

論文の内容の要旨

論文題目 Tailoring Physicochemical Properties of Pentasil Zeolites via Rational Metal Modification
(合理的な金属修飾によるペンタシルゼオライトの物理化学特性の制御)

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Typically, zeolites are a kind of crystalline aluminosilicates with uniform microporous channels. Since the natural zeolites were first discovered in 1756, new zeolites with various topological structures and compositions have been discovered in quick succession due to the rapid development of the synthetic methods and advanced characterization techniques, and their excellent performances in adsorption, ion exchange and catalysis have been widely recognized. Commonly, one Al atom in the siliceous framework produces one negative charge, which is the foundation for the important properties of zeolites, such as Brønsted acidity and guest cation stabilization. Pentasil zeolites, including famous ZSM-5 and ZSM-11 zeolites, are a class of high-silica zeolite material constructed of pentasil units (one pentasil unit consists of eight five-membered rings). Due to the attractive properties, such as high thermal stability, strong acidity, unique channel structure and confined pore size, they have already been applied in many catalytic reactions. However, the physicochemical properties for pentasil zeolites are limited by their low framework Al contents. In previous studies, Al contents and distributions were attempted to directly manipulate to improve their ion exchange capacity and pursue unique catalytic performance, which were proven complicated and difficult. Fortunately, the flexibility in structure and composition of zeolites makes it feasible to introduce metals and bring promising features to zeolites. Therefore, in this thesis, without directly manipulating Al atoms, the physicochemical properties that are usually governed by framework Al atoms in pentasil zeolites were tailored via rational metal modifications.

In Chapter 1, general introductions of porous materials, particularly zeolites and pentasil zeolites, are given, followed by a brief review of modification of zeolites with metal species.

In Chapter 2, high amount of Zn was incorporated into the framework of MFI-type zeolites to enhance their ion exchange capacity. Substitution of divalent Zn in the silicate framework, i.e., zincosilicate zeolites, can produce two negative charges and therefore greatly enhance the cation exchange capacity compared with aluminosilicate analogs. However, introducing transition metals into a zeolite framework is not easy under conventional hydrothermal conditions, especially for MFI-type zeolites with highly siliceous nature. Mechanochemical method is recently involved in the material science, and chemical reactions are believed to occur in the solid state due to the strong mechanical energy. In this study, the Si–Zn oxide composites were first prepared by ball-milling of the mixture of fumed silica and ZnO. After the mechanochemical treatment, the coordination environment of Zn was changed and Zn atoms were dispersed within the silica matrix. In addition, the Al impurity derived from the milling media was negligible. Then zeolites were synthesized using the aforementioned Si–Zn oxide composites as a starting material. All the zeolites showed the typical XRD patterns of crystallized MFI structure. The Si/Zn molar ratio could be as low as ca. 14 calculated by the results of ICP-AES. The successful incorporation of Zn in the framework and negligible presence of extra-framework Zn species were confirmed by several characterization techniques, including DR UV–Vis, FT-IR, XPS and ^{29}Si MAS NMR. It was found that the incorporation of Zn into the silica matrix before the hydrothermal process was crucial to remain Zn in the solids and finally form zincosilicate framework. In contrast, by using the hand-mixed SiO_2/ZnO composite, the crystallization process was hampered and extra-framework Zn species were present. When dissolved Zn source ($[\text{Zn}(\text{NH}_3)_4]^{2+}$) was used, Al source was dispensable and incomplete Zn incorporation was also detected. The ion exchange performance for divalent cation was tested in $\text{Na}^+ - \text{Co}^{2+}$ binary solutions with different $2\text{Co}/(2\text{Co} + \text{Na})$ molar ratios. It was easier for Co^{2+} to exchange Na^+ on MFI-type zincosilicate zeolites than on commercial ZSM-5 (C-ZSM-5) when the solution Co concentration was low ($S_{\text{Co}} < 0.4$). Moreover, the maximum Co^{2+} ion exchange capacity of MFI-type zincosilicate zeolite (6.2 wt%) with similar metal substitution level to that of C-ZSM-5 was much higher than that of C-ZSM-5 (3.5 wt%). These results implied that MFI-type zincosilicate zeolites exhibited superior selectivity and ion exchange capacity for divalent cations compared with aluminosilicate analogs.

In Chapter 3, the catalytic performances of cobalt-exchanged ZSM-5 and ZSM-11 zeolites with different cobalt distributions in non-oxidative methylation of benzene with methane were compared, and the possible active sites were figured out and better catalytic performance was obtained. Recently, Co-exchanged ZSM-5 zeolites were found capable of catalyzing non-oxidative methylation of benzene with methane in fixed-bed continuous flow system, while other Co-exchanged zeolites, including beta, faujasite and mordenite, were inactive. Then, a question is raised that which features are needed to create the active sites for the reaction. In this

study, Co-exchanged ZSM-11 zeolite, which has similar topological structure to that of ZSM-5 zeolite but different distribution of ion exchange sites, were investigated in the target reaction for the first time. ZSM-5 and ZSM-11 zeolites with similar Si/Al molar ratios (high silica and low silica, respectively) and micropore volumes were synthesized from the reactants with the same composition (but different OSDAs). The cobalt contents in the ZSM-11 zeolites were higher than those in the ZSM-5 zeolites in both high and low silica samples. In addition, different from ZSM-5 zeolite, which has α -, β - and γ -type ion exchange sites, ZSM-11 zeolite only possesses α - and γ -type ion exchange sites, and therefore a higher proportion of Co^{2+} cations on α sites was achieved in ZSM-11 zeolites, according to the results of DR Vis–NIR spectra. The sequence of the concentration of the Co^{2+} on the α sites was: $\text{CoZ11-LS} > \text{CoZ11-HS} > \text{CoZ5-LS} > \text{CoZ5-HS}$. The long-term catalytic reactions at 540 °C on these four catalysts showed that the toluene formation rate followed the sequence: $\text{CoZ11-LS} > \text{CoZ11-HS} \approx \text{CoZ5-LS} > \text{CoZ5-HS}$. However, the apparent turnover frequencies (TOFs) of CoZ11 catalysts were always higher than those of CoZ5 catalysts. Moreover, CoZ11 catalysts also showed a higher methane consumption than CoZ5 catalysts. The Lewis acidic divalent cobalt cations on the ion exchange sites in zeolites were believed to be effective for the methane activation, which is the most critical step in the target reaction. In this study, a good positive correlation between the concentration of α -type Co^{2+} and the methane conversion was found, which suggested that the α -type Co^{2+} was the possible active site for the target reaction. Actually, the α -type Co^{2+} had more loosen coordination with the framework oxygen atoms, and therefore should display stronger Lewis acidity to facilitate the activation of methane. Without intentionally manipulating Al distribution, more α -type Co^{2+} can be easily created in ZSM-11 due to its intrinsic nature, which makes it promising candidate for catalyzing non-oxidative methylation of benzene with methane.

In Chapter 4, tailoring acid properties of ZSM-5 zeolites was realized with the assistance of sulfated zirconia. As is well known, zeolites serve as a class of important solid acid catalysts. However, HZSM-5 zeolite, one of the strongest zeolite-type acid catalyst, has relatively low acid density due to its limited Al content. Among other solid acids, sulfated zirconia (SZ) has attracted extensive attention owing to its facile preparation and high catalytic activity, but suffers low surface area, lack of uniform porosity and poor selectivity. Combination of zeolites and SZ seems to be a promising strategy to prepare solid acid catalysts with both enhanced acid density and satisfactory porous structure and shape-selectivity. In this chapter, by using a novel bottom-up method, ZSM-5 zeolites with well-dispersed zirconia were synthesized through hydrothermal conversion of Zr-impregnated MCM-41 precursors. First, zirconia was impregnated onto mesoporous MCM-41, which possessed large surface area to help disperse zirconia species. Then the precursors were hydrothermally treated in the presence of Al source and TPA^+ to synthesize zeolites. The as-synthesized samples displayed typical MFI-type

structure without distinguishable crystalline ZrO_2 . The XPS results suggested that zirconia species were enriched on the zeolite surface. Although the ZSM-5 particles became larger with the increasing amount of zirconia and the zirconia content was slightly higher on the surface of relatively small particles, the dispersion of zirconia species was still better than the sample prepared by direct impregnation method, in which highly aggregated crystalline zirconia could be observed. After the sulfation, sulfate groups were exclusively anchored on the surface of zirconia, which was critical for zirconia to exhibit acidity. The sulfated zirconia–ZSM-5 composites showed enhanced Brønsted acid density with mainly medium acid strength along with the increasing zirconia content, and the acid density was higher than that of zirconia-impregnated ZSM-5 sample with similar zirconia content but much lower sulfate group concentration. These results demonstrated that the increase of Brønsted acid density of ZSM-5 zeolites can be realized by introduction of sulfated zirconia, and one-pot hydrothermal conversion method was superior to conventional impregnation method.

In conclusion, modifying zeolites with metal species is regarded as an effective way to render zeolites desired physicochemical features for various applications. This thesis focuses on pentasil zeolites, whose physicochemical properties are greatly limited by the framework Al contents. Instead of directly increasing the amount or manipulating the distribution of Al atoms in the framework, which is difficult to achieve, rational metal modifications are employed to overcome the disadvantages, and some interesting properties are created, which may further broaden their application fields. In order to effectively realize metal modification, the features of metal species and zeolites should be fully utilized. By incorporating divalent Zn in the framework, ion exchange capacity can be greatly enhanced at a low metal substitution level; while acid properties can be tuned with the help of other solid acid materials. Furthermore, by choosing proper zeolite substrate with natively suitable conformation, more active sites with certain metal configuration may be easily created.

On the other hand, the methods for introduction of metal species into zeolites should also be considered. Through the rational design of preparation methods, the drawbacks of conventional one-pot methods or post-treatment methods can be avoided. The novel synthesis methods proposed in this thesis help to introduce metal species properly into zeolites and promising metal-containing zeolites are obtained. Furthermore, the multifunctional zeolite catalysts with two or more metal species can also be expected to develop. For example, bifunctional bimetal cluster-containing zeolites (like Zn/ZrO_2 -ZSM-5) can be synthesized by conversion of bimetal cluster-containing mesoporous precursors as proposed in Chapter 4, rather than just physically mixing two active components, which may be beneficial for consecutive reactions.