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[Review Paper]

Development of Solid Acid Catalysts for Synthesis of Chemicals from Sugars and Sugar Alcohols

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This review describes our efforts in the development of high-performance solid acid catalysts for synthesis of useful chemicals from sugars and sugar alcohols. We found that zeolite beta, which had both Lewis and Brønsted acid sites, acted as effective bifunctional catalyst for one-pot synthesis of 5-hydroxymethylfurfural (HMF) from glucose. Particularly, by controlling the density of these acid sites in zeolite beta with a high density of Al atoms, a high yield of HMF over 70 % was achieved. We also developed catalysts for derivatizing furfurals into useful chemicals. We established novel synthesis methods for hafnium-containing zeolite beta and titanium suboxide fine particles, and each showed significantly high activity in transfer hydrogenation and acetalization of furfural, respectively. Furthermore, it was found that zeolites with a low density of Al atoms exhibited high activity for dehydration of sorbitol to isosorbide in water. Due to the hydrophobic nature of the solid surface, such zeolites were less likely to be deactivated by water, resulting in the high activity and high durability even under severe conditions in hot water.

Keywords

Acetalization, 5-Hydroxymethylfurfural, Isosorbide, Titanium oxide, Transfer hydrogenation, Zeolite

1. Introduction

In the present days, vast variety of chemical products are effectively produced by the oil refinery. Crude oil is a mixture of hydrocarbons with a wide range of carbon numbers and different carbon chains. Owing to the wide variety of molecular structures, petrochemical products have diverse chemical and physical properties and a wide range of applications. While crude oil and other fossil fuels will be the primary feedstock of chemicals and energy for a couple of decades to come, there is necessity to develop alternative methods for production of chemicals due to the limited and unstable supply of fossil fuels.

Plant biomass is a promising alternative carbon resource, and carbohydrate accounts for a major part of renewable plant biomass. Carbohydrate fraction of biomass is divided into two types of polysaccharides; one is cellulose, which is crystalline linear glucan, and the other is hemicellulose, which is heterogeneously branched amorphous polysaccharides containing pentoses such as xylose and arabinose. In contrast to crude oil, carbohydrate has the limited variety of molecular structures, the low H/C and high O/C ratios, and

low calorific potential. Thus, carbohydrate should be upgraded into value-added molecular structures through effective chemical transformation accompanied with selective deoxygenation. Particularly, there is a need for catalysts that can selectively promote chemical reactions of oxygen functional groups and appropriately reduce the amount of oxygen from carbohydrates. In this context, we have been working on the development of high-performance solid acid catalysts for upgrading carbohydrate into useful chemicals, based on our original material design. This paper briefly reviews our studies, categorized by target reaction and type of catalyst.

2. Conversion of Carbohydrates into Furfurals

Pentoses and hexoses can be converted to furfural and 5-hydroxymethylfurfural (HMF), respectively, with elimination of water in the presence of acid catalysts. Furfural and HMF are the most promising compounds as C5 and C6 building blocks, respectively, for synthesis of bio-based furanic and derivate compounds¹⁾.

As the most abundant monosaccharide obtained from renewable carbohydrate biomass, glucose is a suitable raw material for synthesis of HMF in terms of the availability and cost. However, because of low reactivity to dehydration, it is not easy to synthesize HMF directly

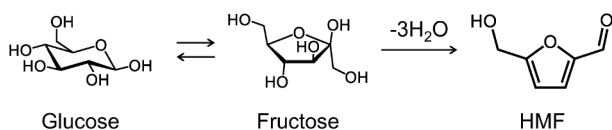
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from glucose. In contrast, fructose is highly reactive to the dehydration, and the development of appropriate catalytic reaction systems has made it possible to synthesize HMF from fructose in high yields²⁾. Therefore, a two-step synthesis strategy has been proposed that consists of isomerization of glucose to fructose and following dehydration of fructose to HMF (Scheme 1). Furthermore, because the isomerization of glucose is a reversible reaction with equilibrium constraints, it is effective to synthesize HMF from glucose in one-pot by combining the isomerization with the irreversible dehydration of fructose. In this strategy, it is important to use a combination of catalysts suitable for each reaction, and it is recommended to use Lewis acid³⁾, base⁴⁾, or isomerase⁵⁾ for the isomerization, and Brønsted acid for the dehydration. We found that zeolite beta calcined at high temperature had both Lewis and Brønsted acid sites, and each acid site promoted the isomerization and dehydration, respectively, thereby making it possible to synthesize HMF from glucose in one-pot^{6)~8)}.

2. 1. Isomerization of Glucose to Fructose over Lewis Acid Sites on Zeolite Beta

Lewis acid sites can be facilely generated on aluminosilicate zeolites by calcination in wet air or steam



Scheme 1 Two-step Conversion of Glucose to 5-Hydroxymethylfurfural (HMF) via Fructose as Intermediate

treatment of precursor zeolites, and so aluminosilicate zeolites are promising materials as Lewis acid catalysts for the isomerization of glucose. We found that zeolite beta with Lewis acid sites, which was prepared by steam treatment of ammonium-form precursor, promoted the isomerization of glucose to fructose in $\sim 70\%$ selectivity in water⁶⁾. The reaction mechanism for the isomerization of glucose was investigated by the isotope experiment using deuterated glucose. The isomerization proceeded through intramolecular hydrogen transfer with the complete retention of deuterium in the produced fructose over the zeolite beta (Fig. 1). This reaction mechanism is characteristically observed for Lewis acid catalysts, being different from the proton abstraction mechanism for base catalysts^{9),10)}. The characteristic reaction mechanism demonstrated that the Lewis acid sites of zeolite beta were active sites for the isomerization of glucose. For the reaction over the zeolite beta, the significant kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} \approx 2$) suggested that the cleavage of a C-H(D) bond was involved in the rate-determining step.

Since zeolite beta originally had Brønsted acid sites, the generation of Lewis acid sites means that the zeolite beta obtained the bifunctionality required for the synthesis of HMF from glucose. Actually, zeolite beta having both types of acid sites were found to be effective single catalysts with bifunctionality; the zeolite beta calcined at 750°C had 0.18 mmol/g and 0.17 mmol/g of Lewis and Brønsted acid sites, respectively, and gave 43% yield of HMF from glucose in one-pot⁶⁾. Di-, oligo-, and poly-saccharides were also able to be converted to HMF in one-pot reaction with the bifunctional zeolite beta⁷⁾.

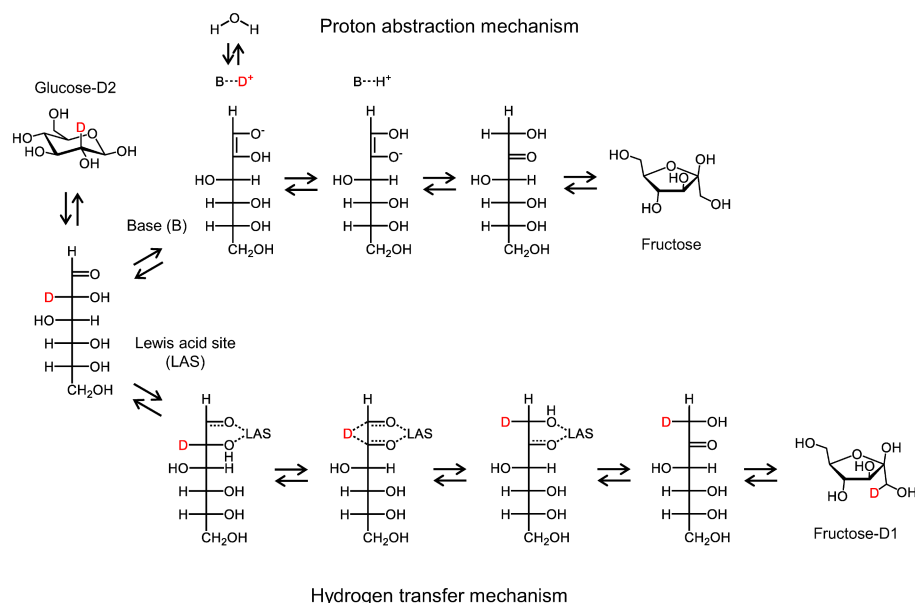


Fig. 1 Mechanism for Isomerization of Deuterated Glucose (glucose-D2) to Fructose over Base and Lewis Acid Catalysts

Table 1 Composition, Acid Properties and Catalytic Performance of Zeolite Beta for Conversion of Glucose to HMF^{a)}

Sample	Si/Al ^{b)} [-]	Acid sites [mmol/g]		Conv. ^{c)} [%]	Selectivity ^{d)} [%]	
		Brønsted	Lewis		Fructose	HMF
Beta-OF-Cal450	5.5	0.61	0.21	81	4	65
Beta-OF-Cal500	5.5	0.71	0.20	86	3	66
Beta-OF-Cal550	5.5	0.62	0.22	88	4	67
Beta-OF-Cal600	5.5	0.31	0.24	86	12	55
Beta-OF-Cal700	5.5	0.20	0.19	80	15	45
Beta-TEA-Cal500	15	0.25	0.13	57	4	36

a) Reaction conditions: Catalyst, 0.1 g; Glucose, 0.67 mmol; Water, 4.5 mL; DMSO, 0.5 mL; THF, 15 mL; Temperature, 180 °C; Time, 3 h.

b) Si/Al atomic ratio.

c) Conversion of glucose.

d) Selectivity to fructose and HMF.

2.2. Synthesis of Al-rich Zeolite Beta and Its Application to Conversion of Glucose to HMF

Although it was confirmed that HMF was produced from glucose using the zeolite beta, two points were to be overcome in order to improve the yield of HMF. One was that unreacted fructose remained due to the small number of Brønsted acid sites on the zeolite beta. The other was side reactions such as decomposition of fructose, some of which might be promoted by Lewis acid sites. Since Lewis acid sites are necessary to promote the isomerization and cannot be decreased, a common countermeasure for these two points was to increase the density of Al atoms and the number of Brønsted acid sites.

In 2008, a breakthrough method was developed to synthesize zeolite beta without the use of organic structure directing agent (OSDA), and such zeolite is called OSDA-free zeolite beta¹¹⁾. Recently, the increasing number of papers have reported the application of OSDA-free beta as catalyst^{12)~16)}. This method provides zeolites with relatively Al-rich compositions, compared to the conventional one that is synthesized with OSDA such as tetraethylammonium (TEA) cation. The OSDA-free synthesis of zeolites has several advantages over the conventional one in terms of cost, CO₂ and NO_x emission, and energy consumption, arising from the use of OSDAs.

In spite of the great effort devoted to the synthesis, the yield of OSDA-free beta usually did not exceed 30 %. Even though OSDA-free synthesis of zeolites has many advantages, such low product yield would tone down its superiority. The conventional OSDA-free synthesis of zeolite beta used fumed silica as silicon source¹¹⁾. Due to its high reactivity, an excess amount of fumed silica was indispensably used to prevent non-selective crystallization, especially in the synthesis of Al-rich zeolites. As a result, the silica-based yield of zeolites became low.

We improved the yield of OSDA-free beta up to 80 % by using colloidal silica with mild reactivity instead of fumed silica and optimizing the composition of

precursor gel¹⁷⁾. The Si/Al atomic ratios of the zeolite beta synthesized by the OSDA-free and conventional methods were 5.5 and 15, respectively (Table 1)⁸⁾. Hereinafter, these zeolites are denoted as Beta-OF and Beta-TEA, respectively.

Calcination of Beta-OF at moderate temperature generated a sufficient number of Lewis acid sites to promote the isomerization of glucose, while retaining majority of the original Brønsted acid sites due to the high density of Al atoms. The number of Brønsted and Lewis acid sites in Beta-OF-Cal500 were 0.71 mmol/g and 0.20 mmol/g, respectively, which were significantly higher than those for Beta-TEA-Cal500. When Beta-OF was calcined at 600 °C or higher, the number of Brønsted acid sites decreased significantly, but no significant change was observed in the number of Lewis acid sites. It was thought that aluminum species exhibiting Lewis acidity were mainly generated by the calcination at 550 °C or lower, and that aluminum species produced by the calcination at higher temperature did not exhibit Lewis acidity.

These Beta-OF samples were applied in the one-pot conversion of glucose to HFM. All Beta-OF catalysts showed conversion of glucose over 80 %, which was higher than 57 % for Beta-TEA-Cal500. This was due to the large number of Lewis acid sites that promote glucose isomerization. Beta-OF-Cal500 showed 66 % selectivity to HMF, while Beta-OF-Cal600 and -Cal700 showed 55 % and 45 %, respectively. Clearly, as the ratio of Brønsted/Lewis acid sites increased, the selectivity to HMF increased (Fig. 2). These results demonstrated that in order to improve the HMF yield, it is necessary to have sufficient Lewis acid sites to promote isomerization, while at the same time to keep an abundance of Brønsted acid sites. Furthermore, it was important not only to balance the numbers of Lewis and Brønsted acid sites, but also to ensure that these two acid sites were located close to each other within the zeolite pores. This preferable distribution of acid sites was achieved by the Al-rich composition. Finally, Beta-OF-Cal500 gave a high yield of HMF over 70 %⁸⁾.

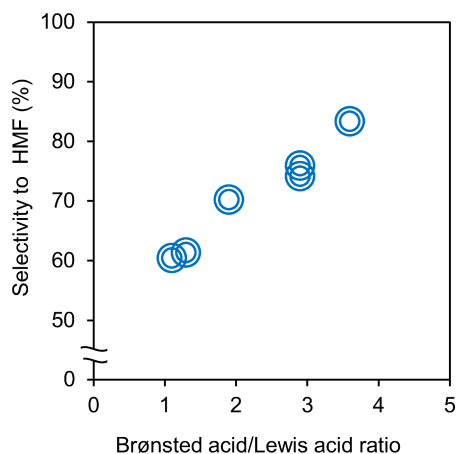


Fig. 2 Correlation between Selectivity to HMF and Brønsted/Lewis Acid Ratio in Dehydration of Fructose to HMF over Beta-OF Catalysts⁸⁾

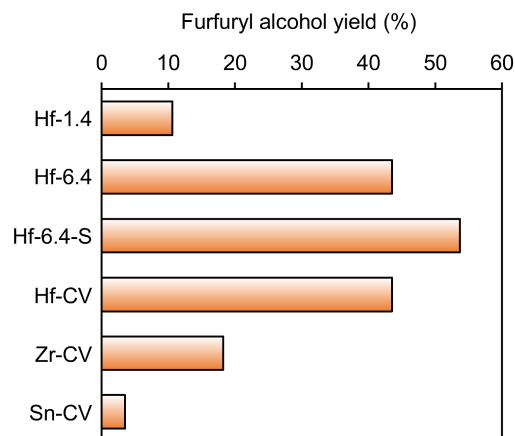
3. Conversion of Furfurals into Value-added Compounds

Once HMF and furfural can be produced in acceptable yields from hexoses and pentoses, respectively, the next challenge is to develop efficient chemical processes for further converting these platform molecules into value-added compounds. A formyl group of furfurals can undergo various chemical reactions to achieve a wide range of derivatizations.

3.1. Rapid Synthesis of Hafnium-containing Zeolite Beta for Production of Furfuryl Alcohol

Furfuryl alcohol, which is a raw material for furanic resins, can be synthesized by selectively reducing the formyl group of furfural. Meerwein-Ponndorf-Verley (MPV) reduction is an effective transfer hydrogenation reaction of carbonyl groups using alcohols as hydrogen donor. Generally, MPV reduction gives the corresponding alcohols from carbonyl compounds in high selectivity. Metallosilicate zeolites are known to exhibit particularly high activity for MPV reduction. Koehle et al. reported that hafnium-containing zeolite beta (Hf-Beta) exhibited the high activity for the MPV reduction of furfural to furfuryl alcohol¹⁸⁾. However, the conventional synthesis of Hf-Beta requires the long-term hydrothermal treatment of several weeks, which has hindered research and development on Hf-Beta.

Generally, for the hydrothermal synthesis of zeolite, crystallization rate increases as the concentration of precursor gel increases. Based on this feature, we attempted to increase the crystallization rate of Hf-Beta by reducing the water content in the precursor gel¹⁹⁾. When the water content of precursor gel was extremely low ($\text{H}_2\text{O}/\text{SiO}_2 = 1.4$), the crystallization of Hf-Beta proceeded significantly fast and completed in 24 h. However, because hafnium has low solubility to basic water and precipitated as hafnium oxide during the hy-



Samples synthesized with seed crystal and by the conventional method are indicated with the phrases -S and -CV, respectively. Reaction conditions: Catalyst, 100 mg; Furfural, 5 mmol; 2-Propanol, 10 mL; Temperature, 70 °C; Time, 3 h.

Fig. 3 MPV Reduction of Furfural over Hf-Beta Synthesized from Concentrated Precursor Gel with $\text{H}_2\text{O}/\text{SiO}_2$ Ratios of 1.4 and 6.4 and Other Metallosilicate Beta Zeolites¹⁹⁾

drothermal treatment, the amount of hafnium incorporated into the zeolite framework became low. As a result, Hf-Beta synthesized in such way showed poor activity for the MPV reduction (**Fig. 3**). In order to increase the amount of hafnium incorporated into the framework, it was necessary not to reduce the water content too much. By adjusting the water content moderately low ($\text{H}_2\text{O}/\text{SiO}_2 = 6.4$), we succeeded in synthesizing highly active Hf-Beta in 72 h, which was much shorter than the synthesis time required for the conventional method. Furthermore, by adding seed crystal, the crystallization period was further shortened to 24 h. The Hf-Beta synthesized in this way showed higher activity for the MPV reduction of furfural than metallosilicate zeolites synthesized by the conventional methods.

For the above two samples synthesized from the precursor gel with different water contents (denoted as Hf-1.4 and Hf-6.4, respectively), acid properties were investigated by IR spectroscopy with CD_3CN as probe molecule (**Fig. 4**). There were two absorption peaks at $\sim 2310\text{ cm}^{-1}$ and $\sim 2275\text{ cm}^{-1}$ in the spectra, which are assigned to CD_3CN adsorbed on framework Hf Lewis acid sites and on silanol, respectively. Due to the relatively large amount of Hf incorporated into the framework, Hf-6.4 had the larger number of Lewis acid sites, leading to the high activity.

3.2. Synthesis of Titanium Suboxide Fine Particles for Selective Acetalization of Furfural

Acetalization is a chemical reaction of formyl group, and is important to obtain surfactants, biofuels, plastic monomers, and etc. from furfurals. We found that Ti_2O_3 , which is a kind of titanium suboxide, was a high-

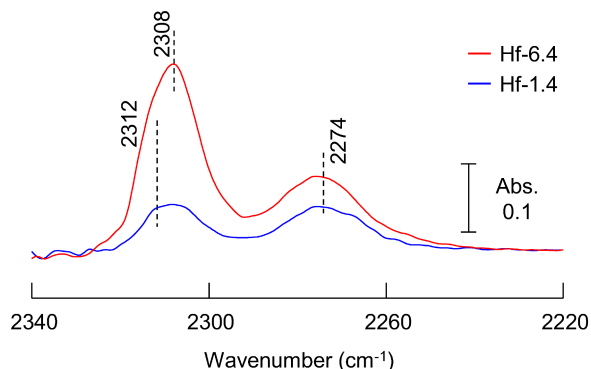


Fig. 4 IR Spectra of CD₃CN Adsorbed on Hf-Beta Samples Synthesized from Precursor Gel with Different Water Contents¹⁹⁾

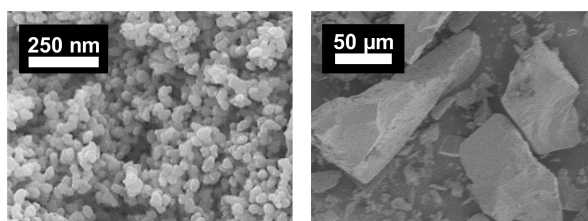


Fig. 5 SEM Images of (left) Ti₂O₃ Synthesized by Our Method with TiH₂ as Reductant and (right) Commercially Available Ti₂O₃

ly active catalyst for the acetalization of furfural²⁰⁾.

We first started to develop a method for synthesizing titanium suboxide fine particles with large specific surface area. The conventional method for synthesizing titanium suboxides is to reduce TiO₂ at high temperature over 1000 °C using oxyphilic metals such as Al as reductant. Consequently, metal oxides such as Al₂O₃ remain in the product as impurities, which has been an obstacle to understanding the physical properties and functional development of titanium suboxides themselves. Furthermore, the high temperature process causes excessive particle growth, making it essentially difficult to obtain fine particles by the conventional synthesis methods. We developed a novel synthesis method in which TiO₂ was reduced with TiH₂ as reductant. Since this method uses only titanium compounds as raw materials, in principle no impurities other than titanium oxides are generated. Taking advantage of the high reactivity of TiH₂, it is possible to synthesize titanium suboxides at a relatively low temperature of 700 °C or less, yielding fine particles smaller than 100 nm (Fig. 5). Furthermore, a series of titanium suboxides such as Ti₂O₃, Ti₃O₅, Ti₄O₇, and Ti₈O₁₅, can be synthesized individually by this method with simply adjusting the amount of TiO₂ and TiH₂.

In the reaction of furfural with 2-propanol, Ti₂O₃ selectively promoted the acetalization (Table 2). Due to the relatively large specific surface area, the synthe-

Table 2 Catalytic Performance of Ti₂O₃ and Other Catalysts for Reaction of Furfural with 2-Propanol^{a)}

Catalyst	$S_{\text{BET}}^{\text{b)}$ [m ² /g]	Formation rate [mmol/g h]	
		Acetal	Alcohol
Ti ₂ O ₃ -syn ^{c)}	10	2.1	0.0
Ti ₂ O ₃ -com ^{d)}	< 0.1	0.2	0.0
TiO ₂ ^{e)}	53	0.0	0.2
Zeolite beta	602	1.8	0.0
ZrO ₂	76	0.0	2.5

a) Reaction conditions: Catalyst, 25 mg; Furfural, 0.50 mmol; 2-Propanol, 2.5 mL; Temperature, 90 °C; Time, 2 h.

b) Specific surface area calculated by the BET method.

c) Ti₂O₃ synthesized by our method with TiH₂ as reductant.

d) Commercially available Ti₂O₃.

e) Catalyst, 100 mg.

sized Ti₂O₃ exhibited higher activity than commercially available Ti₂O₃, clearly demonstrating that this synthesis method was superior to the conventional one. The acetalization activity of the synthesized Ti₂O₃ was comparable to that of zeolite beta. In contrast to Ti₂O₃, TiO₂ showed no activity for the acetalization, but slightly promoted the MPV reduction of furfural. There was clear correlation between the density of Ti³⁺ on the surface of titanium oxides and the acetalization activity, suggesting that Ti³⁺ on the surface formed active sites for the acetalization.

4. Development of Zeolite Catalysts with Hydrophobic Nature for Dehydration of Sorbitol

During the last decade, owing to great research effort, the conversion of cellulose to sorbitol has been achieved in high yields through hydrolytic hydrogenation²¹⁾, and sorbitol has become a platform material for the production of chemicals from cellulose. Thus, increasing research interest has been paid to the conversion of sorbitol into value-added chemicals. Isosorbide is formed through intramolecular dehydration of sorbitol (Scheme 2). Isosorbide has many applications in wide industrial fields because of its high stability and two symmetrical OH groups. For example, isosorbide is a monomer of polyesters, polycarbonates, and epoxy resins with unique functionalities, a part of which has been already commercialized²²⁾.

In the early studies on the dehydration of sorbitol to isosorbide, various homogeneous acids such as sulfuric

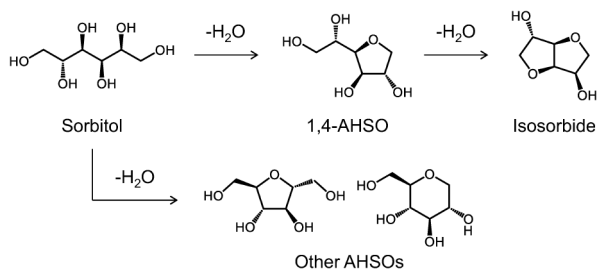
acid were examined as catalysts. However, due to a couple of problems accompanied with the use of homogeneous acids, a considerable research attention has been paid to the development of environmentally benign reaction regime using solid acid catalysts. We investigated ZSM-5, mordenite, beta, and USY zeolites with different Si/Al ratios as catalysts for the dehydration of sorbitol in compressed water at 200 °C (**Fig. 6**)²³⁾. Their catalytic performance was governed by the framework structure, composition, and stability in hot water. High-silica large-pore aluminosilicate zeolites, especially beta, exhibited outstanding catalytic performance and gave isosorbide yield as high as 80 % under optimal conditions.

For a particular type of zeolite, catalytic activity per Al atom was significantly increased with the increase in the Si/Al ratio. This advantage of the Si-rich composition was attributed to hydrophobicity of the zeolites. Diffusion of sorbitol and/or kinetically relevant steps would be unfavorably disturbed by adsorbed and con-

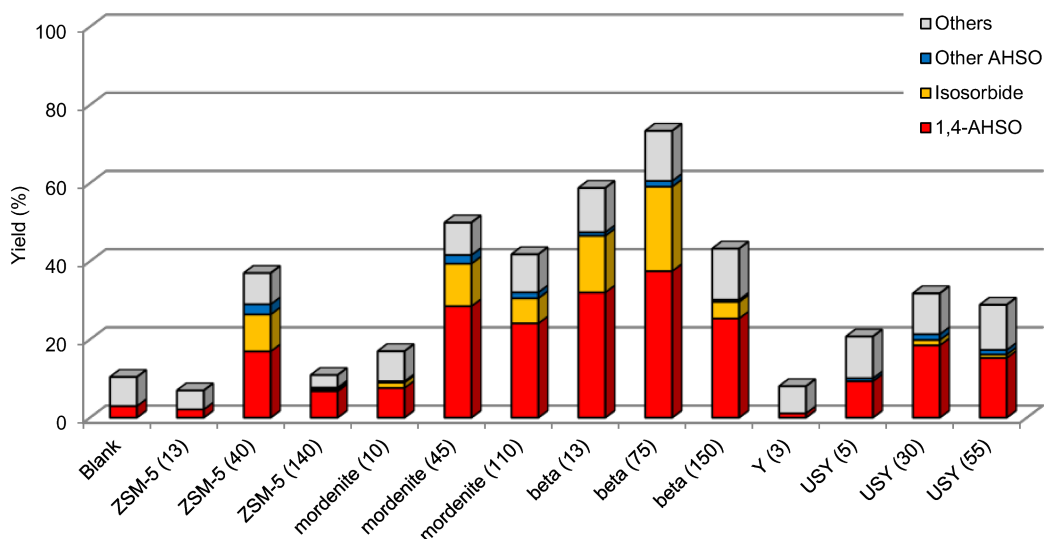
densed water on Al-rich zeolites, while hydrophobic nature of Si-rich zeolites could reduce such unfavorable effects, leading to the high catalytic activity.

Si-rich USY zeolites with the Si/Al ratio over 30 were unstable under the reaction conditions and their framework structures collapsed during the reactions in hot water, while Al-rich Y zeolites were recovered with the complete retention of the structure. The framework structures of Si-rich ZSM-5, mordenite, and beta were also totally retained after the reactions. Generally, USY zeolites have silanol defect sites in their framework that are formed during the preparation. Such silanol sites are the initial sites where the collapse of framework by hydrolysis occurs in hot water, resulting in the low catalytic activity.

Si-rich MCM-68 was found to show better catalytic performance for the dehydration of sorbitol in water than ZSM-5, mordenite, and beta (**Fig. 7**)²⁴⁾. MCM-68 was more effective than beta to keep Al atoms in tetrahedral coordination to form a larger number of effective Brønsted acid sites. Fourier transform infrared spectroscopy (FT-IR) examination with a combination of pyridine and di-*t*-butylpyridine as probe molecules revealed that Si-rich MCM-68 had Brønsted acid sites predominantly in the 10-ring windows and inside the supercage of the MSE-type structure. The void space at the intersection of 10-ring windows and inside the supercage provides enough and suitable space to accommodate bulky transition states in the dehydrations of sorbitol, facilitating the high catalytic activity of Si-rich MCM-68.

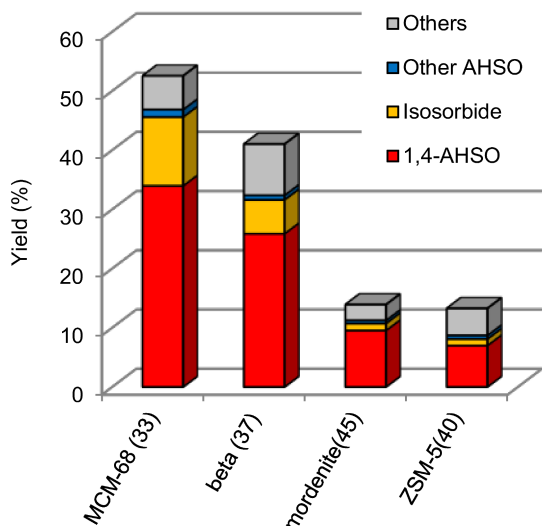


Scheme 2 Dehydration of Sorbitol to Isosorbide and Other Anhydrosorbitols (AHSOs)



The numbers in parentheses are Si/Al atomic ratios. Reaction conditions: Catalyst, 0.5 g; Sorbitol, 7.5 mmol; Water, 15 mL; Temperature, 200 °C; Time, 2 h.

Fig. 6 Dehydration of Sorbitol over Various Types of Zeolites²³⁾



The numbers in parentheses are Si/Al atomic ratios. Reaction conditions: Catalyst, 0.15 g; Sorbitol, 7.5 mmol; Water, 15 mL; Temperature, 200 °C; Time, 2 h.

Fig. 7 Dehydration of Sorbitol over MCM-68 and Other Zeolites²⁴⁾

5. Conclusions

This paper was focused on introducing our development of solid acid catalysts for converting sugars and sugar alcohols into useful chemicals. OSDA-free zeolite beta which had both Lewis and Brønsted acid sites with the controlled density acted as the effective bifunctional catalyst and achieved the one-pot synthesis of HMF from glucose. We also developed catalysts for derivatizing furfurals into useful chemicals. By adjusting the water content in precursor gel, we developed a method to rapidly synthesize Hf-Beta, which showed high activity for the MPV reduction of furfural to furfuryl alcohol. We also established a novel synthesis method that enabled the synthesis of a series of titanium suboxide fine particles at relatively low temperature and discovered that the synthesized Ti₂O₃ exhibited high activity and high selectivity for the acetalization of furfural. Furthermore, various types of zeolites were investigated as catalysts for the dehydration of sorbitol in hot water. MCM-68 as well as zeolite beta, which had a small density of Brønsted acid sites, showed the high activity. The catalytic performance was governed by hydrophobicity of the zeolite surface, structural durability in hot compressed water, and locative distribution of acid sites within the zeolite framework.

In the future, we would like to continue understanding basic physical properties and elucidating the deep principles of the developed materials and developing a wide range of their further applications.

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要 旨

糖および糖アルコールから化学品を合成するための固体酸触媒の開発

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本総説では、糖類や糖アルコール類から有用な化学品を合成するための高性能な固体酸触媒の開発に関する我々のこれまでの取り組みを解説する。ルイス酸点とブレンステッド酸点の両方を有したゼオライトベータがグルコースから5-ヒドロキシメチルフルフラール (HMF) へのワンポット合成に対して有効な二元機能触媒として働くことを見出した。特に、Al 原子密度の高いゼオライトベータのルイス酸点とブレンステッド酸点の密度を制御することで、70 % 以上の高収率で HMF の合成を達成した。また、フルフラール類を有用化学品に誘導体化する

ための触媒の開発にも取り組んだ。ハフニウム含有ゼオライトベータや低原子価チタン酸化物微粒子の新しい合成法を確立し、それぞれフルフラールの移動水素化、アセタール化に極めて高い活性を示した。さらに、Al 原子密度の低いゼオライトが水中でのソルビトールからイソソルビドへの脱水反応に対して高い活性を示すことを見出した。このようなゼオライトは固体表面が疎水的であるため、水による失活が起こりにくく、高温の水中でも高い活性と高い耐久性を発揮した。

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