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Influence of the calcination treatment on the catalytic properties of hierarchical ZSM-5

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ABSTRACT

The effect of the calcination conditions on the properties and catalytic performance of hierarchical ZSM-5 zeolite has been investigated using different reactions as catalytic tests: acylation of aromatic substrates and rearrangement of linear and cyclic epoxides. The hierarchical h-ZSM-5 material was prepared by crystallization of silanized protozeolitic units. The removal of the organics present in the as-synthesized ZSM-5 samples has been carried out using two different calcination procedures: (i) directly under air atmosphere; (ii) following a two-step (nitrogen-air) treatment.

Clear differences are noticed related to the textural properties of the ZSM-5 samples, since the h-ZSM-5 presents higher BET and external surface area than standard ZSM-5 zeolite. Whereas the calcination method does not affect the properties of the reference ZSM-5 sample, noticeable changes were observed over the hierarchical zeolite. The concentration of Brønsted acid sites decreases by half for one-step air calcination, but only a quarter when using a two-step nitrogen/air calcination, showing that the aluminium present in hierarchical ZSM-5 is very sensitive to the calcination conditions as it may undergo framework extraction and dehydroxylation phenomena. For all the studied reactions, the hierarchical sample, calcined by a two-step treatment, presents higher activity than when using direct air calcination.

1. Introduction

Zeolites are crystalline inorganic materials having dimensions in the molecular scale. Zeolites possess singular properties which explain their high interest and potential for being employed in a variety of fields, such as catalysis, ion exchange, separations, adsorption, membranes, optics, etc. Thus, zeolites have found widespread use as heterogeneous catalysts in oil refining, petrochemistry, fine chemistry and pollutant abatement [1].

It is well known that the presence of aluminium in the zeolite framework induces a negative charge that requires a cation to balance it. This is the origin of many zeolite properties, as it is the case of their acidity and capability to catalyze acid reactions. Both Brønsted and Lewis acid sites are typically found in zeolites, their relative proportion depending on the Si/Al ratio, the zeolite structure and the activation and calcination conditions, among others. These sites correspond with bridging Si–OH–Al groups, exhibiting proton-donor Brønsted acidity, and with Lewis electron-acceptor sites connected to the unsaturated coordination of aluminium either bound to the framework or in extra-framework positions [2]. From the ^{27}Al MAS NMR spectra, the framework and extra-framework nature of aluminium present in zeolites can be ascertained, since two peaks centered at ~0 and ~50 ppm, assigned to octahedral and tetrahedrally coordinated aluminium species, respectively, are discerned [3]. Dealumination of the zeolite frameworks, for example by calcination, hydrothermal treatment, or treatment with strong acids makes possible the formation of structural defects and the appearance of extra-framework aluminium species. The acid strength and nature of these different sites can be estimated using adsorption/desorption studies of a variety of probe molecules like CO, hydrocarbons and pyridine and its derivatives, combined with FTIR measurements [4].

On the other hand, aluminium-containing zeolites exhibit unique properties with respect to activity and selectivity. Activity is mostly related to the zeolite acid sites, whereas the shape and size of the micropores may induce various kinds of shape selectivity [5]. A variety of chemical reactions of industrial interest are catalyzed by zeolites, having found application in refinery and petrochemical processes where the shape selectivity properties of the microporous zeolites are exploited [6–10]. However, the location of most

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of the active sites within the micropores produces that zeolite catalysts often suffer from intracrystalline diffusion limitations and steric constraints [11]. To overcome these hindrances, there has been a long-standing drive to either minimize the size of the zeolite crystals, thereby increasing the intercrystalline porosity, or to synthesize novel zeolitic structures with a larger pore size [12]. In this context, zeolites with hierarchical porosity, that is, zeolites featuring multiscale porosity other than microporosity have been found to offer a good solution to this problem [13]. Significant efforts have been devoted to the development of preparation methods for zeolites with a bimodal pore size distribution, such as carbon templating, desilication, zeolite seed assembly, resin templating, recrystallization, mesoscale cationic polymer templating and by using amphiphilic organosilica zeolite precursors [14–22]. Owing to the presence of the hierarchical porous structure, improved diffusion and catalysis properties have generally been observed.

In this work, hierarchical ZSM-5 zeolite obtained by crystallization of silanized protozeolitic units has been employed [22]. This method is based on perturbing the growth of the zeolite crystals by functionalization of the protozeolitic units with organosilanes, in order to prevent their total aggregation. It consists of the following steps: (i) precrystallization of the zeolite synthesis gel with the aim of promoting the formation of zeolite nuclei, (ii) functionalization of the protozeolitic units by reaction with organosilanes, which form a protective organic barrier against aggregation, (iii) crystallization to complete the zeolitization of the functionalized seeds, being subsequently subjected to different calcination procedures. This strategy has led to the synthesis of a variety of zeolites (ZSM-5, ZSM-11, Beta and mordenite) having enhanced both overall and external surface areas [22–25].

Hierarchical zeolites have shown to be very attractive as heterogeneous catalysts for reactions involving bulky molecules, such as polyolefin cracking and the synthesis of chemical intermediates and fine chemicals [23,26]. The latter field constitutes an interesting application as hierarchical zeolites may substitute the homogeneous catalysts conventionally employed.

In a recent work [27], we have concluded that hierarchical ZSM-5 samples, obtained by crystallization of protozeolitic units, present a higher ratio of Lewis/Brønsted sites acid sites, as well as a higher share of extra-framework aluminium, compared with a conventional sample. These results suggested that the nature and coordination of the acid sites located on the non-microporous external surface, or in its vicinity, may exhibit different acidic features and thermal stability. The strength and nature of the acid sites affected both the activity and the selectivity obtained in the different reactions investigated, although the accessibility of the acid sites was another factor playing a key role in the catalytic behaviour of these materials.

In this context, the present work is aimed to investigate how the conditions employed in the calcination treatment, needed to remove the organics present in the as-synthesized materials, influences the acidic and catalytic properties of hierarchical ZSM-5 samples. Thereby, the samples obtained using two different calcinations methods have been tested as catalysts in several fine chemistry reactions: Friedel–Crafts acylation of anisole and 2-methoxynaphthalene, and 1,2-epoxyoctane and isophorone oxide rearrangement. Additionally, the changes induced by these two calcination procedures over the chemical nature and the strength of the acid sites in hierarchical ZSM-5 zeolite have been also studied.

2. Experimental

2.1. Hierarchical zeolite synthesis

Hierarchical ZSM-5 zeolite (h-ZSM-5) was prepared, using tetrapropylammonium hydroxide (TPAOH) as structure directing agent, from a solution having the following molar composition: Al_2O_3:60 SiO_2:11 TPAOH:1500 H_2O [28]. The precursor solution was precrystallized in a round bottom flask equipped with a condenser under stirring at 90 °C for 20 h. Thereafter, phenylaminopropyl-trimethoxysilane (PHAPTMS) was added to the solution in proportion of 5 mol% related to the total silica content of the gel. The final crystallization of the functionalized protozeolitic units was carried out in Teflon-lined autoclaves at 170 °C for 7 days [22]. The solid products obtained from the synthesis were separated by centrifugation, washed out with distilled water and dried overnight at 110 °C.

A reference ZSM-5 sample was synthesized using the same procedure but omitting the silanization step.

2.2. Calcination treatments

Two different calcination methods were applied to both hierarchical and conventional ZSM-5 samples in order to remove the organics contained in the as-synthesized materials. In the first one the materials were calcined under an air atmosphere increasing the temperature from ambient conditions up to 550 °C with a ramp of 1.8 °C/min, the final temperature being kept constant for 5 h. The samples so obtained were named as ZSM-5 (air) and h-ZSM-5 (air). In the second calcination treatment, the as-synthesized materials were subjected first to a nitrogen atmosphere increasing the temperature from ambient conditions up to 400 °C, remaining at this temperature for 4 h, and followed by a second calcination step under air at 550 °C (ramp of 1.8 °C/min and 5 h at the final temperature). The samples so prepared were designated as ZSM-5 (N_2/air) and h-ZSM-5 (N_2/air).

2.3. Characterization

XRD patterns of the different samples were obtained with a Philips X'PERT MPD diffractometer using CuK_α radiation. Argon adsorption–desorption isotherms at −186 °C were 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 distribution was calculated using the adsorption branch of the argon isotherms by applying the NLDFT model (Quantachrome) [29]. The Si/Al atomic ratio of the samples was determined by ICP-AES measurements with a Varian VISTA-AX-CCD equipment. TEM images were obtained in a PHILIPS TECHNAI 20 electron microscope operating at 200 kV.Ammonia temperature programmed desorption (TPD) experiments were carried out in a Micromeritics 2910 (TPD/TPR) equipment.

The coordination of the aluminium atoms in the zeolite samples was determined from the ^{27}Al MAS NMR spectra. They were recorded at 104.26 MHz in a VARIAN Infinity 400 spectrometer at spinning frequency of 4 kHz and intervals ranging from 5 to 30 s between successive accumulations. The external standard reference was $[Al(H_2O)_6{}^{3+}]$ and all measurements were carried out at room temperature. FTIR spectra were recorded with a Bruker Tensor 27 spectrometer. For the pyridine adsorption study, self-supported wafers were prepared and evacuated at 500 °C. Then, 2.4 kPa of pyridine (equilibrium pressure) was adsorbed at 170 °C. Desorption was subsequently performed at increasing temperatures (250 °C, 350 °C, 450 °C and 520 °C) for 20 min each time to determine the acid strength of the sites. Concentration of Brønsted and Lewis acid sites (in μmol/g) were obtained from the experiments of pyridine adsorption, calculated on the basis of the intensity of the 1540 cm^{-1} (pyH+) and 1450 cm^{-1} (pyL) bands, respectively after first desorption step at 250 °C and using the respective absorption coefficients, ε(pyH+) = 0.75 cm/μmol and