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Tailoring the properties of hierarchical TS-1 zeolite synthesized from silanized protozeolitic units

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ABSTRACT

Hierarchical TS-1 zeolites, characterized by having a secondary porosity within supermicro-mesopore range, have been synthesized by silanization of protozeolitic units, previously generated by means of a precrystallization step. The silanization agent anchors over protozeolitic units surface, acting as crystal growth inhibitor during the hydrothermal crystallization treatment and hindering partially the protozeolitic units growth and aggregation. The secondary porosity arises from the voids existing between these protozeolitics units. Both the duration of the precrystallization step and the proportion of the organosilane compound added to the synthesis gel have a significant influence on the physicochemical and textural properties of the resultant materials. Thus, a precrystallization time comprised between 22 and 24 h leads to the highest enhancement of the textural properties. On the other hand, by controlling the organosilane compound proportion added to the synthesis gel, the relative contribution of the secondary porosity can be tailored. The catalytic activity of these materials was evaluated in olefin epoxidation reactions, using tert-butylhydroperoxide (TBHP) as oxidant. The olefin conversion and TOF values reached by hierarchical TS-1 zeolites are remarkably superior to those obtained with the conventional microporous TS-1 zeolite, the best catalytic results being achieved using a 8% mol of silanization agent. Likewise, these zeolites exhibit a high oxidant efficiency and total selectivity to epoxide, parameters which are not affected by the presence of the secondary porosity.

1. Introduction

Zeolitic catalysts offer a broad range of possibilities for performing reactions with high selectivity in the field of organic synthesis. In this sense, the discovery, by Taramasso et al., in 1983 [1], of titanium-silicalite zeolite (TS-1), with the MFI topology, was a breakthrough in heterogeneous catalysis using zeolites, owing to its excellent catalytic features in a large number of selective oxidation reactions under mild conditions [2–6]. This unique activity of TS-1 zeolite is ascribed to the isomorphical substitution of Si atoms by Ti and the hydrophobic character of its surface [7]. However, the small pore size of TS-1 zeolite limits its application to relatively small substrates and oxidants (i.e. H_2O_2) and imposes severe mass transport limitations [8].

Several strategies have been investigated during the last decades in order to overcome these drawbacks, such as the synthesis of Ti-containing zeolites with larger pores (Ti-Beta zeolite) [9] or Ti-containing ordered mesoporous materials (Ti-MCM-41, Ti-SBA-15) [10,11]. Unfortunately, the last materials suffer from low hydrothermal stability and low intrinsic activity of the Ti sites, which is mainly derived to the amorphous nature of their walls [12].

Molecular transport in zeolites can be also improved by the generation of an additional porosity to that of zeolitic micropores, commonly named as secondary porosity. Depending on the synthesis strategy, this secondary porosity may vary from the supermicropore to the macropore region. Therefore, this innovative kind of materials, known as hierarchical zeolites, combines the typical characteristics of zeolites, such as a crystalline structure and high surface area, with other properties usually related to amorphous materials, such as the presence of larger pores. Thus, the hierarchical structure generation not only may solve the micropore diffusional problems but also may modify the selectivity and improve the catalyst lifetime. For this reason, research concerning the hierarchical zeolites development has largely been extended in the last decade, becoming one of the most promising ways to overcome the diffusion limitations in microporous catalysts [13].

The secondary porosity may be generated by post-synthesis treatments such as dealumination, desilication or detitanation of preformed zeolites [14–16] or by the use of templates. These methods, denoted as templating methods, can be classified in three

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