



Amphiphilic property of niobium oxyhydroxide for waste glycerol conversion to produce solketal



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ABSTRACT

Amphiphilic catalysts are synthesized using NbCl_5 in the presence of the CTAB (cetyltrimethylammonium bromide) to generate partial hydrophobicity to the catalysts. The partial hydrophobicity of the niobium oxyhydroxides improved the acetalization reaction of a residual glycerol from biodiesel production by decreasing the interaction between the water molecules and the acid sites of the catalyst. A waste glycerol conversion of 73% with a selectivity to solketal (2,2-dimethyl-[1,3]dioxolan-4-yl)methanol of 95% was obtained. Many reuses of the catalysts showed glycerol conversions between 70 and 80%.

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1. Introduction

Many possibilities for use of the residual glycerol have been investigated, especially employing catalytic processes [1,2]. Catalytic conversion reactions of glycerol, which is a highly reactive molecule, favor obtaining chemical products with high added value, which can be obtained by reactions such as selective oxidation and hydrogenolysis, dehydration, steam reforming, thermal reduction in synthesis gas, oligomerization/polymerization, selective transesterification, etherification and epichlorohydrin synthesis [3–6]. Among these, we highlight the acetalization and etherification of glycerol to obtain fuel additives, which have a lower polarity and viscosity, and therefore greater volatility, which can improve the combustion efficiency [2,7].

In acetalization reactions, through the reaction of glycerol with acetone, the products are cyclic acetals with 5 or 6 ring members, with the solketal ((2,2-dimethyl-1,3-dioxolan-4-yl)methanol) as major product [8,9]. These ketals can act as additives in order to increase the octane level of gasoline.

To obtain solketal, glycerol and acetone catalytic reactions have been studied using homogeneous and heterogeneous processes. In homogeneous catalysis *p*-toluene sulphonic acid [10], hydrochloric acid and sulfuric acid [11,12] have been employed.

In heterogeneous catalysis, different types of catalysts are used in the acetalization reactions of glycerol, mesoporous silicates [13], meso-structured silica functionalized with sulfonic acid [14], ZrO_2 [15], Amberlyst resins [14] and oxides [8,15], among others.

Modified catalysts based on niobium compounds, have received special attention because of their catalytic activity in several important chemical processes [16–20], as a promoter effect in oxidation reactions [21,22], supporting effect in hydrogenation reactions [23], metathesis [24], hydrotreating [25] and acid catalysis [26]. The acetalization reaction occurs through the condensation of a glycerol molecule with one molecule of acetone, resulting in the liberation of water. The formed water can favor the reverse reaction, reducing the formation of solketal [14,27]. Alternatives for these reactions have been the use of distillation processes [27] after the reaction, or hydrophobic catalysts [28], which decrease the interaction between water molecules and the acid sites, without losing catalytic properties.

Niobium oxide shows a good water tolerance property as reported by Okuhara [28], and exhibited the highest activity among the solid acids. Nair et al. [8] shows the water tolerance of niobia acid sites in acetalization reactions. Studies reported by Okuhara [28] and Nair et al. [8], employ niobium oxide calcinated until 773 K. Above 773 K this activity decreases the water tolerance, thus it can be suggest that structural changes in the niobium oxide occur [28]. In this work, we report the synthesis of a new series of catalysts based on niobium oxyhydroxide obtained from the precursor of niobium chloride and surface modification by

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partial hydrophobization with surfactants groups. Preliminary results from our research group have shown success in hydrophobization processes of niobium-based catalysts with excellent results in many types of reactions [29–32].

2. Materials and methods

2.1. Synthesis and characterization of the catalysts

The catalysts were synthesized, starting from the precursor of niobium chloride (NbCl_5 99%, purchased from Sigma–Aldrich). A water:oil:surfactant system was prepared, consisting of a mixture of Milli-Q water, 1-butanol (99%, Vetec), and 1-hexanol (99%, Vetec) in proportions of 17, 22 and 61%, respectively. 41.2 mmol CTAB (cetyltrimethylammonium bromide) surfactant was added and after solubilization 46.2 mmol of (NbCl_5) was added at 60 °C and constant stirring. A solution of NH_4OH (5 mol L^{-1}) was then added, dropwise, under constant stirring for 12 h (S4 catalyst) or 48 h (S4-2D catalyst). Finally, the resulting white solid is filtered, washed and dried at 60 °C for 12 h.

A catalyst without surfactant was also synthesized by dissolving NbCl_5 in 50% alcoholic solutions at 60 °C, after the addition of NH_4OH until it reached pH 7, a solid white is precipitated. This is kept under stirring for 12 h, thus this is filtered, washed, and oven-dried at 60 °C for 12 h. This procedure is from catalyst S4-SS.

The structural properties of materials were investigated by different characterization techniques. The thermal analysis measurements were performed on a Shimadzu-TGA50H thermobalance at 700 °C in air atmosphere and flow of 100 mL min^{-1} , with a heating rate of 10 °C min^{-1} . Analyses of infrared spectroscopy (FTIR) were obtained using a Perkin Elmer RXI FTIR spectrophotometer. The spectra of the samples were obtained in the 4000–500 cm^{-1} region with resolution of 4 cm^{-1} and an average of 64 scan signal. Analysis of X-ray diffraction (XRD) was performed in the range between $2\theta = 20$ and 70 in continuous scan mode of 2.0° min^{-1} using $\text{K}\alpha\text{Cu}$ radiation ($\lambda = 1.542 \text{ \AA}$) in a Siemens D5000 diffractometer. Acidity of the materials was characterized by NH_3 -TPD in a Quantachrome ChemBET-3000, TCD detector with 150 mA current and attenuation value of 32. N_2 adsorption/desorption isotherms were measured at 77 K using a Quantachrome Autosorb IQ2 equipment. Data were analyzed by BET method and pore size distribution using the BJH model. Scanning electron microscopy (SEM) obtained the morphology of the catalysts in a Quanta 200 FEG-FEI scanning electron microscope, operating at 30 kV with a resolution of 1.6 nm.

2.2. Catalytic reactions

Typical acetalization reactions were performed at 70 °C with constant stirring in a batch reactor with an acetone/glycerol molar ratio of 2/1, 0.2 g catalyst and 1 h of reaction. Residual glycerol from biodiesel production and a desalinated one were used in the acetalization reactions, both provided by Petrobras. NMR and GC-MS analyzed the conversion of glycerol and product identification.

^1H , ^{13}C and DEPT, experiments, were performed at 20 °C on an RMN spectrometer Avance DRX 200 at the High Resolution Magnetic Resonance Laboratory of UFMG. With a 5 nm multinuclear probe and procedure to optimize the field homogeneity (shimming), as well as probe tuning in the frequency of ^1H and ^{13}C , in order to have optimal resolution and signal detection.

Analyses by GC-MS in an Agilent Technologies™ Model 7890A, coupled to a mass detector model 5975C, were performed on HP-5MS (5% polymethylphenylsiloxane), 30 m \times 250 μm \times 0.25 μm column. Helium gas was used as carrier gas at a flow of 1.4 mL min^{-1} , split ratio of 130/1, injector temperature of 25 °C and

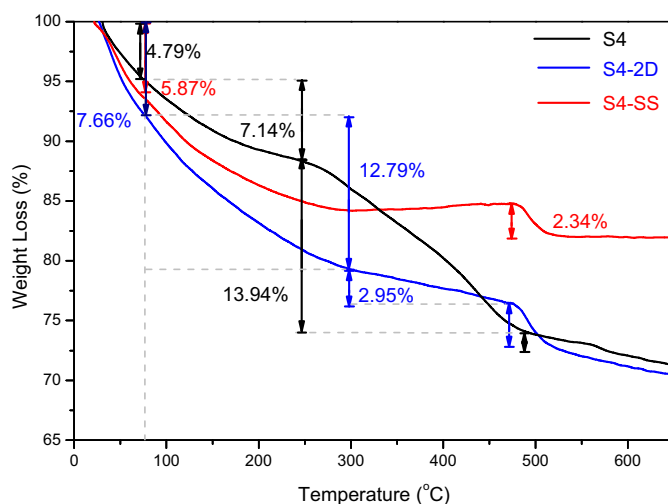


Fig. 1. Thermogravimetric analyses for catalysts based on niobium oxyhydroxide.

oven temperature profile was 80 °C for 5.0 min increasing to 100 °C at 3 °C min^{-1} , maintaining the final temperature for 1 min.

The calculation of the conversion, selectivity and products yield were determined by the calibration curve with standard glycerol PA (Modern Chemical, 99.5%) and solketal PA (provided by Petrobras).

3. Results and discussions

3.1. Characterizations of the catalysts

Thermogravimetric analyses of the catalysts, Fig. 1, showed three mass loss events, which are associated with the surface hydroxyl groups above 110 °C and after 200 °C mass losses associated with the surfactant group.

A mass loss of 14 and 3% was observed related to surfactant group decomposition for S4 and S4-2D, respectively. These results indicate a lower degree of hydrophobization of the catalyst S4-2D compared to S4. Above 450 °C, the event observed in three samples is associated with the loss of hydroxyl groups from the bulk, as suggested by some authors [31,33]. The mass loss for the catalyst SS-S4 suggests that initially, the event with 5.87% loss is due to the humidity and the two following events are related to OH loss (11.74%), from surface and bulk. These data suggests that the molecular formula of the S4-SS catalyst is $\text{NbO}_2(\text{OH})$, referred to as niobium oxyhydroxide [32,34].

Analyses by infrared spectroscopy are shown in Fig. 2. The catalyst S4 presented bands related to $\nu\text{C-H}$ at 2922 and 2852 cm^{-1} , which is a strong evidence of the presence of surfactant groups on the surface of the catalyst.

The S4-2D catalyst presented similar profile compared to S4-SS. The inset of Fig. 2, shows OH bond stretching observed at 3405 cm^{-1} related to surface hydroxyls and at 3123 cm^{-1} due to the OH from bulk, as reported by Schwertman and Cornell [32,34]. This fact gives evidence of the formation of niobium oxyhydroxide. The presence of the surfactant over the catalysts gives them a hydrophobic character, which can contribute to the glycerol acetalization reactions.

X-ray diffraction analyses not show diffraction patterns for catalysts S4, S4-2D and S4-SS. The amorphous character of the catalysts are expected, because these were not calcinated during the synthesis to preserve the surfactant group, as surface and bulk hydroxyl groups, which are characteristic of oxyhydroxides.

The strength of the acid sites and total acidity were determined by NH_3 -TPD. The catalysts showed similar NH_3 desorption profiles, as shown in Fig. 3.

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