

Synthesis and catalytic properties of Ti-silicate form of BEC polymorph of Beta zeolite

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Introduction

Ti-silicates are well-known catalysts considering their broad range of applications in oxidation reactions. From the discovery of TS-1, researchers have tried to introduce Ti species into the framework of alternative structures in order to improve activity and selectivity for manufacturing of oxygenated derivatives. Concretely, epoxidation reactions have attracted a great interest owing to the facility of the oxirane group to be transformed into other important intermediates. The synthesis of large pore Ti-zeolites, as Beta zeolite, or mesoporous Ti-containing materials has allowed overcoming diffusional limitations during the reaction of bulky cycloalkenes.

Beta zeolite, consisting on an intergrowth of two different polymorphs (A, and B), is formed by two large straight channels (6.6x6.7 Å) and the medium-size sinusoidal channel (5.6x5.6 Å). However, a third polymorph of this family, namely polymorph C (BEC) shows three dimensional large straight channels (7.5x6.3 Å), and it could provide less diffusional limitations and higher activities in the epoxidation of heavy olefins. Recently, we presented a new synthetic route for obtaining the pure silica polymorph C of Beta zeolite [1] based on a buffered media with hexafluorosilicate species and K⁺ cations, by using SDA1 (see Figure 1A) as organic structure directing agent (SDA). However, the presence of alkaline cations avoids the incorporation of Ti into the zeolite framework [2]. In present paper, we have found a very selective SDA for synthesizing the pure silica BEC in fluoride media (neutral pH), without K⁺ cations. The new Ti-BEC catalyst has been synthesized and tested in the epoxidation of different olefins, showing high activity and selectivity for reacting large cycloalkenes.

Materials and Methods

Materials and methods can be found in ref. [2].

Results and Discussion

Figure 1A shows the whole family of SDAs explored in the present work for the microporous synthesis. In the selected synthesis conditions, it can be checked that SDA1, which led to the pure silica form of polymorph C in the presence of K⁺, provides Beta zeolite under K⁺-free and neutral conditions. In the same way, other small monocationic SDAs belonging to the same family (SDA2, SDA3, and SDA4) also produce Beta structure. Dicationic SDA5 and SDA6, with similar sizes than SDA1 to SDA4 but with two charges in their structure always yield amorphous materials under the same synthesis conditions. On the other hand, when larger and more rigid dicationic molecular structures were used as SDA, it was found that SDA9, which is twice as large as SDA1, but has two charges, leads to the formation of a polymorph C under K-free conditions, while SDA7 and SDA8 yield Beta and ITQ-24 zeolite, respectively. Therefore, pure silica BEC is synthesized without alkali cations, being possible the introduction of Ti species into the polymorph C structure. UV-Vis diffuse reflectance spectrum

on the calcined material showed the presence of a unique band at ~ 220 nm, which can be assigned to Ti tetrahedrally coordinated into the zeolite framework.

The catalytic behavior of Ti-Beta and Ti-BEC was evaluated for the epoxidation of cyclic and non cyclic olefins with H₂O₂ as oxidizing agent. The intrinsic activity of these catalysts is given as a turnover frequency number (mmol_{alkene converted}/mmol_{Ti}·h), calculated from initial reaction rates. Despite the higher intrinsic chemical reactivity of cyclic compared to linear terminal olefins for epoxidation, Ti-Beta gives similar activity when reacting 1-hexene, cyclohexene and cyclooctenes. The relatively low activity of cyclohexene on Ti-Beta zeolite, indicates that during epoxidation of cyclohexene, diffusional limitations can also play a role. In fact a decrease in activity for the epoxidation of cycloalkenes with respect to linear alkenes is typically observed with medium pore Ti-zeolites, owing to diffusional limitations of cycloalkenes into the medium size pores. In the case of Ti-Beta, it is expected that cyclic olefins, such as cyclohexene, will only diffuse through the two channels with larger pore diameter (6.6 x 6.7 Å), while linear alkenes will also diffuse into the channel with lower pore diameter (5.6 x 5.6 Å). This hypothesis would explain the unusually high ratio 1-hexene/cyclohexene epoxidation observed with Ti-Beta. On the other hand, Ti-BEC, with three large straight pores (7.5 x 6.3 Å and 6.9 x 6.0 Å), is more active than Ti-Beta for the epoxidation of cycloalkenes (Figure 1B), indicating that there are not diffusional limitations for cyclohexene and cyclooctene within the pores of the Ti-BEC zeolite.

Significance

The new large-pore titanasilicate shows much better activity and selectivity for the epoxidation of bulky cycloalkenes towards oxygenated derivatives.

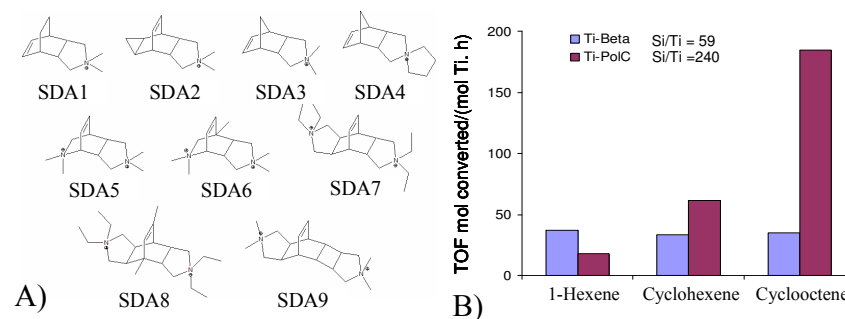


Figure 1. A) SDAs used in the present work. B) Intrinsic activity of Ti-Beta and Ti-ITQ-17, expressed as turnover frequency number (mmol alkene converted/mmol Ti·h)

References

1. Cantín, A., *et al*, *Angew. Chem. Int. Ed.* 45, 8013 (2006).
2. Moliner, M., *et al*, *J. Phys. Chem. C*. ASAP, DOI: 10.1021/jp805400u

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