



Effect of hierarchical porosity and fluorination on the catalytic properties of zeolite beta for glycerol etherification

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ABSTRACT

The effect of hierarchical porosity in Beta zeolite on the catalytic etherification of glycerol with *tert*-butanol or isobutene has been studied by comparing its catalytic behavior with one conventionally synthesized Beta zeolite with similar Si/Al ratio. Additionally, these two samples were fluorinated at mild conditions to modify their acidity and to study the effect of this treatment on the textural and catalytic properties. The higher conversion and higher selectivity to the bulkier glycerol triether obtained for the Beta with hierarchical porosity and its fluorinated form for both reactions compared with their corresponding conventional zeolites can be explained because of their additional porosity, which favors the diffusion of the reactants to the Brønsted acid sites, since these catalysts showed similar acidity amount and strength when compared with the corresponding conventional Beta and fluorinated Beta, respectively. Fluorination of Beta samples led to slight higher selectivity to h-GTBE (di- and triethers of glycerol). This has been related to their slightly stronger acidity, achieved by the inductive effect of the fluorine introduced into the zeolite framework.

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1. Introduction

Beta is a large pore zeolite with a three-dimensional 12-ring pore system (straight channels of diameter $6.6 \times 6.7 \text{ \AA}$ and sinusoidal channels of diameter $5.6 \times 5.6 \text{ \AA}$). In the last years, several works have been focused on the synthesis of either Beta zeolite having crystals in the nanometer range (nanocrystalline zeolite Beta) or Beta zeolite with an additional porosity (hierarchical zeolites) [1,2]. Mesopore-containing zeolites have been prepared by direct synthesis, different post-synthesis treatments, such as dealumination or desilication procedures, and novel dual templating methods [3–5].

The hierarchical structure can be achieved by different strategies. In this work, the employed methodology was based on hindering the growth of the zeolitic crystals by organo-functionalization of protozeolitic units in order to prevent their further aggregation and agglomeration [6,7]. This strategy has been successfully applied to the synthesis of ZSM-5, Beta, TS-1, Mordenite and ZSM-11 zeolites, using phenylaminopropyltrimethoxysilane (PHAPTMS) as the silanization agent. This type of materials possesses improved textural properties regarding to the standard

zeolite, which may affect positively to their performance as catalysts in reactions involving bulky molecules [2,7–10].

Recently, special attention has been focused on the obtention of di- and tri-tertiary butyl ethers of glycerol (h-GTBE), which is an excellent additive with a large potential for diesel and biodiesel reformulation [11–13]. Besides, h-GTBE can replace methyl tertiary butyl ether (MTBE), which is detrimental to the environment. Etherification of glycerol with isobutene (IB) or with *tert*-butanol (TBA) has been studied in the presence of acid catalysts [14–31]. Etherification with isobutene yielded better conversion and selectivity towards h-GTBE than etherification with *tert*-butanol [16,18]. The water formed when using TBA as a reagent seems to have an inhibition effect on glycerol terbutylation. Regarding heterogeneous catalysis, the best activity results were achieved with acid ion-exchange resins of Amberlyst type (Amberlyst 15 and 35) [14–17], with silicas functionalized with organosulfonic groups [18,19] and more recently, with microwave-assisted sulfonic acid-functionalized SBA-15, aerogel and zeolite catalysts [28,30,31]. In the first studies performed with zeolites as catalysts for this reaction, Klepáčová et al. reported that the formation of the triether was sterically hindered in Beta and H-Y zeolites due to their microporosity [17]. In a previous study, three pentasil-type zeolites (Mordenite, ZSM-5 and Beta) were modified by different treatments to be tested as catalysts for the etherification of glycerol with *tert*-butanol [29]. The best catalytic results were achieved using a

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fluorinated beta zeolite resulting in the formation of the glycerol triether in very low amounts. This was explained by the higher amount of stronger acid sites generated by the incorporation of fluorine in the zeolite framework.

The aim of this work was to study the effect of hierarchical porosity by comparing the catalytic behaviour of one conventional Beta sample (Si/Al=27) with that of one Beta zeolite with hierarchical porosity (Si/Al=27), prepared from organofunctionalized protozeolitic units, for the etherification of glycerine with *tert*-butanol or isobutene. Additionally, these two zeolites were fluorinated to modify their acidity and establish the effect of fluorination on the catalytic activity. In order to compare hierarchical porosity with ordered mesoporous materials, two Al-containing ordered mesoporous materials (Al-MCM-41 and Al-SBA-15) with similar Si/Al ratio than Beta and hierarchical Beta were tested as catalysts for the etherification of glycerol with isobutene.

2. Experimental

2.1. Catalyst preparation

Beta zeolite with hierarchical porosity was prepared from a solution with the following molar composition: $\text{Al}_2\text{O}_3:60\text{SiO}_2:15.5\text{TEAOH}:1000\text{H}_2\text{O}$. Fumed silica (Fluka), tetraethylammonium hydroxide (TEAOH, 35%; Alfa), aluminum flakes (Aldrich) and distilled water were used as starting materials [2,32]. The precursor solution was pre-crystallized in a Teflon-lined stainless steel autoclave under autogenous pressure at 408 K for 3 days. The solid obtained was mixed with 8 wt% of an aqueous solution containing the phenylaminopropyltrimethoxysilane (PHAPTMS, 97 wt%, Aldrich) and TEAOH (13% w/w) (TEAOH/SiO₂ = 0.5). The resulting mixture was kept in a reflux system under stirring (100 rpm) at 90 °C for 6 h. Thereafter, the crystallization of the functionalized seeds was carried out in a stainless steel reactor under autogeneous pressure at 135 °C for 7 days. The solid obtained was separated by centrifugation, washed several times with distilled water, dried overnight at 110 °C (h-Beta “as made”) and calcined in air at 550 °C for 5 h (h-Beta).

The previously prepared sample (h-Beta) was fluorinated by adding 3.5 mL of NH₄F 0.1 M to 1 g of the Beta synthesized with hierarchical porosity to incorporate 0.3 wt% fluorine in the final sample. The slurry formed was stirred and kept at room temperature for 42 h. Finally, the sample was calcined at 450 °C for 8 h (h-Beta(F)).

Additionally, one Beta zeolite (Si/Al = 27) was synthesized following the same procedure than for preparing h-Beta but omitting the precrystallization and silanization steps (called Beta “as made” before calcination, and Beta, after calcination). This reference sample was also fluorinated by adding 3.5 mL of NH₄F 0.1 M to 1 g of the synthesized Beta to yield 0.3 wt% fluorine in the final sample. The slurry formed was stirred and kept at room temperature for 42 h. Finally, the sample was calcined at 450 °C for 8 h (Beta(F)).

Finally, two aluminum containing ordered mesoporous materials were synthesized. 1.0 g of calcined pure silica (MCM-41 or SBA-15) was added to 50 ml hexane(dry) containing the required amount of aluminium isopropoxide (Si/Al ratio: 25) and stirred at room temperature (Al-MCM-41) or 70 °C (Al-SBA-15) for 24 h. The resulting powders were obtained by filtration, washed with dry hexane, dried at room temperature and calcined at 550 °C for 4 h.

2.2. Catalyst characterization

Elemental analyses of the samples were obtained with a Philips PW-2400 sequential XRF analyzer with Phillips Super Q software. All measures were made in triplicate.

Structural characterization was completed by powder X-ray diffraction patterns of the samples which were obtained with a Philips X'PERT MPD diffractometer using nickel-filtered Cu K α radiation. Samples were dusted on double-sided sticky tape and mounted on glass microscope slides. The patterns were recorded over a range of 2θ angles from 5° to 40° and crystalline phases were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) files (48-0074 corresponds to Beta). The integrated intensity of the signal at $2\theta = 22.4^\circ$ was used to evaluate the crystallinity of Beta samples.

Argon adsorption–desorption isotherms at –186 °C were also recorded for the zeolite samples using an Autosorb instrument (Quantachrome). Prior to the measurements, the individual samples were outgassed at 300 °C under vacuum. The surface area was determined applying the Brunauer–Emmet–Teller (BET) equation. The pore size distributions were calculated using the adsorption branch of the argon isotherms by applying the NLDFT model (Quantachrome).

Infrared spectra were recorded on a Bruker-Equinox-55 FTIR spectrometer. The spectra were acquired by accumulating 32 scans at 4 cm^{–1} resolution in the range of 400–4000 cm^{–1}. Samples were prepared by mixing the powdered solids with pressed KBr disks in a ratio of 5:95 and dried in an oven overnight.

Solid-state ²⁷Al MAS NMR experiments were performed on a Varian Infinity 400 MHz spectrometer fitted with a 9.4 T magnet. These nuclei resonate at 104.26 MHz. For acquisition, spinning frequency of 4 kHz and intervals ranging from 5 to 30 s between successive accumulations, were employed. ²⁷Al chemical shifts were externally referenced to [Al(H₂O)₆]³⁺.

TEM images were obtained in a PHILIPS TECHNAI 20 electron microscope operating at 200 kV.

¹H NMR spectra were obtained with a Varian Mercury Vx 400 MHz using a probe of 7 mm CPMAS at a frequency of 400 MHz by spinning at 5 kHz. The pulse duration was 2 μ s and the delay time was 5 s. The chemical shift reference was trimethyl silyl-3 propionic acid *d*₄-2,2,3,3 sodium salt.

Ammonia temperature programmed desorption (TPD) experiments were performed in a Micromeritics 2910 (TPD/TPR) equipment. Previously, the samples were outgassed under an He flow (50 N ml/min) by heating with a rate of 15 °C/min up to 560 °C and remaining at this temperature for 30 min. After cooling down to 180 °C, an ammonia flow of 35 N ml/min was passed through the sample for 30 min. The physisorbed ammonia was removed by flowing He at 180 °C for 90 min. The chemically adsorbed ammonia was determined by increasing the temperature up to 550 °C with a heating rate of 15 °C/min^{–1}, this temperature being maintained constant for 30 min. A thermal conductivity detector was employed for monitoring the ammonia concentration in the effluent stream.

Acid capacity of the samples was also measured by cationic-exchange using NaCl as exchanging agent. In a typical experiment, 0.05 g of zeolite was added to 20 g of NaCl (aq, 1 M) maintaining under stirring at 60 °C for 12 h. Released protons were then potentiometrically titrated with a 0.1 M NaOH aqueous solution.

X-ray photoelectron spectra were taken with a SPECS system equipped with an Al anode XR50 source operating at 150 W and a Phoibos 150 MCD-9 detector with pass energy of 25 eV at 0.1 eV steps at a pressure below 6 10^{–9} mbar.

2.3. Catalytic activity test

Etherification experiments were performed in a stainless steel stirred autoclave (150 mL) equipped with a temperature controller and a pressure gauge. Stirring was fixed for all experiments at 1200 rpm to avoid external diffusion limitations. For the etherification of glycerol with *tert*-butanol, the composition of the reaction mixture was: 20 g of glycerol, glycerol/*t*-butanol molar ratio of 0.25,

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