

Immobilization of Mo in BEA zeolite and its application to cyclohexene epoxidation

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Transition elements are known as good catalysts for several important oxidation of hydrocarbon. Among those elements, molybdenum (Mo) shows especially high performance for liquid-phase oxidation of olefins using organic oxidant [1]. However, Mo species leached out from zeolite framework leads to deactivation, high removal cost and environmental problems. Our approach to immobilize Mo on zeolite was to synthesize Mo-BEA by isomorphous substitution for B-BEA. We carried out post-synthesis using Mo(CO)₆ as Mo source. Mo(CO)₆ was fed by chemical vapor deposition (CVD) to insert Mo in silanol-nest site that was formed by B removal with HCl. Cyclohexene epoxidation was performed to evaluate its catalytic property.

B-BEA was synthesized by the dry gel conversion (DGC) method. Si/B ratio in as-prepared sample was 15.5, which was determined by chemical analysis using ICP. To form silanol-nest site, B-BEA was deboronated by treatment with 0.1M HCl at 80°C. The deboronation procedure was carried out 3 times. Subsequently, by the CVD of Mo(CO)₆ at 100°C for 1 h, Mo(CO)_x reacted with Si-O(H) in silanol-nest, and then CO was eliminated by heating at 400°C for 2 h. The XRD pattern indicated that BEA structure was maintained through these procedures. Catalytic activity was examined by cyclohexene epoxidation using TBHP as an oxidant. 0.1 g of Mo-BEA, 40 mmol of cyclohexene, 20 mmol of TBHP (in decane) and 20 g of chlorobenzene (solvent) were used for reaction. Reaction period was 3 h and temperature was 50°C while stirring. Subsequently, to reactivate during the recycle, catalyst was calcined at 500°C for 3 h after reaction. Recycle test was carried out 8 times

and Mo/Si ratio of the reused catalyst was determined by chemical analysis. Fig. 1 shows the levels of conversion of cyclohexene, epoxide yields and Mo/Si ratios of catalyst in the course of recycling tests. Though in the beginning Mo was leached during the reaction, Mo leaching was gradually reduced and ceased by 9 times of reaction. In spite of Mo leaching, the level of conversion of cyclohexene and the yield of epoxide were kept throughout the repeated reactions.

Fig.2 shows the UV-vis spectra of Mo-BEA and catalyst after 9 times of recycling tests. These spectra consisted of mainly 3 signals, T_d Mo⁶⁺ at 230 nm, O_h Mo⁶⁺ at 285 nm and Mo-O-Mo at 330 nm. After 9 times of reactions, the signal corresponding to Mo-O-Mo disappeared, suggesting that such Mo species were leached out in the course of reaction. Since the catalyst after 9 times of recycling kept high activity, we consider that the active sites of Mo-BEA were isolated Mo⁶⁺ species like T_d and O_h Mo⁶⁺ without Mo-O-Mo bond.

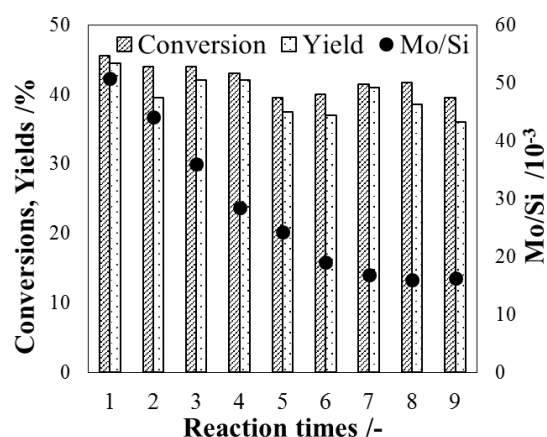


Fig.1 Catalytic activities of Mo-BEA and Mo/Si ratio.

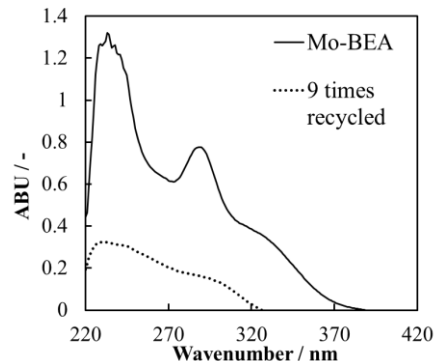


Fig. 2 UV-vis spectra of Mo-BEA.

REFERENCES

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