

Special Contributions

Development of High-performance Zeolite Catalysts for Effective Use of Carbon Resources

Toshiyuki Yokoi, Dr. Eng.
Takashi Tatsumi, Dr. Eng.

OVERVIEW: If the resource, energy, and environmental problems facing the world are to be overcome, it is important that effective use be made of different types of resources. Given the problems of dwindling oil resources in particular and of reducing emissions of CO₂, establishing ways of making effective use of both conventional and unconventional carbon resources is a particularly crucial challenge. With “Environmentally conscious manufacturing – catalysts are the key” as a catchphrase, the authors have focused their research on zeolites, a class of microporous crystalline aluminosilicates with molecular-scale voids in their crystal structures. This article describes their recent work on the development of zeolite catalysts for the effective use of carbon resources.

INTRODUCTION

ZEOLITES^{(1),(2)} are microporous crystalline minerals that are subject to a high level of nano-scale control and that contain voids of uniform size at the molecular scale (0.3 to 1 nm) (see Fig. 1 and Fig. 2). These structural characteristics give zeolites three notable properties, namely their ability to be used as molecular sieves, ion exchangers, and solid acid catalysts. They

have crystal particle diameters in the range of several micrometers and their external surface area is only a few percent of their total surface area. This means that most of their activity is accounted for by their micropores, and when reactants and products have sizes similar to that of the zeolite micropores, the rate and selectivity of the reaction are influenced by the geometrical relationship between the respective shapes of the micropores and the molecules. This

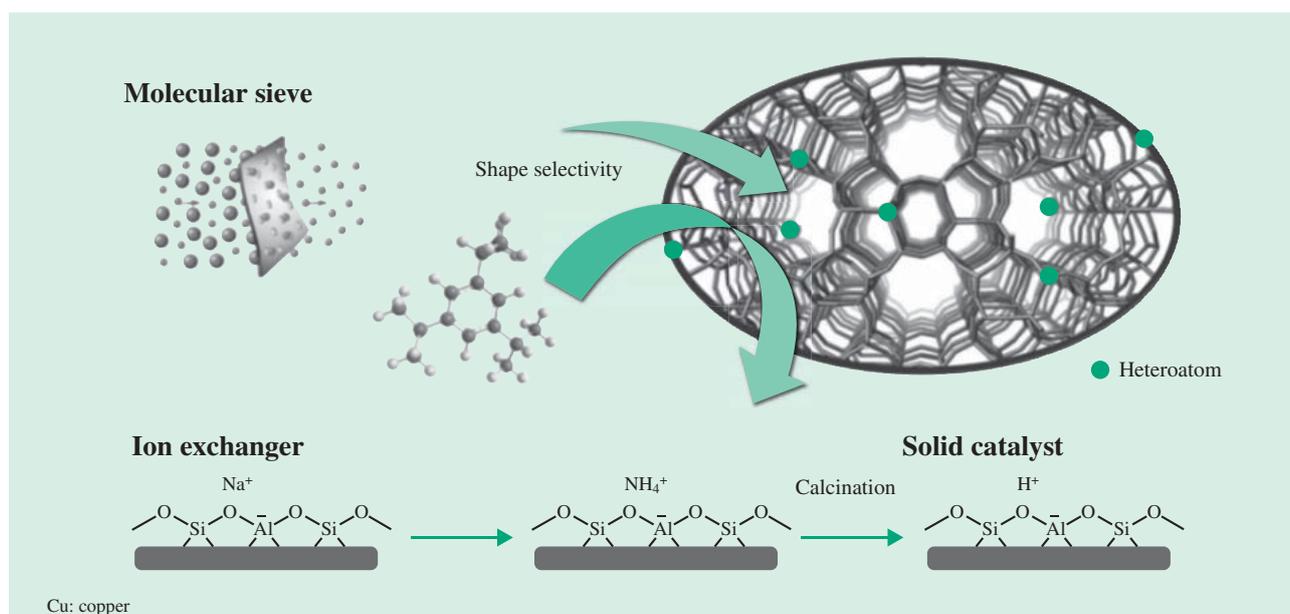


Fig. 1—Properties of Zeolites.

Zeolites are microporous crystalline minerals that are subject to a high level of nano-scale control and can be used as molecular sieves, ion exchangers, and solid catalysts.

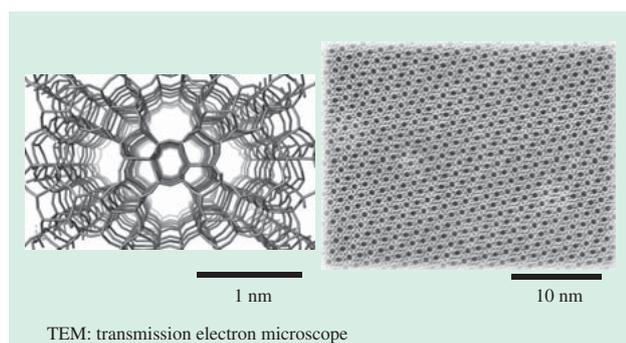


Fig. 2—Structural Model of MFI-type Zeolite (left) and TEM Image (right).

Each stick in the structural model represents a $\equiv\text{Si-O-Si}\equiv$ sequence. The TEM image shows how the zeolite is made up of a regular array of identical micropores.

is called shape selectivity and allows zeolites to act as a molecular sieve, one of their main properties. Most zeolites have a silica framework and are aluminosilicates in which some of the silicon (Si) atoms are replaced with aluminum (Al) atoms. As some other cations are required to maintain the charge balance between Si^{4+} and Al^{3+} , this enables zeolites to act as ion exchangers and solid acid catalysts. Zeolite catalysts are currently used in environmental treatment systems as well as in the production of basic chemical feedstock from oil. Potential is also seen for their use in catalyzing reactions for chemical synthesis by the conversion of biomass.

This article focuses on the use of zeolites as solid acid catalysts and describes the development of a zeolite catalyst for making effective use of carbon resources.

PROCESS FOR CATALYTIC CRACKING OF NAPHTHA

Lower olefins such as ethylene, propylene, and butenes are important petrochemical precursors that are mainly produced by the thermal cracking of naphtha. However, there is also interest in catalytic cracking using zeolite as the catalyst because it allows the reaction to proceed at a lower temperature and can achieve a propylene/ethylene ratio of 0.6 or higher^{(3), (4)}. Unfortunately, catalytic cracking suffers from problems such as acid sites becoming coated due to the production of coke and a loss of catalytic activity due to blocking of the micropores. It has been reported in the past that catalyst life can be improved in various hydrocarbon conversion reactions by increasing the number of entry and exit points to the

micropores by enlarging the external surface area, or by shortening the diffusion length by making the zeolite crystals smaller and creating mesopores inside the crystal^{(5), (6)}. The authors, too, have identified ways of extending the life in catalytic cracking of hexane through the use of nano-sized catalysts by using alkali treatment to form mesopores and control acidity^{(7), (8)}. Recently, they have developed a method for controlling the distribution of Al inside Zeolite Socony Mobil-5 (ZSM-5) micropores and have been working specifically on the influence that the positioning of Al inside the micropores has on acid catalyst activity⁽⁹⁾.

How to minimize catalyst deactivation is an important factor in the catalytic cracking of naphtha. Reasons for this deactivation include structural breakdown, leaching of the Al atoms in the zeolite framework that serve as the site of activity, coating of the site of activity due to the formation of coke, and blocking of the micropores. To solve these problems, it is important to obtain information about the structure and distribution of active sites and about where coke is formed. This means it is helpful if detailed observations can be made of the cross-section of zeolite particles. The authors have analyzed the elements present inside particles of zeolite using an ion milling machine to image the cross-section of zeolite catalysts and using energy-dispersive X-ray spectroscopy (EDX) to determine composition. The following describes an example.

Assessing Coke Distribution Using Cross-sectional Imaging of Zeolite Catalysts

A hexane catalytic cracking reaction over ZSM-5, a zeolite catalyst of framework type MFI, was performed at 650°C. The quantities of coke that had built up on the catalyst after reaction times of 3, 6, and 12 hours were determined by thermogravimetric (TG) analysis to be 5.3 wt%, 6.8 wt%, and 8.8 wt% respectively. Differential thermal analysis (DTA) was also used to determine that the peak exothermic temperatures gradually increased from 600°C to 630°C and 640°C. From this it was concluded that an increasing amount of coke builds up on the ZSM-5 catalyst over the course of the reaction, and that the coke is transformed into other less combustible forms of carbon (with higher molecular mass). This left the question of where the coke was forming on the ZSM-5 catalyst. Was it happening in the micropores of the zeolite or on the outer surfaces of the particles? To investigate this, an ion milling machine was used to view a cross-section of the zeolite catalyst and EDX used to analyze its composition. The main

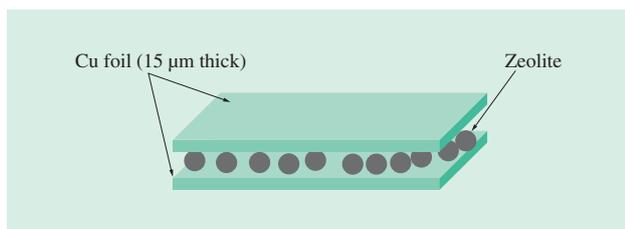


Fig. 3—Sample Preparation for Carbon Mapping. The sample is held together by sandwiching powder between sheets of Cu foil and a cross-section prepared by ion milling.

objective was to perform mapping of coke (carbon). Because the pastes normally used to hold powder in place contain carbon, they are unsuitable for mapping coke. As shown in Fig. 3, the sample was instead prepared by sandwiching it between sheets of copper (Cu) foil for ion milling and EDX analysis.

Fig. 4 shows the carbon maps for an ZSM-5 particle cross-section after reaction times of 3, 6, and 12 hours. These show that, as the reaction progresses, more coke is formed along the outside of the crystal than in its interior. This indicates that the coke is mainly forming on the outer surface or near the micropore entrances, not inside the micropores. Particularly large amounts of carbon were detected from the surface to approximately 400 nm into the interior, with the concentration of carbon near the surface increasing the longer the reaction progressed. However, it was also found that large amounts of coke formed over time in the interior. Currently, the authors are using this to try different catalysts and modify the reaction to build up more knowledge about coke distributions that can be incorporated into catalyst design and used to develop catalysts with longer lives.

DEVELOPMENT OF ZEOLITE CATALYST FOR PRODUCTION OF LOWER OLEFINS FROM NON-OIL RESOURCES

As noted above, the establishment of an alternative to the thermal cracking of naphtha that can produce lower olefins without imposing a large load on the environment plays an important role in terms of making effective use of carbon resources. And, given the problem of future oil scarcity, there is a need to create a process for producing propylene from non-oil resources. This has included interest in methanol-to-olefin (MTO) reactions that produce substances such as propylene and ethylene using methanol as a feedstock. As the methanol feedstock is produced by reacting hydrogen (H_2) with carbon monoxide (CO) or carbon dioxide (CO_2) derived from natural gas or coal, this provides a way to produce lower olefins from resources other than oil.

Zeolite catalysts that demonstrate good performance in MTO reactions include ZSM-5, the MFI-type zeolite with medium-sized micropores; SSZ-13 with small micropores; and SAPO-34, a CHA zeolite⁽¹⁰⁾. However, issues remain with things like lower olefin selectivity and catalyst life and this is currently an active field of research. The authors have succeeded in developing a new CON-type zeolite catalyst that is different from typical catalysts for the MTO reaction. The CON-type zeolites have a unique structure that combines both large and medium-sized micropores. While this gives the catalyst the potential to be used in a wide variety of applications, it has not been widely studied in the past because it is difficult to synthesize. The authors have made improvements to the synthesis

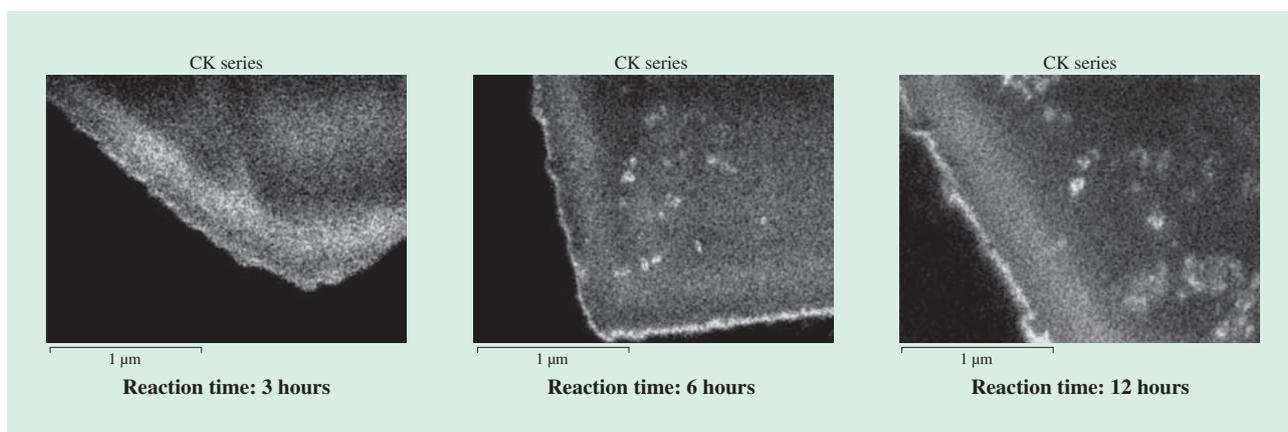


Fig. 4—Distribution of Coke Adhering to ZSM-5 Zeolite Catalyst after Catalytic Cracking of Hexane. These carbon maps show the ZSM-5 particle cross-sections after reaction times of 3, 6, and 12 hours. They show how the amount of coke adhering to the outer surface of the particles becomes larger over time.

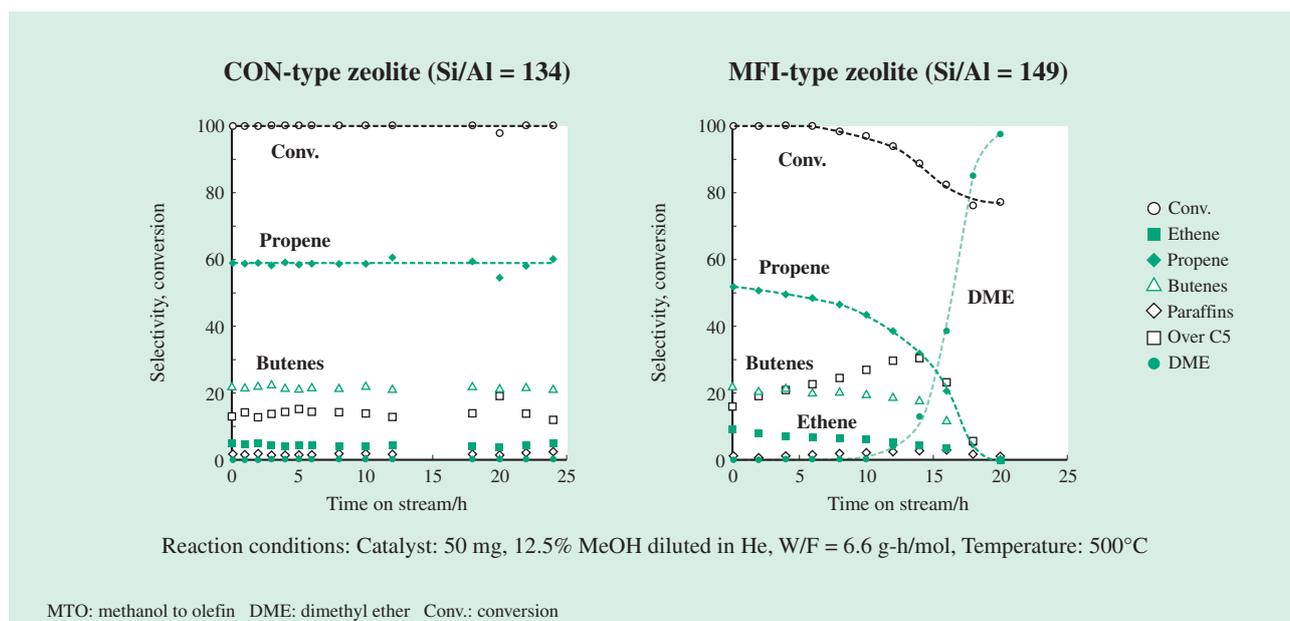


Fig. 5—Results of MTO Reaction Using the CON- and MFI-types Zeolites.

The CON-type zeolite maintains a methanol conversion rate of close to 100% even after 25 hours. It also maintains a propylene selectivity of approximately 60%.

process and developed a technique for introducing Al into the CON zeolite framework that will enable it to be used as an acid catalyst⁽¹¹⁾.

Compared to previous MFI-types, the Al-containing CON-type zeolite is characterized by low ethylene selectivity, high propylene and butenes selectivity, and longer catalyst life (see Fig. 5). Propylene and butenes selectivities are respectively a little under 60% and a little over 20%, high values in comparison to the less than 5% selectivity for ethylene.

The authors are currently participating in an artificial photosynthesis project of the New Energy and Industrial Technology Development Organization (NEDO) and the Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPCChem)⁽¹²⁾. This project aims to use the MTO reaction to produce lower olefins from methanol that has been made from solar hydrogen produced from water using a photocatalyst and the energy of the sun, and CO derived from CO₂ emitted by industrial processes and other sources. In other words, its objective is to make plastics from water by using artificial photosynthesis to enable the manufacture of chemicals without the use of fossil fuels.

CONCLUSIONS

This article has focused on zeolites in their role as solid acid catalysts, describing the catalytic cracking

of hexane and the synthesis of propylene from methanol. These catalytic processes help make the most of carbon resources and are helping overcome the resource, energy, environmental, and other problems facing humanity. If ways could be found to achieve full control over the type, strength, and quantity of acid on zeolite catalysts as well as their micropore structure and particle morphology, the authors believe this would not only lead to improvements in catalyst performance but also expand the range of applications. While there are many problems with zeolite catalysts that remain to be solved, it is hoped that solutions will be found so that they can enter industrial use in a variety of fields.

ACKNOWLEDGMENTS

Some of the results described in this article were obtained from work undertaken under contract to the New Energy and Industrial Technology Development Organization (NEDO). The authors also wish to express their sincere thanks for the assistance with scanning electron microscope (SEM) imaging received from Yoshihisa Orai and Takeshi Sunaoshi of Hitachi High-Technologies Corporation.

REFERENCES

- (1) H. Tominaga (ed.), "Science and Applications of Zeolites," Kodansha Scientific Ltd. (1987), Y. Ono, "Science and Engineering of Zeolite," Kodansha Ltd. (2000) in Japanese, and other sources.
- (2) The Structure Commission of the International Zeolite Association, <http://www.iza-structure.org/databases/>
- (3) Y. Yoshimura et al., *Catal. Surv. Jpn.* **4**, p. 157 (2000).
- (4) K. Kubo et al., "Selective Formation of Light Olefin by n-heptane Cracking over HZSM-5 at High Temperatures," *Microporous and Mesoporous Materials* **149**, Issue 1, pp. 126–133 (2012).
- (5) T. Tatsumi et al., "Recent Development of Zeolite Catalysts," CMC Publishing Co., Ltd. (2004) in Japanese.
- (6) T. Baba ed., "Leading Edge Technology of High Functional Zeolite," CMC Publishing Co., Ltd. (2015) in Japanese.
- (7) H. Mochizuki et al., "Facile Control of Crystallite Size of ZSM-5 Catalyst for Cracking of Hexane," *Microporous Mesoporous Materials* **145**, Issue 1-3, pp. 165–171 (2011).
- (8) H. Mochizuki et al., "Effect of Desilication of H-ZSM-5 by Alkali Treatment on Catalytic Performance in Hexane Cracking," *Applied Catalysis A* **449**, pp. 188–197 (2012).
- (9) T. Yokoi et al., "Control of the Al Distribution in the Framework of ZSM-5 Zeolite and Its Evaluation by Solid-state NMR Technique and Catalytic Properties," *J. Phys. Chem. C* **119**, pp. 15303–15315 (2015).
- (10) U. Olsbye et al., "Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size Controls Product Selectivity," *Angewandte Chemie International Edition* **51**, pp. 5810–5831 (2012).
- (11) M. Yoshioka et al., "Development of the CON-type Aluminosilicate Zeolite and Its Catalytic Application for the MTO Reaction," *ACS Catalysis* **5**, pp. 4268–4275 (2015).
- (12) NEDO, "Carbon Dioxide as Raw Material for Key Chemical Manufacturing Process Technology Development," http://www.nedo.go.jp/activities/EV_00296.html in Japanese.

ABOUT THE AUTHORS



Toshiyuki Yokoi, Dr. Eng.

Assistant Professor, Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology. He is currently engaged in the development of Zeolite catalysts related to the effective utilization of carbon resources. Dr. Yokoi is a member of the American Chemical Society (ACS), the American Institute of Chemical Engineers (AIChE), The Chemical Society of Japan (CSJ), the Catalysis Society of Japan (CATSJ), The Society of Chemical Engineers, Japan (SCEJ), the Japan Petroleum Institute (JPI), and the Japan Association of zeolite.



Takashi Tatsumi, Dr. Eng.

Former Executive Vice President of the Tokyo Institute of Technology; Current Tokyo Institute of Technology Professor Emeritus; and President, National Institute of Technology and Evaluation (NITE).