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Acidity enhancement of niobia by sulfation: An experimental and DFT study

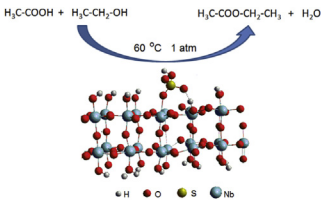
Angela S. Rocha [a, *], Gustavo C. Costa [a], Priscila Tamiasso-Martinhon [b], Célia Sousa [b], Alexandre B. Rocha [b]

[a] Universidade do Estado do Rio de Janeiro, Departamento de Físico-Química, Instituto de Química, Rio de Janeiro, Brazil
[b] Universidade Federal do Rio de Janeiro, Departamento de Físico-Química, Instituto de Química, Rio de Janeiro, Brazil

HIGHLIGHTS

- Sulfation treatment has improved the acidity of niobium oxide.
- A sulfate group on niobia (T-Nb_2O_5) was proposed using DFT method.
- Niobia and sulfated niobia are used for esterification of acetic acid with ethanol.

GRAPHICAL ABSTRACT



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ABSTRACT

Acidic solids are used as catalyst at several industrial processes and studies to improve their activities have been developed by different groups. One method well known is sulfating oxide to create new acid sites, but investigations about sulfated niobia are still scarce. This work studied the influence of sulfation on the niobia acidity by using a very simple reaction model, the esterification of acetic acid with ethanol, performed at 60 °C and 1 atm. Niobia and sulfated niobia samples were characterized by N_2 adsorption, X-ray diffraction, FTIR and titration with *n*-butylamine. To investigate the nature of sulfate groups formed on the surface of niobia, calculations based on the Density Functional Theory (DFT) have been performed for two models: pure niobia with hydroxylated surface and sulfated niobia where one OH^- surface group was replaced by a HSO_4^-. The experimental results indicated that the sulfation treatment leads to an increase in the specific surface area, acidity and, consequently, in the activity of niobia, with small changes in the crystal structure of the solid. The presence of sulfate groups was evidenced by FTIR spectra and calculations have indicated HSO_4^- species bounded to the surface. Density Functional Perturbation Theory (DFPT) was also employed to obtain infrared intensities in the region of sulfate vibration bands.

1. Introduction

Acid catalysts are widely used in several reactions with industrial application [1], as hydration/dehydration [2–4], alkylation [4–6], cracking [7], isomerization [8], esterification [9], etc. Mineral liquid acids can be used in most of these processes but the substitution to solid materials is environmentally and economically appealing, since solid catalysts can be easily separated from the reaction system. Consequently, the purification of products is simple and the material can frequently be reused numerous times. Additionally, acidic solids are in general less corrosive than the liquids, therefore less aggressive.

Several transition metal oxides present noticeable acidity in

* Corresponding author.
E-mail address: angela.sanches.rocha@gmail.com (A.S. Rocha).

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bulk, supported or mixed forms and have been used mainly as support or active phase in catalysts formulation. Alumina as boehmite phase, for instance, is an acid oxide commonly used as bulk catalysts and support [10,11], but silica-alumina and zeolites are solids more versatile [12–14].

The strategies employed to increase the acidity of oxides passes through improve their textural, structural and surface properties. A widely known technique is adding groups to the surface of solids [15–20]. For example, sulfate groups are incorporated to the surface of metal oxide by treating gel oxides with sulfuric acid at specific conditions, such as concentration of the sulfating solution, followed by calcination [21,22].

Arata has summarized the preparation and some properties of sulfated oxides of Fe, Ti, Zr, Hf, Sn, Si and Al [23]. Sulfated solids were obtained by treating the amorphous oxides with sulfuric acid or ammonium sulfate solutions followed by calcination and, it was shown, the sulfated oxides exhibit super acid characteristics. Sulfated zirconia is the most studied superacid solid and its synthesis, as well as its properties, is already well-known [24–27].

Niobia presents both Lewis and Brϕnsted strong acid sites but the sulfated form is less investigated [28–30]. A recent work showed that this material has quite promising features as catalyst for esterification, when compared to others sulfated oxides [31]. Notwithstanding, the identification of surface structures in this type of material was not properly performed.

Niobium oxide exists in many polymorphic forms; TT-Nb_2O_5 and T-Nb_2O_5 are low-temperature phases. H-Nb_2O_5 is the high-temperature phase and is also the most stable, from the thermodynamic point of view. TT-phase is the least stable [32]. It is worth mentioning that TT-Nb_2O_5 changes almost continuously into T-Nb_2O_5 on being heated from 600 to 800 °C [32]. There are also the medium-temperature phases B, M, N, P and R. In what concern applications in catalysis, the low-temperature phases (TT and T) are the most relevant, since these phases present higher specific surface area.

An interesting approach to the study of solid surfaces involves experimental measurements, which provide the basic information on possible surface groups, in conjunction with theoretical calculations, from which the structures of those groups can be proposed. Density Functional Theory (DFT) has proved to be a reliable method to such applications. DFT furnishes results that are commonly in good agreement with the experimental ones. For instance, sulfated zirconia was studied by using DFT in combination with infrared spectroscopy. From that, authors could indicate that sulfate structures change to pyrosulfate after calcination, both of them on zirconia [33].

There are only few studies of Nb_2O_5 by first principle methods. Clima et al. [34] have studied the dielectric properties of Nb_2O_5 and other related compounds at DFT/LDA level. Valencia-Balvin et al. [35] have studied the phase stability of several forms of Nb_2O_5 by DFT/PBE approach. As long as we are concerned, there are no DFT studies concerning catalytic properties of sulfated niobia. This can be understood by considering the complex crystal structures of low-temperature phases. Accordingly, TT phase has not unequivocally been determined, while the T phase, although well characterized, is too much complex to be used in a surface calculation [35], which is essential to describe catalytic properties.

In the present work, a sulfated niobia was synthesized by treatment of niobic acid with sulfuric acid solution. The materials were characterized and tested for esterification of acetic acid with ethanol. The structures of surface groups have been proposed by geometry optimization at DFT level. In order to perform DFT calculations on the T-Nb_2O_5 phase, a modified unit cell has been proposed, which keeps the essence of the true unit cell as will be shown.

2. Methods

2.1. Experimental procedures

The niobium oxide was obtained by calcination of the niobic acid from CBMM company in an oven at 500 °C for 4 h. Sulfated niobia was synthesized by treating the niobic acid with a sulfuric acid solution 0.5 M for 45 min, followed by filtration, drying at 120 °C for 24 h and calcination at 500 °C for 4 h.

The textural characterization was performed by means of nitrogen adsorption on a Micromeritics ASAP 2020 volumetric apparatus. Prior to analysis, the materials were dried under vacuum at 400 °C.

Analysis by X-ray diffraction of the samples was performed on a RIGAKU Miniflex diffractometer by using the K_α radiation of Copper.

The materials were analyzed by FTIR as KBr pellets, using a spectrophotometer Nicolet model Magna IR 760, equipped with DTGS of KBr detector, a KBr beamsplitter, and 32 scans gain of 4.0.

The materials acidity was measured by potentiometric titration. Around 0.05 g of dried solid was suspended in 45 ml of acetonitrile under stirring for 8 min, followed by titration with a solution of *n*-butylamine in acetonitrile (0.025 N) and a flow rate of 0.025 cm^3 min^{-1}. The electrode potential (mV) variation was measured using a Metrohm 827 pHmeter with a glass combined electrode LL Primatrode NTC.

The acetic acid esterification reaction was carried out in a batch system in liquid phase at 60 °C and atmospheric pressure. Anhydrous ethanol and glacial acetic acid at a molar ratio of 3:1 were placed in a three-necked flask connected to a reflux condenser and the reaction was started by addition of dried catalyst (0.5% wt.). To monitor the reaction, aliquots were removed periodically and titrated with standard NaOH to obtain the conversion by acetic acid consumption.

2.2. Theoretical section

Calculations were performed within the density functional theory (DFT), within Perdew, Burke and Ernzerhof (PBE) approximation to the exchange and correlation functional. Periodic boundary conditions and plane wave basis set were used as implemented in the VASP code [36]. Core electrons are treated by the so called projector augmented wave method (PAW). Energy cut-off to define plane wave expansion was 400 eV. Brillouin-zone integrations were done on the Monkhost-Pack 4 × 1 × 6 k-point mesh for bulk and 4 × 1 × 1 k-point mesh for slab.

Density Functional Perturbation Theory (DFPT) was also employed to obtain infrared intensities. As these calculations are computationally intensive, only modes related to sulfate group have been calculated.

The adsorption energy is commonly defined as:

$$E_{ads} = E_{mol/sur} - E_{sur} - E_{mol,} \quad (1)$$

where, $E_{mol/sur}$ is the energy of the system when molecule is adsorbed, while E_{sur} and E_{mol} stand for energy values of surface and isolated molecule respectively. In the present case though, the molecule is not in the gas phase, but in solution, and the reference state has to be changed. One can do this by considering that if there are two adsorption sites on the surface, with energies E_{ads1} and E_{ads2}, each one can be calculated from equation (1) and the reference state of the molecule in the gas phase will be cancel out, as well as the term of the energy of the surface without a molecule. The energy difference would, then, be

$$E_{ads1} - E_{ads2} = E_{mol/sur1} - E_{sur/mol2.} \quad (2)$$

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