Gas phase dehydration of glycerol over, lanthanum-modified beta-zeolite

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ABSTRACT

Glycerol dehydration to acrolein was studied using beta zeolites. Three catalysts were used, the parent catalyst in the protonic form (H-B), and this catalyst after two ion exchanges, both with lanthanum nitrate (LCL-B) and one with lanthanum nitrate and the second with ammonium nitrate (LCH-B). The catalysts were characterized by XRD, XPS, FTIR with pyridine adsorption, pyridine TPD, BET, SEM, ICP, and pulses of 1-butene. Coke was characterized by TPO. Activity tests were carried out in gas phase. It was found that LCH-B and H-B catalysts had similar density of acid sites, but the strength distribution was different, having the former a higher proportion of medium-strength acid sites. Because of this, a better performance in glycerol dehydration was displayed by this catalyst. The changes in acidity were due to the generation of new acid sites that occurred during the preparation, forming acid silanols attached to silica-reach and alumina-reach species. Coke was rapidly formed on the three catalysts, completely blocking the pores. Therefore, after a short time on oil, only the external surface is available for the reaction. Nevertheless, reasonable conversion and stability was obtained with LCH-B catalyst.

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1. Introduction

The reduced availability of fossil raw materials has led to chemical industries to search for alternative feedstocks for different processes. One example is the acrolein production process, which is currently carried out by partial oxidation of propylene, using mixed metal oxides as catalysts [1]. A renewable raw material that can be converted to acrolein by dehydration is glycerol, which is a by-product of the biodiesel production process [2]. Its price has decreased significantly due to the increment of the worldwide production of this fuel. The economics of biodiesel production may be improved if the demand of glycerol increases, for example to obtain other products with added value. Acrolein is one of them, being a chemical intermediate for the production of acrylic acid, acrylic acid esters, superabsorbers, polymers and detergents [3].

The dehydration of glycerol can be carried out both in gas and liquid phase. It was found that in order to avoid excessive loss of selectivity, the conversion has to be limited to 15–25% in the case of the reaction in liquid phase [4]. The conversion of glycerol and the selectivity to acrolein can be easily modulated when the reaction is carried out in gas phase. Several solid acid catalysts have been studied in gas phase, such as metal phosphates [5,6], metal sulphates [7,8], metal oxides [9,10], heteropolyacids supported on metal oxides [11,12] and zeolites [13,14]. The catalytic activity is a function of the acidic properties of the solid and also of the pore size [15]. Catalyst with small pores showed lower activity than catalysts with mesopores ranged between 6 and 10 nm [16]. In terms of acidity, it has been reasonably established that Brønsted acid sites of weak-moderate strength catalyzes acrolein production [14,17], whereas Lewis acid sites increases the selectivity to hydroxyacetone [18–20].

Beta zeolite (BEA structure), which corresponds to the group of large pore zeolites, has a three-dimensional channel structure with rings of 12 oxygen atoms, with pore size of 6.6 Å × 7.7 Å in the direction ⟨1 0 0⟩ and 5.6 Å in the direction ⟨0 0 1⟩. Due to its pore system and high acidity, it is a catalyst that has been used in different reactions such as alkylation [21], cracking [22], isomerization [23,24], and disproportionation [25]. This material has been also studied in the glycerol dehydration reaction. Gu et al. [26] compared the behaviour of a zeolite H-Beta with a Si/Al = 13 with other protonic zeolites such as HY and H-ZSM5. The authors analyzed the effect of the porous structure, noting that deactivation by coke formation decreases in the following order: H-Y ≫ H-Beta > H-ZSM5, which is contrary to the order in which there is an increased in the steric hindrance in the catalysts. Coke is the product of multi-molecular condensation and hydrogen transfer reactions, which are mainly affected by acid sites density and steric hindrance of catalysts [27]. Its formation is favoured in those zeolites with larger pore size. Kim et al. [28] studied the behaviour of H-Beta zeolites with different Si/Al ratio in this reaction. An H-Beta with a relation $SiO_2/Al_2O_3 = 27$ showed the highest glycerol conversion and acrolein selectivity for all reaction times, although at the beginning

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of the reaction (TOS = 2 h) the conversion was slightly higher for an H-Beta with a relation $SiO_2/Al_2O_3 = 25$.

The incorporation of rare earth (RE) elements (e.g. lanthanum) for the modification of catalysts like faujasites, play a significant role, improving its stability and activity in cracking reactions [29]. When hydrolysis of water of solvation of RE^{3+} cations occurs, a higher concentration of Brønsted acid sites is generated, and the catalyst activity is enhanced [30]. Furthermore, the acid strength distribution in the zeolite can also be modified by the presence of highly charged cationic species, due to the polarization of OH groups or to an inductive effect on these groups [29].

The influence of lanthanum and other rare earth elements in faujasites has been well studied, in various reactions such as hydrogen transfer [31], isomerisation [32] and cracking [33]. La^{3+} cations not only can generate Brønsted acid sites by hydrolysis of water [34], but also leads to the modification of the electronic environment and induce a change in the acidity strength of the silanols [35–38].

Nevertheless, there are only few studies about RE influence on Beta zeolite [39]. This catalyst has also been investigated in the isobutane alkylation reaction, obtaining better results with the lanthanum exchanged Beta zeolite than with the protonic form of this zeolite [40].

In this work, the objective was to study different catalysts synthesized from an H-Beta zeolite (Si/Al = 13) incorporating lanthanum in the structure by ion exchange. These catalysts possess analogous textural properties but different acidities depending on the degree of lanthanum exchange. The reactivity of catalysts was tested in the gas phase glycerol dehydration and the acid surface properties were investigated by pyridine temperature-programmed desorption (Py-TPD) and FTIR analyses of adsorbed pyridine (Py-FTIR).

2. Experimental

2.1. Catalyst preparation

A beta-zeolite (from UOP, Si/Al = 13) in protonic form was employed (H-B). This zeolite was exchanged with a 0.5 M $La(NO_3)_3$ aqueous solution, during 3 h in reflux. Then it was filtered and dried at 100 °C, and finally calcined at 550 °C. This material was used for a second ionic exchange with NH_4NO_3 0.5 M during 3 h in reflux, drying and calcining at 550 °C. This catalyst was labeled LCH-B. A similar procedure was followed to prepare another catalyst, but using also $La(NO_3)_3$ in the second ion exchange (LCL-B). Finally, the catalysts were crushed and sieved to 40–80 mesh. The chemicals used in the preparation of catalysts were $La(NO_3)_3 \cdot 6H_2O$ (Merck, >99%) and NH_4NO_3 (Anedra, >99%).

2.2. Coke characterization

Coke deposited during the reaction was characterized by temperature-programmed oxidation (TPO), or by hydrogenation. The experiments were carried out using a modified technique [41] in which the gases coming out of the sample cell passed through a methanation reactor. A H_2 stream was fed to this reactor, which was loaded with a Ni catalyst, and quantitatively converted CO and CO_2 to CH_4. This compound was continuously measured using a flame ionization detector (FID) detector. Under these methanation conditions (400 °C, carrier 5% O_2 in nitrogen at 40 ml min⁻¹) a 100% conversion of CO_x was reached, and in this way the sensitivity of the technique was greatly improved.

The analysis cell was loaded with approximately 10 mg of catalyst and the analyses were performed employing a heating from 20 °C, at a rate of 12 °C min⁻¹, up to 700 °C. The equipment was calibrated using pulses of CO_2 diluted in He.

2.3. Catalyst characterization

2.3.1. BET surface area, pore size and volume

Nitrogen adsorption was employed to determine BET surface area, and pore volumes were estimated by means of t-plots [42]. The determinations were carried out using an Autosorb-1® sorptometer (Quantachrome). Before the measurements, all the samples were degassed under vacuum at 250 °C for 3 h to ensure complete removal of adsorbed moisture. This technique was employed for the fresh catalysts and for the deactivated samples at 1 h and 7 h of time on stream.

2.3.2. Powder X-ray diffraction (XRD)

X-ray diffraction was used to identify the structure of the zeolite catalysts and to evaluate the degree of crystallinity. The XRD measurements were carried out in a Shimadzu XD-D1 instrument with a monochromator, CuK_α radiation (30 kV, 40 mA). The diffractograms were recorded from 5° to 60° at a scanning rate of 0.5° (2θ) per min.

2.3.3. Microscopy analysis

Scanning electron microscopy (SEM) of H-B, LCH-B and LCL-B samples at 25 kV were carried out using an electron microscope (JEOL JSM 35 C). The atomic elemental analyses were obtained using an Energy-Dispersive X-Ray analysis (EDX) system attached to the SEM instrument. In order to ensure that the data collected was representative of the whole sample, scans were carried out at more than one location.

2.3.4. Inductively coupled plasma atomic emission spectroscopy (ICP-OES)

The concentration of metals in the catalysts was evaluated by inductively coupled plasma atomic emission spectroscopy (ICP-OES). Measurements were performed in a Perkin Elmer Optima 2100 DV. Samples were dissolved using a mixture of perchloric and nitric acids.

2.3.5. Pyridine FTIR

The acidic properties of the samples were studied by pyridine adsorption followed by infrared spectroscopy (FTIR). Spectral measurements of pyridine adsorption on the samples were performed on a JASCO FT-IR 5300 spectrometer equipped with a DTGS detector. The range and resolution of acquisition were 4600–400 and 4 cm⁻¹, respectively. A self-supporting wafer for each sample (~20 mg and 13 mm of diameter) was prepared, placed in a thermostated cell with CaF_2 windows connected to a vacuum line, and evacuated for 8 h at 400 °C. The background spectrum was recorded after cooling the sample to room temperature. Afterward, the solid wafer was exposed to pyridine vapours (Sintorgan, 99% purity) until the system was saturated at 46 mmHg at room temperature; the contact time at this pressure was 12 h. The IR spectrum for each sample was obtained after pyridine desorption by evacuation for 1 h at 100, 200, 300 and 400 °C. All the spectra were recorded at room temperature before and after pyridine adsorption and desorption at each temperature. The difference spectrum was finally obtained by subtracting the background spectrum previously recorded.

2.3.6. Pyridine temperature-programmed desorption (TPD)

These experiments were carried out to evaluate the quantity and strength of acid sites in the samples. Approximately 10 mg of catalysts, sandwiched by quartz wool, was loaded in a quartz tube. The catalysts were pretreated in-situ in N_2 flow (30 ml min⁻¹) at 350 °C for 1 h. After cooling down to room temperature, the sample was saturated with pyridine. After this, pure nitrogen was flowed and the temperature was increased up to 150 °C, maintaining this temperature until no physically adsorbed pyridine was detected. The