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Gas phase glycerol conversion over lanthanum based catalysts: $LaNiO_3$ and La_2O_3

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ABSTRACT

The catalytic performance of lanthanum based catalysts: $LaNiO_3$ and La_2O_3 were evaluated in the gas-phase transformation of glycerol. The reaction was investigated in the temperature range of 300–700 °C. At 400 and 500 °C, the production of compounds in liquid phase is favored while at high temperature gases such as carbon monoxide, carbon dioxide and hydrogen are mainly formed. The basic catalysts used in this study favor the production of hydroxyacetone. Additionally 1,2 propanediol, methanol and ethylene glycol were formed in significant amount. The perovskite $LaNiO_3$ and La_2O_3 show no significant deactivation during 10 h at 400 °C, the selectivity to hydroxyacetone only slightly decreased with time on stream most probably due to the formation of heavy products. The catalysts were characterized before and after reaction (XRD, TGA, CO_2-TPD) showing that $LaNiO_3$ was partially reduced into $LaNiO_{2.5}$ during reaction at 400 °C. It is suggested that strong basic sites of La_2O_3 compared to $LaNiO_3$ are particularly active to produce methanol through glyceraldehyde but also acetaldehyde, propionaldehyde and acetone.

1. Introduction

The market of biodiesel as alternative fuel was continuously increasing during the last decade, the production of fatty acid methyl esters reached more than 19 billion liters in 2010. Glycerol is the main by-product of the process, consequently its conversion to higher added value products has received considerable attention [1–3]. A large number of valuable products can be obtained from glycerol, such as esters, oligomers, carbonates, branched alkyl ethers. Behr et al. published a review on this topic in which reduction and oxidation reactions using heterogeneous, homogeneous and bio catalysts were detailed [4]. The hydrogenolysis of glycerol to 1,2 or 1,3-propanediol is an important research subject due to their application as monomer to produce polyester resins. The reaction involves the cleavage of a C—O bond and the addition of hydrogen. The hydrogenolysis of glycerol is commonly conducted in liquid phase under hydrogen pressure using dilute solution of glycerol [5–8]. The solid catalysts active for the reaction are composed of metals (Cu, Pd, Rh, Ni) and supports (ZnO, C, SiO_2, Al_2O_3, ...). Montassier et al. [5] obtained high selectivity to 1,2 propanediol using Raney copper under 300 bar of H_2 at 260 °C. In the presence of CuO/ZnO, 100% selectivity was obtained under 80 bar of H_2 at 180 °C by Chaminand et al. [9]. The authors showed that the best results in terms of conversion and selectivity to 1,3 propanediol was obtained using polar aprotic solvent such as sulfolane. The conversion of glycerol was also studied in gas phase, solid acid catalysts were successfully used for the synthesis of acrolein by dehydration of glycerol [4,10]. Dubois et al. [11] reported that the reaction proceeds in the presence of strongly acidic solid catalysts with a Hammett acidity H_0 between −10 and −16. High catalytic activity in glycerol dehydration to acrolein was obtained with heteropolyacids [12], WO_3/ZrO_2 doped with SiO_2 [13], zeolithes [14]. The dehydration of glycerol can be initiated by the removal of either the central or the terminal —OH leading to the formation of respectively 3-hydroxypropionaldehyde and 1-hydroxyacetone [15]. The 3-hydroxypropionaldehyde is very unstable at the reaction temperature (about 300 °C) and leads to the formation of acrolein. The 1-hydroxyacetone (or acetol) is a product of great importance and there are needs to produce selectively acetol as a first step in the production of 1,2 propanediol. The dehydration of glycerol in gas phase was reported on different transition metal oxides such as MO_x-Al_2O_3-PO_4 [16], acid-base properties were changed by the addition of Na, K, Ni, Co...oxides [17,18].

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Solid base catalysts are not effective for the formation of acrolein from glycerol while weak basic sites of ZrO_2 are active for the dehydration of glycerol to hydroxyacetone [13,19].

The mechanism of glycerol dehydration to acetol on acid catalysts is well described in the literature, Alhanash et al. presented mechanistic schemes on Lewis and Bronsted acid sites [20]. The use of basic metal oxide catalysts to perform the reaction in gas phase using a continuous fixed bed process was reported by Kinage et al. [21] the authors showed that the catalyst: 5%Na doped CeO_2 exhibited good performances with high selectivity to acetol at 350 °C but a poor stability was observed the glycerol conversion being divided by two after only 3 h of reaction. In this study glycerol was diluted with water, the selectivity to acetol was maximum with 12% glycerol concentration in feed. Chiu et al. [22] investigated the vapour-phase hydrogenolysis of glycerol to acetol over copper-chromite catalysts, they showed that both acetol and propylene glycol were produced, high hydrogen feed increasing the selectivity to propylene glycol. Recently, Xia et al. [23] showed that the catalytic activity for hydrogenolysis of glycerol increased with the basicity of the material.

In this work, we studied the conversion of pure glycerol in gas phase using basic catalysts: lanthanum oxide and the perovskite $LaNiO_3$, with or without reduction prior to the reaction. The target was to investigate the role of basic and metallic sites in gas phase glycerol transformation. Special attention was given to the nature of products formed to propose mechanisms of reactions at the surface of the catalysts. To the best of our knowledge, the use of perovskites to convert glycerol in gas phase has never been reported. The influence of the reaction temperature and catalyst pre-treatment (reduction) was investigated.

2. Experimental

2.1. Catalyst preparation

The perovskite $LaNiO_3$ and lanthanum oxide (La_2O_3) were prepared by the self combustion method [24]. In the synthesis, $La(NO_3)_3{\cdot}6H_2O$ (Rhodia), $Ni(NO_3)_2{\cdot}6H_2O$ (Aldrich), and glycine (Merck) were used.

Glycine ($H_2NCH_2CO_2H$) used as ignition promoter was added to an aqueous solution of metal nitrates with appropriated stoichiometry, in order to get a $NO_3^-/NH_2 = 1$ ratio. The resulting solution was slowly evaporated at ~100 °C until a vitreous green gel was obtained. The gel was heated up to around 250 °C, temperature at which the ignition reaction occurs producing a powdered precursor which still contains some carbon residue. A calcination at 700 °C for 6 h eliminates all of the remaining carbon.

For a set of experiments, the perovskite $LaNiO_3$ was reduced under a flow of pure hydrogen (100 mL min^{-1}) at 700 °C during 30 min.

2.2. Characterization

The catalysts were characterized by X-ray diffraction (XRD) using a Siemens D-5005 diffractometer with Cu $K\alpha = 1.5417$ Å, operated at 40 kV and 30 mA. The diffraction patterns were recorded in the 2θ range of 10–90° with a step interval of 0.02° and period of 1 s.

The specific surface areas of the catalysts were determined from adsorption–desorption isotherms of nitrogen at −196 °C using a Tristar apparatus (Micromeritics) and applying the BET method.

Temperature-Programmed Desorption of adsorbed CO_2 (CO_2-TPD) was performed using an Autochem 2910 apparatus (Micromeritics). 100 mg of catalyst was pretreated at 700 °C under helium (50 mL min^{-1}) for 30 min. After cooling down to 50 °C, a 5% CO_2–He gas mixture was flowed for 30 min at 50 mL min^{-1}. The catalyst was then heated under helium flow (50 mL min^{-1}) up to 800 °C with a heating rate of 10 °C min^{-1}.

Table 1
BET surface area and results from CO_2-TPD measurements.

Catalyst	A_{BET} ($m^2\,g^{-1}$)	XRD phases	CO_2 adsorbed amount	
			μmol CO_2/g	μmol CO_2/m^2
$LaNiO_3$	13	$LaNiO_3$	196	15.1
Reduced $LaNiO_3$	13	Ni, La_2O_3	196	15.1
La_2O_3	15	La_2O_3	250	16.6

Thermogravimetric analysis (TGA) was carried out with a SDT 2960 thermobalance TA Instruments analyser in Pt crucibles to determine the stability of the catalyst. The measurement was performed under an airflow of 100 mL min^{-1} on heating from room temperature to 800 °C with a heating rate of 5 °C min^{-1}.

XPS analysis were performed using an Axis ultra Kratos spectrometer equipped with Al $K\alpha$ X-ray radiation source in a vacuum of 2×10^{-9} Torr. La 3d, Ni 3p, O 1s and C 1s signals were measured.

2.3. Catalytic reaction

Catalytic decomposition of glycerol was carried out at atmospheric pressure by passing a continuous flow of 20% (v/v) pure glycerol in N_2 as the carrier gas over the catalyst bed, employing a two zone reactor, pure glycerol (99.9%) was vaporized in the first zone before arriving to the reaction zone.

The temperature in the first reactor was maintained at 300 °C, while the temperature in the second reactor was varied between 300 °C and 700 °C. Liquid phase products were recovered by condensation in two cold traps located at the reactor outlet for further analysis, whereas gas phase was analyzed by gas chromatography during the reaction. Separation and quantification of main organic compounds in liquid phase were performed using a gas chromatograph (Varian 430 GC) equipped with a capillary column (50 m × 0.25 μm × 0.2 μm, CP WAX 58 CB) and a FID detector. Quantification was performed by using butanol as internal standard. The products of the glycerol decomposition were identified by GC-MS (Varian 3800, injector 1079) coupled with a mass spectrometer (Analyser triple quadrupole Varian 1200L with an electric impact source of 70 eV).

Conversion of glycerol and product selectivity was calculated according to the following equations:

$$\text{glscerol conversion}(\%) = \frac{\text{mols of glycerol reacted}}{\text{mols of glycerol in the feed}} \times 100$$

$$\text{product}\ \ i\ \ \text{selectivity}(\%) = \frac{\text{mols of carbon in}\ \ i\ \ \text{product}}{\text{mols of carbon in glycerol reacted}} \times 100$$

The carbon balance was calculated as the sum of product selectivity (in liquid and gas phase).

3. Results and discussion

3.1. Catalyst characterization

The specific surface areas of the catalysts $LaNiO_3$ and La_2O_3, calcined at 700 °C, are respectively equal to 13 and 15 $m^2\,g^{-1}$ as shown in Table 1. After reduction of the perovskite $LaNiO_3$ under hydrogen at 700 °C its specific surface area is not modified. The conditions of reduction were chosen in order to obtain a complete reduction of the perovskite into metallic nickel and lanthanum oxides. The behavior of $LaNiO_3$ under reductive atmosphere is not reported in this study since it was largely described in previous papers [25,26].

CO_2-TPD profiles collected in Fig. 1 show a desorption peak of CO_2 at temperatures between 200 and 400 °C in the case of $LaNiO_3$,