Synthesis and catalytic application of FER/MOR composite zeolite

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Abstract

A series of FER/MOR composite zeolites are synthesized through an organic template free route, with the MOR to FER ratio being well controlled. FER/MOR is quite different from its corresponding mechanical mixture and the intergrowth happens between [010] plane of both MOR and FER. FER/MOR composite zeolite shows superior performances in DME carbonylation reaction due to its high Brϕnsted acid density and good pore connectivity.

1. Introduction

Composite zeolites, especially micro/microporous composites, have been paid more and more attention due to their synergistic performances in catalytic reactions. The most successful one is ZSM-5/ZSM-11, which exhibits high activity, good selectivity and excellent resistance to impurity in the alkylation reaction of benzene with dilute ethylene in FCC off-gas [1-2]. Composite zeolites with binary structure not only combine the advantages of the two zeolites, but also induce the formation of special structure which could improve its catalytic performance. Thus, exploration of new composite zeolite systems attracts more and more interest in scientific and industrial field. Here, attempt on the organic template-free hydrothermal synthesis of FER/MOR composite zeolites has been done. More emphasis was put on controlling the phase composition of composite zeolite and its application in catalytic reactions compared with mechanical mixture.

It is well known that ferrierite (FER) zeolite contains a two dimensional channel structure consisting of 8 MR (8-membered ring) channel (3.5 × 4.8Å) along the crystallographic [001] direction and perpendicular 10 MR (4.2 × 5.4 Å) along the [010] direction. Mordenite (MOR) consists of one dimensional channel system with parallel 8 MR (2.6 × 5.7 Å) and 12 MR (6.5 × 7.0 Å). The existence of 8 MR channel guaranteed them as the best catalyst candidates for dimethyl (DME) carbonylation with CO to methylacetate (MA) reaction [3]. Intergrowth of FER and MOR phase may enhance the diffusion property of the zeolite which could bring unexpected catalytic performance [4]. FER shares the common feature with MOR zeolite in the secondary building unit (SBU) of 5-1 unit. And FER cage could be decomposed into a MOR cage and 5 MR. The difference between FER and MOR lies in the linkage of SBU in topology. Due to the similarity between their structures, there is a possibility to form intergrowth structure. Up to now, few report is concerned the synthesis of FER/MOR composite zeolite. Sometimes, FER (or MOR) is considered as impurities during the pure zeolite synthesis. It has thus been the aim of the present work to investigate whether FER/MOR composite zeolite could be synthesized, especially through an organic template free route.

2. Experimental

The raw materials used included colloidal silica (25.6 wt% SiO_2, 0.3 wt% Na_2O, 0.1 wt% Al_2O_3, Qingdao Haiyang Chemical Co. Ltd.), sodium aluminate ($NaAlO_2$, 51.5 wt% Na_2O, 43.0 wt% Al_2O_3, China Medicine (Group) Shanghai Chemical Reagent Co.), sodium hydroxide (96.0 wt% NaOH, China National Medicine Group Shanghai Chemical Reagent Co.) and de-ionized water.

3. Results and discussion

Seed zeolites play an important role in the zeolite synthesis, especially for organic template free route. FER/MOR composite zeolites with MOR ratio in the full range could be obtained through controlling the initial gel composition and content of the seed zeolites as shown in Fig. 1. MOR phase is more thermal dynamically favored than that of FER. Intergrowth takes place along both [010] planes of the FER and MOR zeolite evidenced by HRTEM images and DFT calculation results. FER/MOR composite zeolite is quite different from the mechanical mixture. In the HP-^{129}Xe NMR spectra, xenon atoms undergo much faster exchange between FER and MOR analogues in the composite zeolites indicating FER and MOR analogues in composite zeolites may be stacked much closer than that in the physical mixture and some parts of intergrowth may be formed due to the partially similar basic structure of FER and MOR. This could be further proved by the UV-Raman spectra results which reveal the difference of T-O-T vibration peaks. On basis of ^{1}H MAS NMR quantitative analysis results, the Brϕnsted acid density in FER/MOR was higher than that of the corresponding mechanical mixture.

FER/MOR composite zeolite exhibits quite unique catalytic behavior in the DME carbonylation reaction. Two induction periods are observed on the catalyst and MA yield is higher than that of the mechanical mixture. It should be pointed out that the MA yield on FER/MOR is even higher than that on FER which means FER/MOR exhibits better carbonylation activity than FER on premise of its good catalytic stability. Correlation between the catalytic performance and properties of FER/MOR is established.

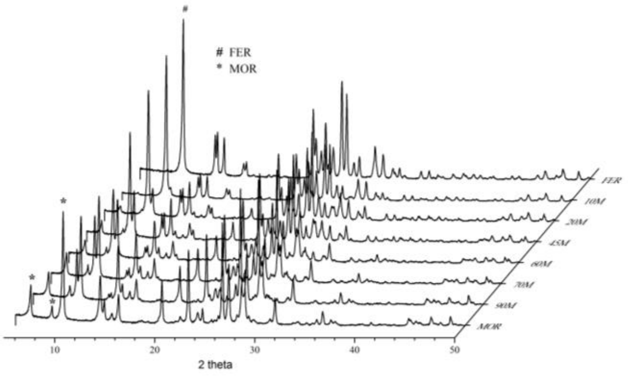

Figure 1. XRD patterns of FER/MOR composite zeolites.

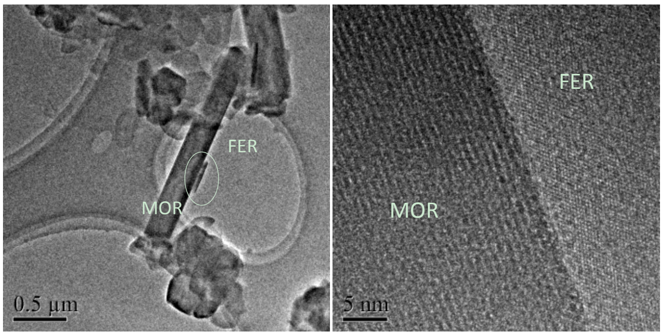

Figure 2. HRTEM image of FER/MOR composite zeolite.

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