



# Amphiphilic niobium oxyhydroxide as a hybrid catalyst for sulfur removal from fuel in a biphasic system



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## ABSTRACT

Here, we show that a new niobium oxyhydroxide, NbO<sub>2</sub>OH, can be synthesized and modified with a surfactant to be used as a heterogeneous catalyst for oxidative desulphurization. The material was treated with hydrogen peroxide to generate oxidizing groups (peroxo species) on the surface. Furthermore, this material was converted to a family of solid catalysts that can stabilize water/oil emulsions and catalyze reactions at the liquid/liquid interface by anchoring a surfactant to the catalyst. The material was then able to efficiently remove a sulfurous compound under mild conditions.

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## 1. Introduction

Desulphurization of fuel oils has become an environmentally urgent subject worldwide. Environmental regulations have limited the sulfur levels in diesel fuels to less than 15 ppm since 2006 in the United States [1]. However, it is very difficult with current technology to decrease the sulfur content from several hundred mg/L to only a few mg/L [2,3]. In the conventional hydrodesulphurization process (HDS), the use of high temperatures and pressures, large amounts of very active catalysts, long residence times, and large volume reactors are needed to effectively reduce the sulfur content to these low levels. Selective catalytic oxidation combined with extraction is one of the most promising desulphurization methods. Liquid/liquid extraction has been effectively utilized to remove sulfur and/or nitrogen molecules from petroleum distillates and synfuels [4]. However, this process is relatively inefficient due to the similar chemical characteristics of both sulfurous and nonsulfurous compounds. The more polar sulphones can be better extracted by polar solvents than sulphides; therefore, the efficiency of desulphurization via extraction can be significantly increased by oxidizing sulphides to sulphones [5,6]. Many oxidative systems

have been created, however, these systems have not been selective enough to oxidize only sulphides present in the fuel mixture. Furthermore, a large quantity of oxidant is required, increasing operating costs [7]. The amphiphilic catalyst (Nb-amp) reported in this work can selectively oxidize dibenzothiophene to the corresponding sulphone with stoichiometric amounts of H<sub>2</sub>O<sub>2</sub> under mild conditions. Furthermore, the sulphone is removed in situ from hexane by acetonitrile during the reaction, and the catalyst can be recycled.

The solid structure that was obtained in this work permitted the generation of highly oxidizing surface groups by H<sub>2</sub>O<sub>2</sub> treatment (Nb-hyd). These groups, peroxo-species, which have only been reported before in homogenous systems, can act as an effective oxygen donor in oxidation reactions [8–10]. However, some important reactions need more than an active catalyst. As reported in *Science* recently by Cole-Hamilton [11] and Crossley et al. [12], a catalyst that can simultaneously stabilize emulsions during the reaction would be highly advantageous in streamlining processes such as biomass refining. Both of these works and others [13] have used noble metals as the active catalyst. Here, we report a new family of solid catalysts based on the more common metal niobium that can stabilize water–oil emulsions by incorporating a hydrophobic surfactant on the catalyst and can catalyze reactions at the liquid/liquid interface in oxidative desulphurization processes.

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## 2. Experimental

### 2.1. Synthesis and characterization

The catalyst was prepared by first treating 0.26 M  $\text{NH}_4[\text{Nb}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})_n$  with 1 M  $\text{NH}_4\text{OH}$  (14.0 mL), followed by heating at 70 °C for 72 h. This material was used as a precursor for the preparation of hydrophilic  $\text{NbO}_2\text{OH}$  (Nb-hyd), obtained by treating pure niobia (300 mg) with 30% aqueous  $\text{H}_2\text{O}_2$  (4 mL) in  $\text{H}_2\text{O}$  (80 mL) for 30 min. The yellow solid was then filtered, washed with distilled water, and dried at 60 °C for 12 h. Then, the surfactant compound cetyltrimethylammonium bromide (CTAB, 4.47 mmol, Vetec) was added to a suspension of  $\text{NbO}_2\text{OH}$  (Nb-hyd) in  $\text{H}_2\text{O}$ , and the mixture was refluxed for 4 h to prepare the amphiphilic hybrid material (Nb-amp). The resulting catalyst (yellow powder) was filtered, washed with water and dried at 60 °C. The materials were characterized by transmission electron microscopy (TEM) with a JEOL transmission electron microscope (model JEM 2000EXII).

A DIGIDROP-DI goniometer (GBX Instruments) was used to perform contact angle measurements. This system is equipped with a CCD camera and an automated liquid dispenser. The contact angle was determined by placing  $\text{H}_2\text{O}$  droplets (10  $\mu\text{L}$ ) on the surface of the samples using a syringe. The pure specimens were pressed to obtain disks. An image was taken and then analyzed to give an average angle between the droplet and the surface. Three consecutive measurements were made at room temperature using the Surface Energy mode of the software, which allows direct measurement of contact angle (in degrees).

Fourier transform infrared spectroscopy (FTIR) measurements of the catalyst were carried out with a Shimadzu Prestige 21 spectrophotometer equipped with an attenuated total reflectance (ATR) accessory. The spectra of the samples were obtained in the region from 4000 to 240  $\text{cm}^{-1}$  using a CsI crystal with a resolution of 1  $\text{cm}^{-1}$  and 100 signal-averaged scans.

Thermogravimetric analysis (TG/DTG) was performed using a DTG60 SHIMADZU. The samples were heated from room temperature to 800 °C using a heating ramp of 100 °C  $\text{min}^{-1}$  under air flow (150  $\text{mL min}^{-1}$ ).

### 2.2. Catalytic tests

The extraction–oxidation desulphurization experiments were conducted in a 20 mL round-bottom flask. For the catalytic studies 500 mL of a solution containing 1000 mg/L of dibenzothiophene dissolved in n-hexane (model compound of a fuel) was prepared. Of this solution, 10 mL was used to prepare the mixture with acetonitrile (extraction liquid) and the catalyst. The mixture, 1 mL  $\text{H}_2\text{O}_2$  (30%, v/v) and 2 mL of acetonitrile was stirred vigorously at 25 °C in the presence of 10 mg of catalyst. After the reaction, the resulting mixture was placed in a static state to form two layers. The upper apolar phase (hexane) was separated easily from the nonpolar phase (acetonitrile) by decantation and its sulfur content analyzed by gas chromatography. Reuse of the catalyst tests: After 300 min of reaction, the catalyst was recovered by filtration of the modified mixture, followed by washing 3 times to remove the solvents. The material was then dried in an oven for 12 h at 70 °C.

The reaction products were analyzed by GC–MS (Agilent). The percentage of dibenzothiophene conversion was quantified by integrating the dibenzothiophene peak to the total ion content obtained before and after the reaction with the catalyst. GC–MS analysis was carried out with an injector temperature of 250 °C, an injection volume of 0.2 mL, and a flow rate of 1.4  $\text{mL min}^{-1}$  with an HP-5 column (5% polymethylphenylsiloxane). Each run used a heating curve of 110 °C for 5 min then increasing by 3 °C  $\text{min}^{-1}$  to 250 °C. The concentration in percentage of remaining DBT was monitored

using a calibration curve (5 points) constructed with various concentrations of this compound. The calibration curve was performed in the two solvents, acetonitrile and hexane with a good linearity ( $R^2 > 0.99$ ).

## 3. Results and discussion

### 3.1. Synthesis and characterization

Fig. 1(A) shows images of  $\text{H}_2\text{O}$  droplets on the Nb-amp and Nb-hyd surfaces. The Nb-hyd surface was completely wetted by  $\text{H}_2\text{O}$ , and the contact angle was measured as approximately 0°. However, the contact angle measured for Nb-amp was 76°, showing that the surfactant-containing catalyst had a significantly different surface composition compared to the catalyst without the surfactant. These results emphasized that the addition of a surfactant increased the hydrophobic character of the catalyst, suggesting that the surface groups are less available to make interactions with the droplet. This can, in turn, stabilize emulsions at the liquid–liquid interface, as confirmed by optical microscopy (Fig. 1(B)). This indicates that the size and type of quaternary ammonium cations play a vital role in the formation of a metastable emulsion droplet. We found that these metastable droplets are readily formed when the modified  $\text{NbO}_2\text{OH}$  is stirred with acetonitrile and hexane. These emulsion droplets can be easily separated by centrifugation, and the catalyst can then be recycled. Furthermore, it is seen that Nb-amp preferentially migrates to the biphasic interface of this solvent system (Fig. 1(D)), while Nb-hyd shows no such propensity. The material without the presence of surfactant is not stable at the polar/nonpolar interface of the solvents.

To observe possible morphological changes in the material due to the use of the surfactant, the samples were analyzed by transmission electron microscopy, with images shown in Fig. 1(C) and (D). As shown in Fig. 1(C), the material (Nb-hyd) presents the regular morphology of agglomerated particles. Fig. 1(D) (Nb-amp) shows poor image contrast, which is typical of nanoparticles dispersed in the presence of surfactant. This effect of a surfactant on the surface of catalysts has been described in the literature [14].

The presence of the surfactant molecule over the catalyst was identified by infrared spectroscopy (Fig. 2). The more intense bands in the CTAB spectrum are located in the region between 3050 and 2700  $\text{cm}^{-1}$ . The bands at approximately 2916 and 2848  $\text{cm}^{-1}$  are associated to the symmetric ( $\nu_s$ ) and asymmetric ( $\nu_a$ ) stretching modes of  $\text{CH}_2$ , respectively. These bands appear in the spectrum of Nb-amp sample, indicating the presence of the surfactant in the catalyst structure. To identify the possible bonding between the surfactant and the catalyst, specific regions of the Nb-hyd and Nb-amp FTIR spectra were evaluated. The two main spectral regions of interest are at 3600–3000  $\text{cm}^{-1}$  and 950–500  $\text{cm}^{-1}$ . The first is the sum contribution of different hydroxyl group absorptions at the hybrid catalyst surface. The bands at about 3412  $\text{cm}^{-1}$  and 3140  $\text{cm}^{-1}$  are assigned to the O–H stretching vibration localized at the surface and in the bulk structure, respectively [16]. The extent of O–H bulk or surface groups can be evaluated based on the ratio between the area below each hydroxyl band and total area of the bands ( $A_{\text{O-Hsurface}} + A_{\text{O-Hbulk}}$ ). A fraction of O–H bulk groups ( $A_{\text{O-Hbulk}}/A_{\text{total}} = 0.67$ ) is significantly larger than the O–H surface groups ( $A_{\text{O-Hsurface}}/A_{\text{total}} = 0.32$ ) to Nb-hyd. The ratio between these fractions is approximately 2. After the addition of surfactant to the catalyst, the inversion of relative intensity of these bands followed, for Nb-amp the high frequency band at 3186  $\text{cm}^{-1}$ , became more intense. Moreover, two new bands centred at 3541  $\text{cm}^{-1}$  and 3323  $\text{cm}^{-1}$  besides those present were revealed by the deconvolution of the O–H stretching region related to Nb-amp (Fig. 2). These bands in high frequencies, when compared to the

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