Remarkable catalytic properties of hierarchical zeolite-Beta in epoxide rearrangement reactions

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A B S T R A C T

Hierarchical Beta zeolites with enhanced accessibility obtained by crystallization of silanized zeolitic seeds were synthesized and investigated as catalysts for epoxide rearrangement reactions. On the other hand, hybrid zeolitic–mesoporous materials prepared from Beta protozeolitic units, and later assembled around cetyltrimethyl ammonium bromide (CTAB), were also synthesized for comparison purposes. Textural and structural properties were studied by N_2 and Ar adsorption isotherms, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The coordination and stability of the Al atoms were investigated by ^{27}Al MAS NMR. The acidic properties were analyzed by NH_3 temperature programme desorption (TPD), and by FTIR probe pyridine adsorption–desorption to get insights on their acidic features and population of Brønsted and Lewis acidity. These zeolitic type materials featured additional porosity and enhanced textural properties compared with the conventional Beta zeolite and Al-MCM-41. Likewise, their acidic properties were modified, the distribution and strength of Brønsted and Lewis acid sites being different compared to the reference samples. These materials were tested in the liquid phase rearrangement of cyclic, branched, and linear epoxides with different sizes to explore how the acidity and the improved diffusion of the substrates through the channels influence their catalytic behaviour. In overall, hierarchical Beta zeolite exhibits the best combination of catalytic activity and selectivity due to enhanced accessibility and appropriate balance of Brønsted and Lewis acid sites. These results confirm that the hierarchical Beta zeolite is a potentially interesting catalyst for epoxide rearrangement reactions.

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1. Introduction

Zeolite Beta was first synthesized by Mobil Oil in 1967 [1]. Owing to its unique three-dimensional microporous system with 12-ring openings, together with its suitable physicochemical properties, zeolite Beta has been widely used as catalyst for petrochemical processes, such as cracking [2], isomerization [3], alkylation [4] and acylation [5]. However, the major disadvantage in the catalytic properties of this microporous material is the slow diffusion of

bulky molecules, which may limit the reaction rate and accelerate the catalyst deactivation.

Conversely, mesoporous molecular sieves with size-tuneable mesopores have been well developed since their discovery by Mobil researchers [6], attracting a great deal of attention because of their controllable structures and compositions. Thus, these materials are suitable for a wide range of potential applications in catalysis, adsorption, separation, chromatography, etc. In this sense, ordered mesoporous materials could be used in reactions with bulky molecules that cannot enter into the micropores of zeolites. However, unlike zeolites, the walls of mesopores are amorphous and, therefore, the acidity of ordered mesoporous aluminosilicates is significantly weaker than that of zeolites [7]. Moreover, their hydrothermal stability is lower than that of zeolitic materials. Accordingly, the commercial application of ordered mesoporous materials as catalysts is rather limited to date [8].

Much research work and great attention have been devoted in recent years to overcome the limitations of both types of materials trying to combine the advantages of zeolites and the benefits of

ordered mesoporous materials [9–11]. Methodologies to minimize diffusion limitation and enhance catalyst effectiveness include the synthesis of zeolites with larger micropores [12,13], the reduction of the intracrystalline diffusion path length by decreasing the zeolite crystal size [14], and recently the synthesis of two-dimensional zeolites [15]. Likewise, a widely applied strategy to obtain materials that allows a rapid diffusion of bulky species consists of introducing a secondary pore system, in the range of mesopores (2–50 nm), inside the zeolite crystals [16,17]. In this way, different synthetic routes have been proposed for the preparation of zeolitic materials with improved accessibility, such as (i) the crystallization of zeolites from organofunctionalized seeds or protozeolitic units [18,19] and (ii) the synthesis of zeolite seeds or protozeolitic units and their further self-assembly into mesoporous structures [20,21]. Both types of zeolitic materials were compared in a previous work [22], employing protozeolitic MFI units as starting building blocks. They were tested as catalysts in acylation and isomerization reactions, denoting clearly the strong influence of the textural properties and acidic features on their catalytic activity and selectivity. The induced modifications in the zeolite properties by both strategies provide positive effects due to lower steric and diffusional hindrances, accelerating the reactant diffusion towards the active sites and attenuating their deactivation.

The present work focuses on the comparison of the physicochemical, morphological and acidic properties, as well of the catalytic activity in epoxides rearrangement, of two types of zeolitic solids prepared from Beta protozeolitic units: hierarchical Beta zeolite and hybrid zeolitic–ordered mesoporous materials. Pore sizes of zeolite Beta are larger than those of the MFI materials used in our previous work [22], as the BEA structure is constituted by channels of (0.73×0.67) (0.56×0.56) nm, while the MFI one has channels of (0.51×0.55) (0.56×0.53) nm. Examples of successful catalytic applications of zeolite Beta include aromatic and aliphatic alkylation and aromatic acylation [23,24]. Nevertheless, bulky species are either hindered or slowly diffuse into the Beta zeolite micropores, restricting their use as catalysts in important reactions, as it is the case of many chemical transformations of relevance in fine chemistry. However, as a result of textural, accessibility and acidity improvements, the hierarchical Beta and hybrid zeolitic–mesoporous materials, obtained from BEA protozeolitic units, can be considered as porous solid catalysts with high potential in processes involving bulky molecules.

Epoxides rearrangement is a well-known reaction that leads to useful intermediates in organic syntheses, and that has been widely studied using both homogeneous and heterogeneous catalysts [25,26]. Epoxides activation by ring opening reactions leading to aldehydes, ketones, ethers or alcohols can be catalyzed either by Brønsted (addition of a proton to the epoxide oxygen) or Lewis acid sites (coordination of the epoxide oxygen to a multivalent cation) [27]. These reactions are used for the synthesis of a variety of fine chemicals and are conventionally performed with homogeneous catalysts such as metal halides or mineral acids. However, substitution of these homogeneous systems by heterogeneous catalysts is becoming increasingly attractive because they can be easily separated from the product and reused, while they do not usually cause environmental problems. Brunel et al. briefly reviewed the use of zeolites as catalysts in the isomerization of aliphatic epoxides [28]. Thus, a variety of zeolite structures (FAU, BEA, OFF) have been employed in the liquid phase rearrangement of 1,2-epoxyoctane, in which octanal was the main product along with other condensation products. Likewise, very high selectivities to aldehydes have been obtained in the isomerization of styrene oxide and derivatives over various zeolites [29].

Based on this context, the present work is focused on the comparison of the textural and acidic properties of two different zeolitic materials synthesized from Beta protozeolitic units and having

enhanced accessibility. Thus, hierarchical BEA zeolite and hybrid zeolitic-ordered mesoporous materials have been prepared and deeply characterized by different techniques, being also compared with standard reference samples (conventional zeolite Beta and Al-MCM-41). Moreover, the catalytic behaviour of these materials has been probed in the liquid phase rearrangement of three different epoxides varying in molecular size and chemical nature, showing the strong effect of the steric and diffusional hindrances, as well as of the acidic features required to afford the final products.

2. Materials and methods

2.1. Materials synthesis

2.1.1. Hierarchical Beta zeolite

The hierarchical Beta zeolite (h-Beta) sample was prepared from a solution with the following molar composition: Al_2O_3:60 SiO_2:15.5 TEAOH:1000 H_2O [30]. Fumed silica, tetraethylammonium hydroxide, aluminium flakes and distilled water were used as starting reagents. The precursor solution was precrystallized in a Teflon-lined stainless steel autoclave under autogenous pressure at 135 °C for 3 days under static conditions. The solid obtained was mixed with an aqueous solution containing the organosilane and TEAOH (13% w/w) (TEAOH/SiO$_2$ = 0.5). Phenylaminopropyltrimethoxysilane (PHAPTMS) was employed as silanization agent [31], being added to the precrystallized solution in a proportion of 8 mol% with respect to the total silica content in the gel. The resulting mixture was kept in a reflux system under stirring (100 rpm) at 90 °C for 6 h. The crystallization was carried out in a stainless steel reactor under autogenous pressure at 135 °C for 7 days under static conditions. The solid products obtained were separated by centrifugation, washed several times with distilled water, dried overnight at 110 °C and calcined in air at 550 °C for 5 h.

For comparison purposes, a reference Beta zeolite sample was synthesized following the same procedure but omitting the precrystallization and silanization steps.

2.1.2. Hybrid zeolitic–mesostructured material

Protozeolitic units obtained in the early stages of Beta zeolite crystallization were assembled around cetyltrimethylammonium bromide (CTAB) micelles to obtain a hybrid zeolitic–ordered mesoporous material (MCM-BEA). The Beta zeolite synthesis gel was prepared according to a procedure earlier reported [30]. The gel was aged for 20 h at room temperature in order to promote the generation of the protozeolitic units. Thereafter, the formation of the mesostructure was achieved by the addition of the surfactant (CTAB) and water to the seed solution, obtaining a mixture with the following molar composition: Al_2O_3:60SiO_2:10.8 TEAOH: 15 CTAB:2400 H_2O. After an additional ageing period of 4 h at room temperature, the mixture was transferred into an autoclave and heated at 110 °C for 2 days under static conditions [32]. The solid products obtained were separated by filtration, washed several times with distilled water, dried overnight at 110 °C and calcined in air at 550 °C for 5 h.

A reference Al-MCM-41 sample was also synthesized according to a previously published procedure [33].

2.2. Characterization

XRD patterns of the different samples were recorded with a Philips XíPERT MPD diffractometer using CuKα radiation (λ = 1.54056). Both low- and wide-angle X-ray patterns were collected in order to characterize the mesoscopic ordering and the zeolite crystallinity of the samples, respectively.

The textural properties of the mesoporous materials were obtained by nitrogen adsorption–desorption isotherms at −196 °C