

Preparation of interlayer-expanded zeolites having high catalytic performance through silylation of layered zeolitic precursors

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Introduction

While zeolites are generally crystallized under hydrothermal conditions, the structural conversion of a layered zeolitic precursor into a zeolite by the topotactic dehydration-condensation of silanols on both sides of the interlayers has been reported [1-4]. For instance, a typical layered zeolitic precursor is the MCM-22 (framework type code: **MWW**) aluminosilicate precursor (denoted by **MWW(P)**) possessing a layered structure consisting of the stacking of **MWW** sheets [5,6], which is transformed into MCM-22 upon calcinations through the condensation of the silanols located on the surface of **MWW** layers, resulting in the formation of 10-membered ring (10MR) interlayer micropores.

The structural conversion of such a layered zeolitic precursor into a high performance catalyst could be attained by expanding the space between the layered sheets with the original zeolitic structure maintained. Our group has developed the preparation of a novel titanosilicate denoted by Ti-YNU-1 from an **MWW**-type layered precursor [7]. Ti-YNU-1 has an expanded pore window (12MR) between the crystalline **MWW** sheets. It was supposed that a part of silica “debris” originating from the framework and produced by the acid treatment constructs monomeric silica puncheons between **MWW** sheets, resulting in the formation of interlayer-expanded micropores in Ti-YNU-1. Recently, we have developed a novel general methodology of preparing a large-pore zeolite material named interlayer-expanded zeolites (IEZ) through the interlayer-silylation of layered zeolitic precursors [8]. Here we report in detail the preparation of an interlayer-expanded zeolites **MWW** (IEZ-**MWW**) via pillaring the interlayers of **MWW(P)** by using monomeric silylating agents and their catalytic properties.

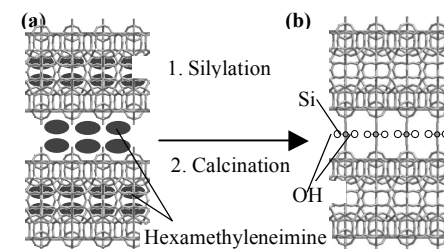
Materials and Methods

The layered precursor of the **MWW** aluminosilicate, denoted by Al-**MWW(P)**, was hydrothermally synthesized from fumed silica (SiO₂, Cab-O-Sil M5, Cabot Inc.), NaAlO₂ (33% Al₂O₃, 36.5% Na₂O), NaOH, hexamethylenimine and distilled water. The silylation of Al-**MWW(P)** was performed under liquid or vapor phase conditions. After silylation, the solid products were recovered, rinsed with ethanol and distilled water, dried at 100°C, and then calcined at 550°C for 6 h to give Al-IEZ-**MWW** materials, which were subjected to catalytic reactions.

Results and Discussion

The XRD patterns of as-made **MWW(P)** show a peak at $2\theta = 6.50^\circ$, due to the [002] reflection. Calcination of Al-**MWW(P)** shifted the [002] reflection peak to $2\theta = 6.90^\circ$, overlapped with the strong [100] reflection peak at $2\theta = 7.14^\circ$; the **MWW** structure was obtained by the dehydration-condensation of hydroxyl groups between the **MWW** layers. On the other hand, the interlayer-expanded structure was maintained not only after the silylation treatment but also after the following calcination, as evidenced by the presence of the [002] reflection at $2\theta = 6.46^\circ$. The preservation of the interlayer spacing in Al-IEZ-**MWW** is obviously due to the intercalation of silylene units between the **MWW** layers and subsequent formation of monomeric silica puncheons by their condensation with silanol groups on the layers. Me₂Si(OEt)₂ or Me₂SiCl₂ molecules are suitable as silylating agents, which can connect with silanol groups on both side of layers without their self-condensation.

The silylation reaction can be carried out under both liquid and vapor phase conditions. In addition to Al atoms, heteroatoms such as Ga, Fe, and Ti can be incorporated into the IEZ-**MWW** materials. They show high catalytic performance in the acylation of anisole (Al), the Baeyer-Villiger oxidation of cyclohexanone (Ga), and epoxidation of cyclohexene (Ti), because of the expanded space that can accommodate bulky substrates. Furthermore, this strategy can be adopted to expand the pores of zeolites having frameworks such as CDO, FER, and NSI.



Significance

We have developed a new methodology of synthesizing zeolites with expanded pores that are useful as catalysts for the conversion of larger molecules.

References

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