text{NbCl}_5:\text{EtOH} = 1:6$ was prepared in a dry box at room temperature. This solution was fluxed with dry-air for 20 min, to allow the HCl removal and the formation of partially substituted $\text{Nb}(\text{OEt})_{5-x}(\text{Cl})_x$ species. An alcoholic solution of TEOS with molar ratio $\text{TEOS}:\text{EtOH} = 1:4$ was stirred for 5 min, and then mixed with the first one. The resulting clear solution was hydrolyzed, under stirring, at room temperature using a HCl hydro-alcoholic solution so to obtain the final molar ratio $\text{TEOS}:\text{H}_2\text{O}:\text{HCl} = 1:4:0.01$. A transparent gel was obtained from this final solution, with gelation occurring no later than 2 days. The gelled systems were kept for 2 days more at room temperature before drying. The gels were fully dried in air at 110°C , in an electric oven for 3 days. The catalyst was obtained by finely grounding the hardened dry gel, and then calcining it at 400°C for 3 h. The final sample contained a nominal amount of Nb_2O_5 equal to 18.9 wt%. Hereafter this sample will be indicated as Nb_{sgII} .

The Nb_2O_5 catalyst was obtained by calcining commercial Nb_2O_5 powders (from Aldrich) at 900°C for 6 h.

2.2. Characterization catalysts

The actual Nb_2O_5 content of the prepared catalysts (see Table 1) was evaluated by different methods. Inductively coupled plasma optical emission spectroscopy (ICP) (Aurora M90, Bruker) was used for Nb_{imp} , utilizing a microwave digestion apparatus for the mineralization of the sample. The surface of Nb_{sgI} was quantitatively analyzed by X-ray photoelectron spectroscopy (XPS), according to the procedure described in [11]. Spectrophotometry was used for Nb_{sgII} , according to the procedure described in [12].

XRD patterns were recorded using a Bruker 2D phaser with a $\text{Cu K}\alpha$ radiation of 1.5418 \AA (40 kV and 20 mA). A 2θ range from 5° to 80° was scanned, at a velocity of $0.02^\circ 2\theta \text{ min}^{-1}$.

Ultra violet and visible light diffuse reflection (UV-DRS) spectra were recorded in the range of 200–800 nm on a doubled beam Jasco spectrophotometer. Barium sulfate was used as a reflectance standard. The measured intensity was expressed as the value of the Kubelka–Munk function $F(R)$.

Surface areas were determined from N_2 adsorption and desorption isotherms at liquid nitrogen temperature, by using the BET method. The N_2 isotherms were obtained in an automatic analyzer (Sorptomatic 1900 instrument). The samples were previously treated in the sample cell at 350°C under vacuum, up for 16 h up to complete degassing.

Microstructure and chemical composition of the samples were investigated by NOVA/NANOSEM 450 FEI scanning electron microscopy (SEM), equipped with an energy dispersive X-ray analyzer (EDX) at an accelerating voltage of 30 kV.

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