



High catalytic performance of surfactant-directed nanocrystalline zeolites for liquid-phase Friedel–Crafts alkylation of benzene due to external surfaces



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ABSTRACT

Beta zeolite is known as an efficient catalyst for Friedel–Crafts alkylation. In liquid phase reactions, however, beta zeolite catalyst is often deactivated rapidly. We discovered that the maximum possible catalytic turnovers in benzene alkylation with benzyl alcohol could be increased by six times by using a beta zeolite with a nanosponge-like morphology, in comparison to bulk beta zeolites. The nanomorphous zeolite was obtained using a hydrothermal synthesis method which uses multiammonium surfactants as a meso–micro hierarchical structure-directing agent. The origins of the high catalytic performance were investigated by measuring the catalytic conversions after selectively poisoning acid sites located on external surfaces and in internal micropores selectively. The result indicated that the high catalytic performance was due to the alkylation reactions occurring on external surfaces. External active sites were able to perform the catalytic function even after active sites inside the zeolite micropores were deactivated. Similar results were obtained with other nanomorphous zeolites such as MFI nanosheets, MTW nanosponge and MRE nanosponge.

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1. Introduction

Friedel–Crafts (FC) alkylation is one of the most important chemical processes to produce value-added aromatic compounds through the formation of new C–C bonds between aromatic molecules and alkylating agents such as olefins, alkyl halides and alcohols [1–3]. Many FC alkylated aromatic products are used as key intermediates for the production of petrochemicals, cosmetics, dyes and pharmaceuticals [2–5]. FC alkylation can be catalyzed by both Lewis and Brønsted acids. The catalysts can be used as homogeneously dissolved components in reaction media (i.e., homogeneous catalysts), or as solid acids (heterogeneous catalysts) [1–3,6–9]. Among the heterogeneous FC alkylation catalysts, zeolites are widely used in industrial processes, due to many advantages such as strong acidity, shape selectivity, high stability and easy regenerability [10].

In petrochemical processes, FC alkylation for easily volatile products such as cumene synthesis and toluene alkylation are operated in gas phase, continuous plug-flow mode using beta zeolite

catalyst [11–15]. The advantage of this mode is high producibility and long catalytic lifetime. However, for low volatile organic products, FC alkylation is difficult to operate in gas phase. Instead, the alkylation can be operated in liquid phase using a batch reactor [16,17]. In many previous works on liquid phase FC alkylation, the conversion of reactants was often reported to reach almost 100% using beta zeolite as a catalyst [18]. The benzylation of benzene with benzyl alcohol is a typical example. This reaction is often reported to go to almost 100% conversion with zeolites or mesoporous aluminosilicate catalysts [19–24]. If a limited amount of catalyst is used, however, high conversion is difficult to achieve in liquid phase. The conversion does not increase beyond a certain value even if a very long reaction time is given. To show this, we measured the conversion of benzyl alcohol (limiting agent) with various amounts of reactants per catalyst using a conventional aluminosilicates beta zeolite. The result indicated that the maximum possible benzyl alcohol conversion (%) decreased against the reactant-to-Al ratio. We then converted the maximum conversion to the number of benzyl alcohol molecules per Al atom contained in the zeolite, and plotted the conversion per Al (CPA) as a function of the reactant amount. This plot showed that the CPA stopped increasing after reaching a maximum value about 40. That is, the zeolite catalyst was completely deactivated after CPA reaching 40.

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The purpose of the present work was to investigate why the liquid-phase FC alkylation zeolite catalyst was so rapidly deactivated, and therefore, to seek a solution to the deactivation problem. We approached the problem, focusing particularly on the effect of zeolite particle size. We noted that zeolites for catalytic applications are normally composed of crystallites on a micrometer scale ($\sim 1 \mu\text{m}$). Despite so small particle sizes, even such micro-crystallites are still much larger than the diameter of the internal micropores ($< 1 \text{ nm}$) that constitute the crystal structure. Such zeolites are called bulk zeolites, and their external crystal surface area is very small as compared to internal surfaces corresponding to a large number of micropores. When a bulk beta zeolite is used as a catalyst, the benzyl alcohol–benzene reaction can occur mostly inside the micropores. Reactions on the external surfaces can be disregarded, due to the relatively small surface area. The phenomenon is similar in various reactions where bulk zeolites are used as catalysts [25,26]. On the other hand, in nanomorphous zeolites (i.e., zeolites with nanoscale morphologies), the catalytic function of the external surfaces can be quite significant, as recently reported by Kim et al. [27]. Kim et al. synthesized MTW, MRE and beta zeolites with nanosponge-like morphologies via a recently-developed synthesis route which used multiammonium surfactants as meso–micro dual structure-directing agents (SDAs). These nanomorphous zeolites exhibited superior catalytic performance to their bulk counterparts in a gas-phase cumene synthesis study. It was particularly notable that the nanomorphous zeolites maintained high catalytic activities for a long time, whereas bulk zeolites lost activity almost completely. Kim et al. were able to separate the catalytic deactivation curve into two exponential functions. Based on this analysis, they attributed the high catalytic performance of the nanomorphous zeolites to benzene alkylation reactions occurring mainly at catalytic sites that were located at external surfaces. If this was correct, the catalytic reactions in these zeolites should have occurred dominantly at the external active sites rather than the internal acid sites. In addition, the external active sites exhibited much longer catalytic lifetimes than the internal sites. Nevertheless, such effects of external acid sites to the catalytic performances were not yet generally confirmed in other zeolite catalysis, particularly in liquid-phase FC alkylation.

For the purposes of the present research, four structure types of zeolite (i.e., beta, MTW, MRE, and MFI) with nanosponge morphologies were synthesized via the multi-ammonium surfactant route [27,28]. These nanomorphous zeolites were characterized in terms of their catalytic conversion rates and the maximum possible conversions in liquid-phase FC alkylation of benzene with benzyl alcohol. Efforts were made to quantify the catalytic conversions taking place on the external surfaces in comparison to reactions occurring inside micropores, using a nanomorphous beta zeolite sample. One strategy to this end was to treat the zeolite sample with triphenylphosphine before benzylation reaction measurement. Triphenylphosphine was a strong base molecule so that it could poison acid sites in a zeolite by strong chemisorption. The poisoning was limited to the external surfaces as the molecule was too large to enter a micropore aperture in a beta zeolite. Another strategy was to expose the zeolite sample to a high-temperature gas flow containing benzene and *i*-propene, prior to benzylation. This treatment could deactivate the internal catalytic sites more rapidly than the external sites due to the preferential deposition of coke in micropores [29,30]. We analyzed the result of the catalytic reaction measurements after such selective deactivation treatments. This investigation indicated that the cause for the rapid catalytic deactivation of bulk beta zeolites in liquid-phase FC alkylations was due to internal pore blockage by the bulky side products. Compared to the internal sites, the external sites were very slowly deactivated. Thus, zeolite synthesis in nanomorphous form turned out as an

effective means of achieving high catalytic turnovers in the liquid-phase benzyl alcohol reaction.

2. Experimental

2.1. Material preparation

Nanomorphous zeolite samples were synthesized with multi-ammonium surfactant SDAs as described elsewhere [27,28]. Beta, MTW and MRE zeolites were synthesized using the same SDA, $[\text{C}_{22}\text{H}_{45}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-CH}_2\text{-(C}_6\text{H}_4\text{)-CH}_2\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-CH}_2\text{-(C}_6\text{H}_4\text{)-CH}_2\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-C}_{22}\text{H}_{45}](\text{Br}^-)_2(\text{Cl}^-)_4$. Tetraethylorthosilicate (TEOS, 95%, Junsei) was used as the silica source for the nanomorphous zeolite samples. Sodium aluminate (53 wt%, Sigma-Aldrich) was the alumina source. The details of the synthesis conditions were differently optimized for each zeolite structure. The optimized synthesis conditions are the same as described by Kim et al. [27]. For MFI zeolite, the SDA was $[\text{C}_{16}\text{H}_{33}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{13}(\text{Br}^-)_2]$. Sodium silicate solution (Si/Na = 1.75, 15 wt% SiO_2) was used as a silica source for the MFI zeolite. Sodium aluminate (53 wt%, Sigma-Aldrich) was used as an alumina source. The synthesis conditions were the same as those reported by Kim et al. [28]. These nanomorphous zeolite samples are denoted as nanozeolites. Their corresponding bulk samples were also synthesized following the procedures [28,31–33]. An Al-MCM-41 sample was prepared via the postsynthetic incorporation of Al, following a procedure reported in the literature [23]. All zeolite and Al-MCM-41 samples were calcined in air at 853 K after hydrothermal synthesis.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were measured with a Rigaku Multiflex diffractometer equipped with $\text{Cu K}\alpha$ radiation (30 kV, 40 mA). The Ar adsorption isotherms were measured at the liquid argon temperature with an ASAP 2020 volumetric adsorption analyzer [34]. Si/Al ratios were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using an OPTIMA 4300 DV instrument (Perkin Elmer). Scanning electron micrographs (SEM) images were taken with a Hitachi S-4800 microscope operating at 2 kV without a metal coating. Transmission electron micrographs (TEM) images were obtained using a TecnaiG2 F30 at an operating voltage of 300 kV. ^{31}P NMR spectra were acquired in a solid state with magic angle spinning (MAS) using a Bruker AVANCE400WB spectrometer at room temperature, following the method reported in the literature [35].

2.3. Catalytic measurements

Calcined zeolites in powder form were slurried in a 1-M NH_4NO_3 solution three times in total for the ion exchange into NH_4^+ . The zeolites were calcined again in air at 823 K to convert to a H^+ -ion-exchanged form. The liquid-phase FC alkylation reaction was performed using a Pyrex batch reactor. Typically, 50 mg of H^+ -form zeolite was degassed at 573 K. This sample was added to a Pyrex glass reactor that contained 190 mmol of benzene and (7.2, 14.4, or 28.8) mmol of benzyl alcohol. The mixing was carried out in a glove box to prevent moisture contamination. The reactor temperature was quickly ($< 3 \text{ min}$) increased to 353 K under magnetic stirring. Small aliquots (0.1 ml) of samples were taken at various times afterward. At each sampling, the solid catalysts were filtered out after immediate cooling to room temperature. The liquid phase was analyzed on a gas chromatograph equipped with a flame

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