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Glycerol dehydration catalyzed by MWW zeolites and the changes in the catalyst deactivation caused by porosity modification

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ABSTRACT

Members of the layered MWW family, including microporous MCM-22, pillared MCM-36 and delaminated ITQ-2 zeolites, were used as catalysts for the gas phase dehydration of glycerol. The chemical, structural and surface properties of the catalysts were characterized by X-ray diffraction, N_2 adsorption–desorption isotherms, SEM, TEM, NH_3-TPD and pyridine chemisorption followed by IR spectroscopy. The results clearly showed that the modified zeolites with designed mesopore structure enabled rapid diffusion and consequently improved the glycerol conversion. Characterization of the acid sites revealed that the relative abundance of Brønsted and Lewis acid sites influenced the efficiency of the catalysis performed by these materials. ^{13}C NMR spectra of the spent catalysts confirmed that differences in the nature and amount of carbonaceous deposits are related to the pore structures of the catalysts, with greater formation of polyaromatic compounds inside zeolite pores, while polyglycols are preferentially formed at the external surfaces of the MCM-36 and ITQ-2 zeolites, as expected for the more exposed sheets.

1. Introduction

Renewable fuels are increasingly in demand due to the depletion of fossil fuel resources combined with greater global fuel consumption. Biodiesel, which production grows every year [1], is an attractive option, but 1 kg of glycerol is generated as a byproduct for every 9 kg of biodiesel manufactured. This feature results in a substantial availability of glycerol as a raw material for industrial purposes, so that the effective use of glycerol is essential to improve the profitability of biodiesel production [2]. The glycerol molecule shows in each carbon a functional group, thus, several applications are possible to chemical industries [3].

The conversion of glycerol can be achieved using oxidation, reforming, hydrogenolysis, esterification and etherification. Another method is the dual intramolecular dehydration of glycerol to acrolein, which is an intermediate in the production of acrylic acid, widely used in the manufacture of adhesives, paints, plastics, and super-absorbents [4–6].

Dehydration of glycerol in the gas phase is advantageous, because the adjustment of parameters such as temperature and contact time enables the tailoring of the conversion and the selectivity [6]. Many solid catalysts have been employed in this reaction and it has been found that catalytic conversion and stability depend on characteristics of the material including the strength, distribution, and type (Brønsted or Lewis) of acid sites, as well as the pore size and access of reactants to the internal active sites. Mesoporous catalysts show better performance compared to purely microporous ones. Sorption of reactants at weak Lewis acid sites favors the single intramolecular dehydration of glycerol to hydroxyacetone, while strong or moderate Brønsted acid sites are more efficient for the production of acrolein. A negative aspect of the Brønsted sites is that they not only favor the production of acrolein, but also of carbonaceous deposits that are responsible for strong catalyst deactivation by deposition of non-reactive compounds that obstruct the pores and cover the active sites [6,7]. This is a major problem that needs to be overcome in catalysts design.

Acid catalysts that have been tested for gas-phase glycerol dehydration at temperatures ranging from 275 to 350 °C include TiO_2, SiO_2/Al_2O_3, and pure Al_2O_3. However, these materials do not provide selectivity toward acrolein. Improved selectivity has been achieved using Nb_2O_5, WO_3/ZrO_2, metal phosphates (Al_2O_3–PO_4

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and TiO_2–PO_4), and heteropolyacids, although the catalysts showed poor stability due to the formation of coke [4,6].

Zeolites have attracted attention because of their stability under a range of catalytic conditions, together with the selectivity provided by their pore systems and the strong Brønsted acid sites that are produced by substitution of silicon by aluminum atoms in the framework. Nevertheless, a microporous framework is unfavorable because it hinders the access of bulky molecules, and the diffusion and mass transport of reactants and products are restricted [8–10]. Furthermore, the deposition of coke readily blocks the micropores, so that the internal acid sites become inaccessible and useless.

MCM-22 zeolite is an interesting structure by having MWW framework with some particularities. This was the first lamellar zeolite to be synthesized in 1990, and has a unique pore structure that enables its use in a variety of different applications. Layered zeolites provide a combination of the chemical characteristics of conventional microporous zeolites, together with access to inner active sites, which makes them attractive for use in catalysis [11–14]. The main distinct aspect between conventional and layered zeolites comes from the fact that adsorption and catalysis in lamellar zeolites occur almost expressly at the surface and not inside pores [15]. Moreover comparing 2D zeolites and layered material in general, zeolites exhibit an advantage in porosity since there are pores in own layers [16].

The lamellar precursor MCM-22 can be pillared and delaminated under suitable conditions giving rise to the MCM-36 and ITQ-2 zeolites, respectively. The three zeolites have different porosities and belong to the same MWW framework family [8,17–20]. MCM-36 is a pillared layered structure built of inorganic layers with inorganic pillars appended on both sides of the sheets. The pillars preserve the interlayer separation, while the void space created after removal of the swelling agent produces mesopores. The pillared zeolite has an advantage due to its mesopores distribution which facilitates the catalysis with large molecules, besides keeping MWW sheets physico-chemical characteristics. Delaminated ITQ-2 consists of thin MWW sheets of approximately 2.5 nm thick, showing an extremely high external surface area combined with an acidity and hydrothermal stability common to zeolites, without a long-range order. The random spatial distribution of sheets yields aggregation mesopores between the layers. This mesoporosity is very interesting for reactions that involve large molecules [21,22].

In this study, we compare and discuss the gas-phase dehydration of glycerol to acrolein catalyzed by an assemblage of lamellar MWW zeolites. The effect of catalyst porosity on the distribution of products, on the control of diffusion constraints and accessibility to the acid sites and, finally, on the catalyst deactivation and coke speciation is shown.

2. Experimental

2.1. Synthesis of the MCM-22P zeolite precursor

The procedure used to synthesize the MCM-22 precursor (denoted MCM-22P) was adapted from Ref. [23]. The synthesis mixture was prepared by adding 0.531 g of NaOH to 35.8 g of deionized water under constant stirring until complete dissolution, and then by adding 0.425 g of sodium aluminate (Sigma–Aldrich). After this, 6.58 g of the organic template, hexamethylenimine (HMI, Sigma–Aldrich) was added drop by drop under constant vigorous mechanical stirring at 50 °C for 30 min. Addition of 6.65 g of fumed silica (200 m^2/g, Sigma–Aldrich) was then performed slowly under the same conditions of temperature and stirring, allowing 30 min for complete homogenization. The final mole composition of the synthesis mixture was 50 SiO_2:1 $NaAl_2O_3$:6 NaOH:30 HMI:900 H_2O. This mixture was transferred to a Teflon-lined autoclave and heated at 150 °C for 5 days under static and autogenous conditions. The precipitated product was washed with acidified water (0.1 wt.% acetic acid) until pH 7.0, and then dried at 100 °C for 1 day prior to production of the MCM-22 zeolite. For the other zeolites (ITQ-2 and MCM-36), the MCM-22P precursor was not dried to avoid any partial condensation of the layers that might hinder the subsequent swelling process.

2.2. Synthesis of the MCM-22 zeolite

The dried MCM-22P zeolite was calcined at 550 °C for 3 h, using a heating rate of 2 °C/min, resulting in the formation of MCM-22 zeolite.

2.3. Synthesis of the MCM-36 and ITQ-2 zeolites

Prior to the synthesis of MCM-36 and ITQ-2, the wet MCM-22P zeolite sheets were swollen using a procedure based on Ref. [18]. Briefly, 5.0 g of MCM-22P and 28.2 g of CTABr (hexadecyltrimethylammonium bromide, Sigma–Aldrich) were mixed with 97.4 g of deionized water, followed by addition of 61.2 g of a 20 wt.% solution of TPAOH (tetrapropylammonium hydroxide, Sigma–Aldrich). The mixture was kept under reflux at 80 °C and pH 12.3 for 24 h.

The pillaring procedure used to produce MCM-36 was adapted from Refs. [24,25]. The swollen MCM-22P zeolite (MCM-22S) was gradually dried at 25 °C for 7 days. Mild conditions were used in order to avoid condensation of the layers. A mass of 3.0 g of the dried zeolite was then mixed with 15 g of TEOS (tetraethyl orthosilicate, Sigma–Aldrich) and refluxed at 80 °C for 24 h under nitrogen atmosphere and continuous stirring. The resulting material was dried at 25 °C and then hydrolyzed at 80 °C for 24 h with an amount of water corresponding to ten times the mass of zeolite. During the hydrolysis, the pH was adjusted to 8 with a concentrated NaOH solution. The solid was filtered, washed, dried, and calcined under air flow at 450 °C for 3 h and then at 550 °C for 6 h, using heating rates of 2 °C/min.

For the production of ITQ-2 by delamination of swollen MCM-22P, the balloon flask used for the swelling procedure was immersed in an ultrasonic bath at 50 °C for 2 h. After the layers had been forced apart, hydrochloric acid was added until the pH reached 2. The mixture was then washed, centrifuged, and dried at 100 °C for 12 h. The resulting material was calcined at 550 °C for 3 h, using a heating rate of 2 °C/min [26,27].

The synthesized zeolites were converted in the H-form by three consecutive ion exchanges of 1 g of zeolite in 50 mL of 0.1 mol/L NH_4NO_3 solution at ambient temperature for 3 h and subsequent calcination at 500 °C (heating rate of 5 °C/min) for 2 h under air atmosphere.

2.4. Characterization

The solid crystalline structures were analyzed by X-ray diffraction (XRD) using a Siemens D5000 diffractometer and Cu Kα radiation selected by a curved graphite monochromator. Data were collected in a 2θ range from 2° to 40°, using a step size of 0.01° and a counting time of 1 s.

The crystal size and morphology were examined by scanning electron microscopy (SEM) performed using a Philips FEG XL 30 instrument. The samples were previously deposited in aluminum sample holders and sputtered with gold. Transmission electron microscopy (TEM) analyses were performed using a JEOL 3010 microscope operating at 300 kV in high-resolution mode. The images were acquired for the layered zeolite crystals supported on a copper grid.

The chemical compositions of the samples were determined by atomic absorption spectroscopy (Model 240FS, Agilent).