Zeolite ITQ-22 as multipurpose alkylation catalyst

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Introduction

Zeolites are microporous materials characterized by their crystalline structure containing channels and cavities of molecular dimensions. One of the most interesting properties of zeolites derived from their microporous structure is their shape selectivity when used as heterogeneous catalysts. The most successful zeolite based catalysts up to now are those containing either medium (10MR) or large pores (12MR) [1], but in the last years the synthesis of zeolites with pores of different dimensions within the same structure has gained interest, not only from a fundamental but also from an applied point of view. In fact, one could expect a potential molecular traffic control occurring within the different pores when reacting or forming molecules with different size and shape, with the correspondent effect on the final selectivity. Here we study the catalytic behaviour of ITQ-22, a zeolite with a very interesting system of pores that includes unconnected 8 MR pores and connected 10 and 12 MR pores, in the alkylation of benzene with ethylene (or ethanol) and propylene (or isopropanol) for ethylbenzene (EB) and cumene (IPB) production. These reactions are not only of industrial interest [2, 3], but also very useful as test reactions for studying zeolite topology [4].

Materials and Methods

ITQ-22 ((Si+Ge)/Al=50) was synthesized following the procedure detailed in [5]. Commercial ZSM-5 and BETA zeolites (CBV8020 and CP-811, respectively, from Zeolyst Int.) have been used as reference catalysts. A Beta containing germanium ((Si+Ge)/Al=50) has also been used for comparison purposes, and synthesized in fluoride media. Alkylation of benzene with ethanol and 2-propanol was performed in the vapor phase within a continuous glass down-flow reactor (11 mm internal diameter) at atmospheric pressure [4]. Alkylation of benzene with ethylene and propylene was carried out in the liquid phase at 35 bar within a stainless steel fixed bed reactor [6].

Results and Discussion

It is well known that ZSM-5 is a much more selective catalyst for EB and diethylbenzene (DEB) production than the large pore Beta zeolite [2], more selective to polyalkylated products. The p/o-DEB (p/o-DEB) ratio is also clearly affected by the pore size of the zeolite, and much higher ratios are obtained in the case of the 10MR ZSM-5. Results obtained with ITQ-22 in the alkylation of benzene with ethanol are compared with that of the reference ZSM-5 and BETA zeolites and activities are similar, whereas selectivity to EB and EB+DEB (figure 1-a) obtained with ITQ-22 is much higher than the one obtained with BETA and even higher than the one obtained with ZSM-5. Thus, in the alkylation of benzene with ethanol zeolite ITQ-22 behaves like a medium pore zeolite.

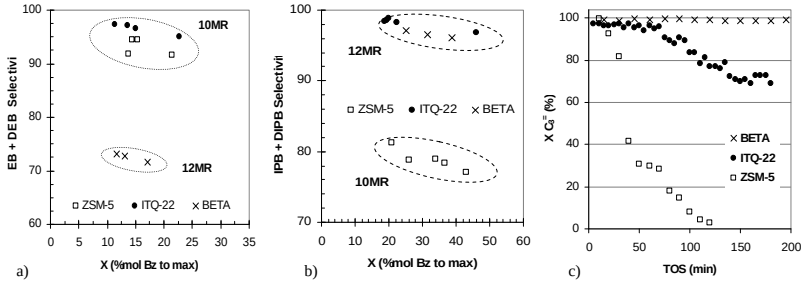

Figure 1. Selectivity to (EB+DEB) (a) and (IPB+DIPB) (b) in gas phase alkylation of benzene with ethanol and 2-propanol, and activity Vs TOS in liquid phase alkylation of benzene with propylene (c)

When benzene was alkylated with 2-propanol for production of cumene (IPB) in similar experimental conditions we obtain activities with ITQ-22 close to those of ZSM-5 and BETA, but again selectivity to IPB is maximum for ITQ-22, considerably above the values obtained by ZSM-5 and BETA. When the IPB+DIPB fraction is considered the selectivity obtained with ITQ-22 is slightly higher than that of the beta zeolite (figure 1-b), and ITQ-22 behaves clearly as a large pore zeolite, with selectivities far from those obtained with ZSM-5.

Commercial cumene processes operate in the liquid phase to increase catalyst life, In those conditions medium pore zeolites present serious diffusion constrains, and the high temperatures necessary for alkylation to occur result in high levels of the undesired n-propylbenzene (NPB). Figure 1-c shows ITQ-22 is much more active than ZSM-5 and more selective to IPB than Beta, with similar levels of NPB as those obtained by Beta. Thus it is able to catalize the alkylation of benzene with propylene with high IPB selectivity in conditions used in commercial cumene plants. It is most interesting to observe that ITQ-22, which behaves more like a 10MR zeolite for the synthesis of EB+DEB, behaves like a 12MR for the synthesis of IPB+DIPB, during alkylation of benzene with ethylene and propylene respectively. The good performance of this multipore zeolite has also been verified for IPB production in the liquid phase, representative of industrial operation conditions.

Significance

Zeolite ITQ-22 has been shown to be an active catalyst for the synthesis of ethylbenzene and cumene by alkylation of benzene with ethylene (ethanol) or with propylene (2-propanol), both in the gas and in the liquid phase. Moreover, the selectivity to the desired products is higher than the one obtained with the industrially used ZSM-5 and BETA. Thus, ITQ-22 marks a unique behavior as a multipurpose alkylation catalyst.

References

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