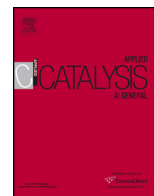




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Properties of hierarchical Beta zeolites prepared from protozeolitic nanounits for the catalytic cracking of high density polyethylene

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ABSTRACT

Hierarchical Beta zeolites have been prepared employing two strategies of synthesis for the generation of mesopores with different size distribution. In both cases, the starting gel was subjected to pre-crystallization to induce the formation of protozeolitic nanounits. The first strategy involves the reorganization of the protozeolitic nanounits by incorporation of a surfactant (cetyltrimethylammonium bromide, CTAB), whereas the second one is based on the use of a silanization agent (phenylaminopropyltrimethoxysilane, PHAPTMS) that it is grafted to the outer part of the nanounits to avoid their total merge during the crystallization process. In addition, conventional Beta zeolite and ordered mesoporous aluminosilicates have been prepared and employed as reference samples. All materials have been characterized by a number of techniques, whereas their catalytic behavior has been evaluated in the cracking of high density polyethylene (HDPE). The h-Beta (CTAB) sample shows a narrower mesopore size distribution, more uniform and stable tetrahedral Al species and a higher acid strength than the material obtained from silanized nanounits, although the latter exhibits a larger accessibility as denoted by its higher mesopore/external surface area (351 m²/g in h-Beta (PHAPTMS) versus 228 m²/g in h-Beta (CTAB)). While the ordered mesoporous aluminosilicates were almost inactive in HDPE cracking (<5 wt% of conversion) due to its weak acidity, high plastic conversions were obtained over the zeolite Beta samples (>50 wt% of conversion). The results obtained indicate that the overall catalytic activity depends mainly on the accessibility to the active sites, whereas the product selectivity is rather determined by the acid strength of the zeolite catalysts. Thus, h-Beta (CTAB) sample promoted in a great extension both end-chain cracking and aromatization reactions due to its high acid strength.

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1. Introduction

Hierarchical zeolites have recently attracted great interest as they show improved properties derived from the enhanced accessibility associated to the presence of a secondary porosity, usually in the mesopore range, in addition to the typical zeolitic micropores [1,2]. Thus, relevant benefits have been identified by the use of hierarchical zeolites as catalysts in a wide range of reactions when compared with conventional purely microporous zeolites: faster intracrystalline diffusion, lower steric hindrances for the con-

version of bulky compounds and higher resistance to deactivation by coke deposition. Moreover, the mesopore volume provides an ideal space for the deposition of metal and/or metal oxides phases with a high dispersion in order to obtain bifunctional catalysts with enhanced activity.

A number of strategies have been developed to prepare zeolitic materials with hierarchical porosity [1–6]. In a previous work [2] these methods have been classified according to the following categories: i) Removal of framework atoms; ii) Dual templating with surfactants; iii) Methods based on hard templates; iv) Zeolitization of pre-formed solids; v) Methods based on the use of silanization agents; vi) Mixed Approaches. Likewise, other strategies of synthesis based on 2D layer zeolite precursors, such as swelling, delamination, pillaring and stabilization, have been reported in the literature [7,8].

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One of the most direct routes for the preparation of hierarchical zeolites is the dual templating method that is based on the incorporation into the synthesis gel of both a zeolitic-structure directing agent and a surfactant, the latter acting as porogen for the formation of mesoporosity. However, this strategy has very often led to the preparation of products which are really a mixture of phases since ordered mesoporous materials, with amorphous walls, are usually observed segregated from the zeolite crystals. Thus, tetrapropylammonium and cetyltrimethylammonium cations (TPA⁺ and CTA⁺, respectively) were combined with NaOH to optimize mesopore generation in ZSM-5 zeolite [9]. Inclusion of TPA⁺ in the alkaline solution led to the largest preservation of the intrinsic zeolite properties, whereas CTA⁺ facilitates the reassembly of dissolved species during alkaline treatment. However, the cationic surfactant CTA⁺ also generates amorphous ordered mesoporous phases and the final product results in a composite of hierarchical zeolite and ordered mesoporous amorphous material with diminished catalytic properties [10].

On the other hand, silanization-based methods [11–15] have shown to be able of producing hierarchical zeolites with high crystallinity and a significant contribution of the mesoporosity to the textural properties. In particular, the method based on the silanization of protozeolitic units followed by their hydrothermal crystallization has shown to be a versatile route for the preparation of different zeolites (ZSM-5, ZSM-11, TS-1, Beta and Mordenite) with hierarchical porosity and a high proportion of mesopore/external surface area with values of the latter even over 300 m²/g. However, organosilanes are relatively expensive reagents, which may limit the commercial development of the hierarchical zeolites prepared by this route.

Cracking of polyolefins is a reaction that has been reported to be very useful for probing the catalytic properties of nano-zeolites, hierarchical zeolites and ordered mesoporous materials since it is very sensitive to changes in the porosity and acidic features of the catalysts. Thus, when the polyolefin cracking is performed at temperatures well below 400 °C, amorphous aluminosilicates are not capable of catalyzing it whereas zeolites show still significant activity. Moreover, polyolefin catalytic conversion is a process of practical interest for the transformation and valorization of plastics wastes to obtain products useful as fuels or chemicals [16]. Thus, in previous works, the catalytic cracking of polyethylene has been studied over BEA, FAU, MWW, MOR, MFI and USY zeolites [17–19], concluding that the product distribution was directly related to the pore diameter and external surface area of the zeolite catalysts. Nevertheless, the acid properties of the zeolite have been also proposed as key factors in the catalytic conversion of polyolefins. In this way, zeolite Beta exhibits a set of properties that make it a promising catalyst for the conversion of polyolefins, such as its relatively large micropore size and the presence in significant amounts of both Brønsted and Lewis acid sites, making it possible to adjust the nature and concentration of the zeolite acid sites. Likewise, hierarchical zeolite Beta has been already prepared using organosilanes [12,13,20,21], which has led to materials with enhanced accessibility and, therefore, with high potential for the catalytic conversion of plastics wastes.

In this context, the present work compares the properties of hierarchical Beta zeolites prepared employing two strategies of synthesis, which has made possible to control the mesopore size distribution. In both cases a gel, which has been previously subjected to pre-crystallization to induce the formation of protozeolitic nanounits, is employed as raw material. The first strategy involves the reorganization of the protozeolitic nanounits by incorporation of cetyltrimethylammonium cations (CTAB⁺), whereas the second one is based on the use of phenylaminopropyl-trimethoxysilane (PHAPTMS) as silanization agent that it is grafted to the outer part of the former to avoid their total merge during the crystalliza-

tion process. In addition, conventional Beta zeolite and ordered mesoporous aluminosilicates have been prepared and employed as reference samples. A number of characterization techniques have been applied for ascertaining the physicochemical properties of these materials, whereas their catalytic behavior has been evaluated in the cracking of high density polyethylene (HDPE). Interestingly, the results here discussed indicate that the HDPE cracking activity is proportional to the mesopore/external surface of both types of hierarchical zeolites despite they were prepared by different approaches, although the synthesis method does really modify the product selectivity.

2. Experimental section

2.1. Synthesis of materials

2.1.1. *h*-Beta (CTAB)

A first sample of hierarchical Beta zeolite (*h*-Beta (CTAB)) was synthesized by incorporation of a commercial cationic surfactant (cetyltrimethylammonium bromide, CTAB – Aldrich) to a gel containing Beta protozeolitic nanounits. The latter was prepared according to a procedure earlier reported [12,22]. Thereby, a solution containing aluminium flakes (Aldrich, 99.9%), fumed silica (Aldrich), tetraethylammonium hydroxide (TEAOH, Alfa, 35% aqueous solution) and distilled water was aged at room temperature for 20 h and precrystallized in Teflon lined steel autoclave reactors at 408 K for 3 days in order to promote the formation of Beta protozeolitic nanounits [23,24]. Thereafter, the addition of the surfactant (CTAB) and water was carried out, a mixture with the following molar composition being obtained: 1.5 Al₂O₃: 60 SiO₂: 15.5 TEAOH: 15 CTABr: 2400 H₂O (Si/Al = 20). After an additional ageing period of 4 h at room temperature, the mixture was transferred to an autoclave and heated at 383 K for 2 days under static conditions. The solid product finally obtained was separated by centrifugation, washed with distilled water, dried overnight at 383 K and calcined in air at 823 K for 5 h.

2.1.2. *h*-Beta (PHAPTMS)

A second hierarchical Beta zeolite (*h*-Beta (PHAPTMS)) was synthesized from silanized protozeolitic nanounits following the procedure published elsewhere [12,23]. Thereby, the raw solution containing protozeolitic Beta nanounits was prepared as above described. Then, the silanization agent (phenylaminopropyl-trimethoxysilane, PHAPTMS, Aldrich, +97%) was added in a proportion of 8 mol% (with regard to the silicon content) and left reacting at 363 K for 6 h under reflux. The resulting mixture was crystallized in an autoclave at 408 K for 7 days. The solid product so obtained was separated by centrifugation, rinsed with distilled water, dried overnight at 383 K and oven calcined in static air at 823 K for 5 h.

2.1.3. *Beta* (conv)

A conventional Beta zeolite sample (*Beta* (conv)) was synthesized using the same chemical composition and procedure previously mentioned, but without adding any surfactant or organosilane agents to the synthesis gel. Therefore, this sample was prepared by direct crystallization at 408 K for 7 days of the protozeolitic nanounits solution.

2.1.4. *Al*-OMS

This material was prepared using the procedure earlier described for the synthesis of the *h*-Beta (CTAB) sample starting from a gel containing both TEA and CTAB, but omitting the pre-crystallization step, a mixture with the following molar composition being achieved: 1.5Al₂O₃: 60 SiO₂: 15.5 TEAOH: 15 CTAB: 2400 H₂O. As later discussed, characterization of this material

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