

博士論文(要約)

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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## Chapter 1 General Introduction

Typically, zeolites are a kind of crystalline aluminosilicates with uniform microporous channels. Since the natural zeolites were first discovered in 1756, people were curious about their microporous features and great progresses were achieved in the past six decades. Thanks to the rapid development of the synthetic methods and advanced characterization techniques, more and more new zeolites with various topological structures and compositions have been discovered in quick succession, and their excellent performances in adsorption, ion exchange and catalysis have been widely recognized [1]. 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 are a class of high-silica zeolite material constructed of pentasil units (one pentasil unit consists of eight five-membered rings). ZSM-5 zeolite, the first member of the pentasil zeolite family, was synthesized in the presence of tetrapropylammonium compounds in 1969. Till 1978, other pentasil zeolites, including ZSM-11 zeolite, and pure-silica zeolite silicalite-1 and silicalite-2, were developed successively. Due to the attractive properties, such as high thermal stability, strong acidity, unique channel structure and confined pore size, ZSM-5 zeolite has already been applied in many catalytic reactions, including hydrocarbon isomerization and alkylation [2]. 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 modulate their physicochemical properties through one-pot synthesis or post-treatment methods. Introduction of heteroatoms, especially metal species, is an alternative way to modify the physicochemical properties of zeolites, such as acidity, pore size and catalytic performance.

Therefore, in this thesis, without directly manipulating Al atoms, the

physicochemical properties of pentasil zeolites (mainly ZSM-5 and ZSM-11 zeolites) that are usually governed by framework Al atoms, such as ion exchange capacity, catalytic activity and acid property, are tailored via different 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, the incorporation of high amount of Zn into the framework of siliceous MFI-type zeolites is realized with the help of a mechanochemical method, and overwhelming ion exchange selectivity and capacity for divalent cations ( $\text{Co}^{2+}$ ) compared with aluminosilicate counterparts are obtained. 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 are evaluated, and the possible active sites are figured out and better catalytic performance is obtained. In Chapter 4, ZSM-5 zeolites with well-dispersed zirconia are synthesized through one-pot hydrothermal conversion of Zr-impregnated MCM-41 precursors, and the sulfated sample displays enhanced Brønsted acid density and is superior to the sample prepared by conventional impregnation method. In Chapter 5, general conclusions are summarized, accompanied with a future prospective on the field of tailoring physicochemical properties of zeolites via rational metal modification.

## **Chapter 2 Synthesis of MFI-Type Zincosilicate Zeolites with High Zinc Content for Enhanced Ion Exchange Capacity**

### **2.1 Introduction**

Zeolites with Zn(II) in the silicate framework, i.e., zincosilicate zeolites, not only possess larger cation exchange capacities than aluminosilicate analogs, but also have activity to trigger certain catalytic reactions due to the unique Lewis acid properties [3, 4]. However, introducing transition metals into a zeolite framework is not easy due to the highly basic conditions commonly involved in the hydrothermal synthesis. Moreover, the highly siliceous nature of some zeolites, e.g., MFI-type zeolite, also brings an obstacle for heteroatoms incorporation via conventional methods. In this chapter, for the first time, MFI-type zincosilicate zeolites with high Zn contents are

successfully synthesized by using the mechanochemically treated Si–Zn oxide composites as the starting material, and superior ion exchange selectivity and capacity for divalent cations ( $\text{Co}^{2+}$ ) are confirmed.

## 2.2 Experimental

A milled Si–Zn oxide composite was prepared by mechanically grinding fumed silica and ZnO in a certain ratio for 24 h using a planetary ball mill equipped with silicon nitride balls and pot. The milled Si–Zn oxide composites were named as M-5, M-8, and M-12 (nominally called M-*x*), corresponding to the molar percentages of Zn/(Si + Zn) of 4.8, 8.1, and 12.5 mol%, respectively.

For the synthesis of MFI-type zirconosilicate zeolites, a mixture with following molar ratio, T (Si and Zn) :  $\text{NH}_4\text{Cl}$  : TPABr :  $\text{H}_2\text{O}$  = 1 : 0.8 : 0.09 : 5, was hand mixed in a mortar for 10 min. Then, the mixture was hydrothermally treated at 170 °C. Further calcination of the as-synthesized samples was conducted at 500 °C for 5 h and the final samples were designated as Zn-MFI(M-*x*).

## 2.3 Results and discussion

After the mechanochemical treatment of the mixture of fumed silica and ZnO, the XRD peaks derived from crystalline ZnO disappeared. Meanwhile, the absorption band of ZnO was negligible in the DR UV–Vis spectra of M-*x*, while the intensity of the absorption bands at around 190–200 nm was gradually enhanced with increasing Zn content. These results could be assigned to the change of coordination environment of Zn and the dispersion of Zn atoms within the silica matrix to form Si–Zn oxide composite. The results of high-energy X-ray total scattering measurement also approved aforementioned conclusion. In addition, the Al impurity derived from milling media was negligible.

Zn-MFI(M-*x*) zeolites showed the typical XRD patterns of crystallized MFI structure. Their micropore volumes were decreasing with increasing zinc contents in the zeolites. DR UV–Vis spectra of Zn-MFI(M-*x*) did not show the distinct absorption band derived from ZnO, indicating few zinc atoms migrated from the lattice to form detectable extra-framework Zn species, and the absorption band at ca. 200 nm corresponded to the isomorphous substitution of Zn atoms into the framework of zeolite.

In the XPS spectra, the binding energy of  $\text{Zn}2p_{3/2}$  in  $\text{Zn-MFI(M-x)}$  is higher than that of bulk  $\text{ZnO}$ , because of a lowered valence electron density of Zn in  $\text{Si-O-Zn}$  bond and an increased binding energy. 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  $\text{SiO}_2/\text{ZnO}$  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  $\text{Co}^{2+}$  to exchange  $\text{Na}^+$  on  $\text{Zn-MFI(M-x)}$  than on commercial ZSM-5 when the Co concentration in solution was low ( $S_{\text{Co}} < 0.4$ ). Moreover, the maximum  $\text{Co}^{2+}$  ion exchange capacity of  $\text{Zn-MFI(M-x)}$  (e.g., 6.2 wt% for  $\text{Zn-MFI(M-12)}$ ) was much higher than that of C-ZSM-5 (3.5 wt%). These results implied that zincosilicate zeolites exhibited superior selectivity and ion exchange capacity for divalent cations compared with aluminosilicate analogs.

## 2.4 Conclusion

By using the mechanochemical method, Zn was incorporated in the silica matrix before the hydrothermal synthesis, which is beneficial for forming zincosilicate framework without detectable extra-framework Zn species. The MFI-type zincosilicate zeolites have high Zn contents, and the ion exchange capacity and selectivity for divalent cations are enhanced with less substitution level compared with aluminosilicate analogs, which is favorable for Si-rich zeolites, like MFI-type zeolite.

## Chapter 3 Comparative Study of Cobalt-Exchanged ZSM-5 and ZSM-11 Zeolites in Catalyzing Direct Methylation of Benzene with Methane

### 3.1 Introduction

Metal cations on different ion exchange sites usually exhibit different chemical states and catalytic activities. 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 [5, 6]. Then, a question is raised that which features are needed to create the active sites for the reaction. In this chapter, for the first time, cobalt-exchanged ZSM-11 zeolite, which possesses a close topological structure to that of ZSM-5 zeolite, is found to show excellent activity in non-oxidative methylation of benzene with methane. By characterizing and comparing these two cobalt-exchanged zeolite catalysts, it is found that the different distributions of ion exchange sites for  $\text{Co}^{2+}$  cations play a critical role in the catalytic reaction.

### 3.2 Experimental

ZSM-11 (Z11) and ZSM-5 (Z5) zeolites were synthesized through the conventional hydrothermal method with the same reactant composition:  $x\text{SiO}_2 : 1.23\text{Al}_2\text{O}_3 : 12\text{Na}_2\text{O} : 2(\text{TBA}_2\text{O (ZSM-11) or TPA}_2\text{O (ZSM-5)}) : 3600\text{H}_2\text{O}$ , where  $x = 95$  and  $50$  for the products with high (HS) and low (LS) Si/Al molar ratios, respectively. The as-synthesized products were calcined at  $550\text{ }^\circ\text{C}$  for  $5\text{ h}$ , followed by ion exchange with  $\text{NH}_4\text{NO}_3$  solution ( $1\text{ M}$ ) once and  $\text{Co}(\text{NO}_3)_2$  solution ( $0.05\text{ M}$ ) twice to obtain cobalt-exchanged zeolites.

The non-oxidative methylation of benzene with methane at  $540\text{ }^\circ\text{C}$  was carried out in a fixed-bed flow reactor with  $0.3\text{ g}$  catalyst. After the pretreatment in  $\text{N}_2$  flow at  $550\text{ }^\circ\text{C}$  for  $1\text{ h}$ , the system was cooled down to  $540\text{ }^\circ\text{C}$ . Then, the gas flow was changed to a mixture of  $\text{He}$  ( $84.6\text{ }\mu\text{mol min}^{-1}$ ),  $\text{CH}_4$  ( $1.23\text{ mmol min}^{-1}$ ) and  $\text{C}_6\text{H}_6$  ( $53.1\text{ }\mu\text{mol min}^{-1}$ ) to initiate the experiment.

### 3.3 Results and discussion

ZSM-5 and ZSM-11 zeolites synthesized from the reactants with the same composition (but different OSDAs) possessed similar Si/Al ratios (high silica and low silica, respectively) and micropore volumes. 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  $\alpha$ -,  $\beta$ - and  $\gamma$ -type ion exchange sites, ZSM-11 zeolite only possesses  $\alpha$ - and  $\gamma$ -type ion exchange sites, and therefore a higher proportion of  $\text{Co}^{2+}$  cations on  $\alpha$  sites was achieved in ZSM-11 zeolites, according to the results of DR Vis–NIR spectra. The sequence of the concentration of the  $\text{Co}^{2+}$  on the  $\alpha$

sites was: CoZ11-LS > CoZ11-HS > CoZ5-LS > CoZ5-HS.

According to the results of temperature-programmed reaction, target reaction did not proceed below 400 °C on either cobalt-exchanged ZSM-5 or ZSM-11 zeolites, while the toluene formation rates increased rapidly with the increasing temperature above 500 °C. The long-term catalytic reactions on these four catalysts showed that the toluene formation rate followed the sequence: CoZ11-LS > CoZ11-HS  $\approx$  CoZ5-LS > 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  $\alpha$ -type  $\text{Co}^{2+}$  and the methane conversion was found, which suggested that the  $\alpha$ -type  $\text{Co}^{2+}$  was the possible active site for the target reaction. Actually, the  $\alpha$ -type  $\text{Co}^{2+}$  had more loosen coordination with the framework oxygen atoms, and therefore should display stronger Lewis acidity to facilitate the activation of methane. The ZSM-11 zeolites could create more  $\alpha$ -type  $\text{Co}^{2+}$  than ZSM-5 zeolites, which were promising candidates for catalyzing non-oxidative methylation of benzene with methane.

### 3.4 Conclusion

Cobalt-exchanged ZSM-5 and ZSM-11 zeolites with the same Si/Al molar ratio were synthesized and tested in non-oxidative methylation of benzene with methane. Despite their similarity in the topological structure, their catalytic performances were different. It was found that the distribution of  $\text{Co}^{2+}$  cations on the ion exchange sites was different, and the possible active site for the target reaction, namely the  $\alpha$ -type  $\text{Co}^{2+}$ , was figured out. Without intentionally manipulating Al distribution, more  $\alpha$ -type  $\text{Co}^{2+}$  can be easily created in ZSM-11 due to its intrinsic nature, which makes it promising catalysts in this reaction.

## Chapter 4 One-Pot Synthesis of Zirconia–ZSM-5 Composites and Evaluation of Acid Properties

## 4.1 Introduction

Acid catalysts play an indispensable role in many industrial processes. 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 [7]. However, bulk SZ catalysts suffer 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 are synthesized through hydrothermal conversion of Zr-impregnated MCM-41 precursors, and the acid properties of the sulfated products are evaluated.

## 4.2 Experimental

MCM-41 was prepared by a conventional hydrothermal method. Then, the loading of Zr into the calcined MCM-41 (namely ZrM) was conducted by incipient wetness impregnation method, and further calcined at 350 °C.

The zirconia–ZSM-5 (ZrZ) composites were synthesized by hydrothermal conversion of corresponding ZrM precursors. ZrM was dispersed in a clear solution containing TPAOH, NaOH and sodium aluminate, and hydrothermally treated at 180 °C for 24 h to obtain the products, which were further calcined at 550 °C.

The calcined ZrZ composites were ion exchanged with  $(\text{NH}_4)_2\text{SO}_4$  solution at 70 °C, and then soaked with  $(\text{NH}_4)_2\text{SO}_4$  solution, dried and calcined at 550 °C to obtain the sulfated zirconia–ZSM-5 (SZrZ) composites.

## 4.3 Results and discussion

MCM-41 had typical small-angle XRD pattern and  $\text{N}_2$  adsorption–desorption isotherm, indicating uniform mesoporous structure. After zirconia was impregnated, no crystalline zirconia could be observed. The mesoporous structure was intact, while the pore volume decreased slightly, suggesting the uniform dispersion of zirconia in MCM-41 precursor. The lower zirconia content detected by XPS than that by ICP-AES also



approved aforementioned conclusion.

The as-synthesized ZrZ samples displayed typical MFI-type structure without distinguishable crystalline  $\text{ZrO}_2$ . 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 as confirmed by SEM and EDX maps, 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. The DR UV–Vis spectra and Zr3d XPS spectra also approved the good dispersion of zirconia species in the ZrZ composites.

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.

#### **4.4 Conclusion**

This study proposed a one-pot method to synthesize zirconia–ZSM-5 composites by direct hydrothermal conversion of zirconia-impregnated MCM-41 precursors. The dispersion of zirconia species was better than the sample prepared by direct impregnation method, which contained crystalline zirconia. After the sulfation, the sulfated zirconia–ZSM-5 composites showed enhanced Brønsted acidity, and the acid density was higher than that of sulfated zirconia-impregnated ZSM-5 sample with similar zirconia content. These results demonstrate that the increase of 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.

### **Chapter 5 General Conclusions and Future Perspective**

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 Chapter 2, MFI-type zincosilicate zeolites with high content of Zn were prepared with the assistance of mechanochemically treated Si–Zn oxide composite. Outstanding divalent cation exchange capacity was achieved, which overcame the disadvantage deriving from its highly siliceous nature. In Chapter 3, a series of cobalt-exchanged ZSM-5 and ZSM-11 zeolites were prepared and tested in the non-oxidative methylation of benzene with methane. Due to their similar topological structure but different catalytic performance, the different cobalt distributions of these two kinds of zeolites were investigated and the possible active sites, namely the  $\alpha$ -type  $\text{Co}^{2+}$ , were figured out, which could guide the design of efficient catalysts with desired active sites. In Chapter 4, zirconia–ZSM-5 composites with good dispersion of zirconia species were synthesized through one-pot hydrothermal conversion of Zr-impregnated MCM-41 precursors, and increased Brønsted acid amounts were obtained after sulfation, superior to that of sulfated zirconia-impregnated ZSM-5 zeolite.

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<sub>2</sub>-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.

## References

- [1] V. Van Speybroeck, K. Hemelsoet, L. Joos, M. Waroquier, R.G. Bell, C.R. Catlow, *Chem. Soc. Rev.* 44 (2015) 7044-7111.
- [2] P.A. Jacobs, H.K. Beyer, J. Valyon, *Zeolites* 1 (1981) 161-168.
- [3] M.A. Deimund, J. Labinger, M.E. Davis, *ACS Catal.* 4 (2014) 4189-4195.
- [4] M. Orazov, M.E. Davis, *Chem. Sci.* 7 (2016) 2264-2274.
- [5] K. Nakamura, A. Okuda, K. Ohta, H. Matsubara, K. Okumura, K. Yamamoto, R. Itagaki, S. Suganuma, E. Tsuji, N. Katada, *ChemCatChem* 10 (2018) 3806-3812.
- [6] H. Matsubara, E. Tsuji, Y. Moriwaki, K. Okumura, K. Yamamoto, K. Nakamura, S. Suganuma, N. Katada, *Catal. Lett.* 149 (2019) 2627-2635.
- [7] M. Hino, S. Kobayashi, K. Arata, *J. Am. Chem. Soc.* 101 (1979) 6439-6441.