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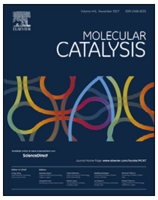

Editor's choice paper

Etherification of different glycols with ethanol or 1-octanol catalyzed by acid zeolites

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ABSTRACT

New routes for transforming biomass-derived glycols into value-added products through innovative catalytic processes are of great relevance in the chemical industry. The etherification of these glycols with alkyl alcohols is a process to produce oxygenated fuel additives, antimicrobial and antiseptic agents, and non-ionic surfactants. In this work, the etherification reaction of glycerol, 1,2-propylene glycol or ethylene glycol with ethanol or 1-octanol using USY, H-Beta and HZSM-5 zeolites as catalysts was investigated. The catalytic activity expressed as glycol conversion was correlated with the zeolite hydrophobicity index, that is, higher conversions were achieved with more hydrophobic zeolites. Considering glycol conversion and monoether distribution, HZSM-5 showed a good catalytic performance for the studied etherification reactions. The hydrophobicity/hydrophilicity of reactants and catalysts, and the framework structure of the zeolites are crucial properties for the catalytic behavior of the studied zeolites in the etherification reaction of glycols and alkyl alcohols.

1. Introduction

Recently, the use of biomass as raw material for chemical industry has attracted great interest, mainly due to concerns about environmental issues. Platform molecules can be obtained from biomass via chemical and/or enzymatic processes and further used as starting materials for bulk and fine chemicals. An important example of a platform molecule is glycerol. Converting glycerol into value-added products, such as propylene glycols and ethylene glycol, provides an alternative for its disposal and surplus problems due to biodiesel production. These glycols have numerous important applications for the synthesis of several valuable chemicals. Besides, the development of new routes for transforming these biomass-derived glycols into value-added products through innovative catalytic processes is of great relevance in the chemical industry.

One possibility to increase the value of these glycols (glycerol, 1,2-propylene glycol, 1,3-propylene glycol and ethylene glycol) is through their transformation into ethers that are stable and have many applications. When the etherification reaction occurs with short chain alcohols, such as ethanol, the produced ethers can be directly used as oxygenated fuel additives and solvents [1–6], and when the reaction is carried out with long-chain alkyl alcohols [7–9] or alkenes [10–14], like 1-octanol or 1-octene, the monoalkyl ethers are applied as amphiphilic bioderivatives, which can be used as precursors for polymers, intermediates in pharmaceutical and agrochemical industries, antimicrobial and antiseptic agents, solvents and non-ionic surfactants.

The etherification of alcohols is an acid catalyzed reaction. Several heterogeneous acid catalyst materials including resins (Amberlyst A15, A35, A70), clays (K-10), grafted silica samples and several zeolites (Beta, ZSM-5, Y, USY) were screened as catalysts [1–5,10,11]. Among these materials zeolites are more suitable to etherification reactions due to their tunable properties such as acidity, hydrophobicity/hydrophilicity, texture, chemical composition, shape selectivity, pore dimension, and also to their easy recovery and reusability. According to the literature, textural, acid and hydrophobicity/hydrophilicity properties are crucial to achieve good glycol conversions and ether selectivities [1,6–8].

To the best of our knowledge, the etherification reaction of glycols and ethanol or 1-octanol is not widely investigated. For ethanol, there are some catalyst screening studies [1–5], but no report on using different glycols. On the other hand, for 1-octanol there are only a few reports using specific Lewis acid mesoporous catalysts [7–9].

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Due to the great potential of direct etherification reaction to increase the value of glycols derived from biomass, in this work the catalytic performance of a USY series, H-Beta and HZSM-5 zeolites on the etherification reaction of glycerol, 1,2-propylene glycol or ethylene glycol with ethanol or 1-octanol was investigated. The catalysts were characterized according to their physical, chemical and textural properties in order to explain their catalytic performance.

2. Experimental

2.1. Catalyst preparation

A series of USY zeolites was prepared through a process of steaming followed by an acid leaching. First, an NH_4Y zeolite was submitted to steaming at 550 and 650 °C. Then, the steamed samples were leached with H_2SO_4 (10 wt%) to eliminate extra-framework aluminum (EFAL) species. The materials were named USY-T-L-X, where T is steaming temperature, L indicates that the material was submitted to an acid leaching, and X is the number of cycles of full treatment (steaming + acid leaching). More details on the preparation of these samples can be found elsewhere [6].

A Beta zeolite (commercial TEA-Beta – Valfor CP806B-25) was supplied by PQ Corporation. It was calcined at 500 °C, under N_2 flow, in order to remove its template. Then, it was ion exchanged with NH_4Cl (2 mol L^{-1} NH_4Cl solution, with NH_4^+/Na^+ ratio = 7.7) and finally calcined under air flow at 500 °C for 4.5 h to produce a material named H-Beta. HZSM-5 sample was obtained from an NH_4ZSM-5 zeolite with nominal Si/Al molar ratio = 15, provided by CENPES/PETROBRAS, by thermal treatment under air flow at 500 °C for 4.5 h.

2.2. Chemical, structural and textural characterization

The identification of crystalline phases was performed using X-Ray Powder Diffraction (XRPD) patterns obtained in a Rigaku Miniflex X-ray diffractometer using CuKα radiation, 30 kV and 15 mA. Data were recorded in 2θ range of 5–60° with an angular step width of 0.05° and a counting time of 2 s per step.

The bulk chemical composition of the zeolites was determined by X-Ray Fluorescence (XRF) in a Rigaku spectrometer (Supermini model) equipped with a Pd X-ray generator and controlled through ZSX software.

The framework Si/Al molar ratio and EFAL content of dealuminated USY zeolites were determined by Attenuated Total Reflectance (ATR) infrared spectroscopy. A Perkin-Elmer spectrophotometer (Frontier model) was used to acquire spectra in the region between 600 and 4000 cm^{-1} at a resolution of 4.0 cm^{-1} at room temperature.

Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE-400 NMR spectrometer equipped with a 7.0 mm VT CP/MAS probe operating at a magnetic field of 9.4 T. The ^{27}Al MAS-NMR spectra were obtained at 103.9 MHz using 1.0 ms (180°/20) pulses and 0.5 s delay, a total of 5000 pulses were accumulated. The magic angle spinning speed was 12 kHz. The ^{27}Al chemical shift was referred to $AlCl_3.6H_2O$.

N_2 adsorption/desorption at −196 °C was used to determine textural properties in a Micromeritics ASAP 2020. Before nitrogen adsorption, samples were pretreated under vacuum for 12 h at 300 °C. Specific area was calculated using BET (Brunauer-Emmett-Teller) equation. Microporous area and volume were determined using t-plot method and Harkins & Jura equation, while mesoporous area and volume were set using BJH (Barrett-Joyner-Hallenda) method.

2.3. Acidity characterization

Temperature-Programmed Desorption (TPD) of NH_3 was used to measure the density and strength distribution of acid sites. The sample was submitted to an in situ thermal treatment at 150 °C for 1 h and then at 500 °C for 1 h under a flow of 30 mL min^{-1} of He, with a heating rate of 10 °C min^{-1}. Then, the sample was cooled down to 150 °C and exposed to a flow of NH_3/He (2.91%) gas mixture (30 mL min^{-1}). The physisorbed molecules were removed under He (30 mL min^{-1}) at the same temperature. Another cycle of NH_3/He adsorption and desorption under He was carried out to determine the amount of physically adsorbed ammonia. After the second cycle, the sample was heated from 150 to 500 °C under He flow (30 mL min^{-1}) using a heating rate of 10 °C min^{-1}, so that desorption profiles of chemisorbed ammonia were obtained. The acid site density was calculated using the amount of ammonia chemically adsorbed at 150 °C calculated by the difference between the total and physically adsorbed amount.

2.4. Hydrophilicity/hydrophobicity assessment

The hydrophobicity index of the zeolites was determined using a non-competitive adsorption of water and toluene. The analyses were performed in a temperature-programmed desorption unit equipped with a thermal conductivity detector.

In a typical procedure, 50 mg of sample was pretreated in situ at 150 °C for 1 h and then at 500 °C for 1 h under He flow (30 mL min^{-1}) to remove adsorbed substances. Then, the sample was cooled to 30 °C and the first adsorption step was started under a saturated mixture of water (0.92 vol%) or toluene (1.77 vol%) vapor and He using a flow rate of 30 mL min^{-1}. After adsorption, the probe molecule desorption was carried out at 30 °C under He (30 mL min^{-1}). In order to quantify the amount of physically adsorbed probe molecule, a new cycle of H_2O or toluene/He adsorption and desorption under He was carried out. The amount of chemically adsorbed probe molecule at 30 °C was obtained by the difference between total and physically adsorbed amount. The partial pressures of water and toluene were 10 and 11 mmHg, respectively.

The hydrophilicity/hydrophobicity (polarity) of the reactants was assigned as the normalized molar electronic transition energies (E_T^N) of dissolved pyridinium N-phenolate betaine dye, measured in kilocalories per mole (kcal mol^{-1}) at room temperature (25 °C) and normal pressure (1 bar) [15].

2.5. Catalytic tests

The etherification of different glycols with alkyl alcohols was performed in a 50 mL batch reactor (Parr reactor model 4843) equipped with temperature, pressure and stirring control. The catalysts underwent to an ex-situ heat treatment under N_2 flow (50 mL min^{-1}) at 500 °C for 3 h. After that, the catalyst was quickly added to the reactor containing the mixture of glycol and alkyl alcohol. The system was then heated up to reaction temperature. The catalytic tests were carried out in the liquid phase, under autogenous pressure and stirring rate of 600 rpm. Experimental conditions were selected based on the literature [1]. The experimental tests for the etherification of glycols with alkyl alcohols of were performed at 200 °C, using an alkyl alcohol/glycol molar ratio equal to 9, a reaction time of 6 h, and 3.5 wt% of catalyst concentration, defined according to glycol amount. These experimental conditions were varied to better understand the catalytic process. After the reaction time, the reactor was cooled to room temperature and the catalyst was separated by decantation. The products were monitored by gas chromatography on a Varian 3800 gas chromatograph using a 30 m capillary column CP Wax 52 CB and a flame ioniza-

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