Journal of Research and Development on Nanotechnology **Review**

On The Effectiveness of Hierarchical Zeolite Catalyst for Isomerization of Biomass-Derived Compound

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The expansion of catalytic technologies in biomass conversion has received increasing attention due to their promising in the sustainable economy. As the solid acid catalyst, zeolite becomes an excellent catalyst for the isomerization reaction of biomass conversion. Nevertheless, the diffusion limitation results from the micropore channel in zeolite rendering the development of zeolite with the additional pores, known as hierarchical zeolite. Up to now, hierarchical zeolites attract much attention appertain with their outstanding properties in the isomerization reaction. Accordingly, many efforts to fabricate hierarchical zeolites, such as top-down and bottom-up methods, have been conducted and grown over the decades. This review examines the current strategies in designing hierarchical zeolite for biomass isomerization. We mainly dwell on the isomerization process of biomass from cellulosic and fatty acids. This review also provides the future challenges and opportunities of the hierarchical zeolite for further improvement in biomass isomerization research.

Keywords: biomass; cellulosic sugars; fatty acid; hierarchical zeolite; isomerization.

Introduction

Nowadays, green and sustainable research has gained significant attention due to the global energy shortage and environmental issues (Li et al., 2017). Efforts have been made to realize the balance-concept between economic growth and the environmental-safety goals (Verboekend and Pérez-Ramírez, 2014). Currently, the valorization of biomass as a renewable feedstock has been developed to produce value-added chemicals and fuels through several processes, i.e., hydrolysis (Zhou et al., 2016), pyrolysis (Qiao et al., 2019), condensation (Su et al., 2019), oligomerization (Corma et al., 2013), esterification (Gomes et al., 2019), transesterification (Rezayan and Taghizadeh, 2019), isomerization (Tang et al., 2020), etc. Isomerization is one of the crucial processes in biomass conversion. For instance, the global production of high-fructose corn syrups (HFCS) was obtained by enzyme-catalytic isomerization of glucose (Molliner et al., 2010). Furthermore, the production of other essential platform molecules such as HMF (5-Hydroxymethylfurfural) (Nandiwale et al., 2014), methyl levulinate (Yang et al., 2019), methyl lactate (Tang et al., 2020), Iso-stearic acid (Bolsakhov et al., 2020), fatty acid methyl ester (FAME) (Zhang and Zhang, 2007), etc. involved the isomerization process as the important part of the various consecutive reaction.

As the solid acid catalyst, zeolite has been reported as the promising catalyst for isomerization reaction (Izutsu et al., 2013). The presence of micropore and the tunable of acidity and hydrophobicity of zeolite offer a wide range of applications in biomass conversion (Taarning et al., 2010). However, the diffusion limitation was often observed due to the restricted micropore channel in zeolite catalyst (Perego et al., 2017). For instance, the very low conversion of glucose or other higher sugar isomerization in MFI zeolite was attributed to the larger kinetic diameter of glucose molecules, which cannot access the active site in the MFI pore (Cho et al., 2014). In this case, the so-called hierarchical zeolite has been devoted to resolving this problem. Several papers have been published mentioning the superior activity of hierarchical zeolite in isomerization rather than the conventional one (Dapsens et al., 2014; Yang et al., 2019; Zhang and Zhang, 2007). Herein, recent advances on the hierarchical zeolite application in biomass isomerization were reviewed. Several strategies to design hierarchical zeolite catalysts and the correlation between zeolite properties and catalytic performance in the isomerization of biomass were scrutinized. Furthermore, we also provide the future insight for further development.

Design of Hierarchical Zeolite Catalyst for Isomerization Reaction

Isomerization is defined as a chemical process with the goal to transform the structure of a molecule into a different isomer. The isomerization of olefins consists of skeletal isomerization, which occurs at higher temperatures, and double-bond isomerization, which proceeds faster at the lower temperatures (Zhao et al., 2016). The skeletal isomerization can be catalyzed by the strong Bronsted acid catalyst. On the other hand, double isomerization can be catalyzed by acid and/or base catalysts. Generally, the isomerization reaction can be catalysed by the standard Pt/chlorinated alumina with high chlorine content and the Pt/zeolite catalyst (Fahim et al., 2010). Moreover, because the

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standard isomerization catalyst is sensitive to impurities, it made the zeolite catalyst attract attention to develop.

Zeolite, as an aluminosilicate arranged by tetrahedral SiO_4 and AlO_4. It posses acid sites, hydrophobicity, and micropores (<2 nm). Nevertheless, zeolite structures with the sole micropore leading to coke formation and low conversion, especially in the isomerization reaction of biomass regarding its bulky molecules. To solve these problems, the presence of additional mesopores and/or macropores, which are known as hierarchical zeolites, is needed. To be noted, the auxiliary pores must allow the increasing of transport function in zeolites.

Several reviews on the realization of hierarchical zeolites have been widely reported (Hartmann et al., 2021; Maghfirah et al., 2020; Pérez-Ramírez et al., 2008; Schwieger et al., 2016). In general, there are two strategies to prepare hierarchical zeolites, i.e., top-down methods and bottom-up methods. Top-down as a destructive approach introduces the auxiliary pores into the zeolite via desilication (alkaline treatment) (Wardani et al., 2019) or dealumination (acid treatment) (Maghfirah et al., 2019).

Originally, the bottom up method fabricates the hierarchical zeolite using the constructive approach that the additional pores created during the synthesis process. In this method, a template (porogen) is needed which consists of the hard and soft template. In the terms of sustainable research and economic point of view, the development of fabrication hierarchical zeolites could be classified by the green synthesis approach. It consists of a solvent-free route (Kadja, Azhari, et al. 2021; Kadja, Rukmana, et al., 2021), using sustainable starting materials (Kadja et al., 2017), green mesoporogen (Chen et al., 2018), and mesoporogen-free (Kadja et al., 2016). From the numerous synthesis strategy of hierarchical zeolites, we have the innumerable choices about methods, synthesis condition, also both economic and industrial opportunities to obtain the desired design of hierarchical zeolite.

Isomerization of Biomass Over Hierarchical Zeolite Catalyst

Isomerization of Cellulosic Sugars

The isomerization of cellulosic sugars has become an essential process in converting biomass to fuels and chemicals (Moliner et al., 2010). For instance, an important platform for producing biochemicals and biofuel, HMF, was obtained from the isomerization of glucose to fructose followed by the dehydration process. The isomerization was mediated by the Lewis acid, where the Bronsted acid was needed to perform the dehydration reaction (Menegazzo et al., 2018). In this case, the use of zeolite catalyst was very suitable because it serves both the Bronsted and Lewis acid site. Moreover, there has been reported the one-pot synthesis of HMF from biomass over a zeolite catalyst. The zeolite catalyst could immediately catalyze the three-consecutive reaction, including hydrolysis, isomerization, and dehydration (Nandiwale et al., 2014). However, the sole micropore of zeolite leads to low conversion, especially for the bulky molecules containing in biomass feedstock.

Lew et al. evaluated the pore size limitation of zeolite in cellulosic sugars isomerization, i.e., dihydroxyacetone (DHA), xylose, and glucose. They employed two different topologies of zeolites, i.e., Sn-BEA (12-membered ring) and Sn-MFI zeolite (10-membered ring). The result showed that Sn-BEA zeolite has the higher conversion for all three sugars, but a huge different conversion was observed for glucose conversion. Only 4% conversion was obtained for the Sn-MFI catalyst and 65% for the Sn-BEA catalyst. It was associated with the mass transfer limitation of the small pore of MFI zeolite (0.56 nm) to accommodate the larger size of glucose molecule (0.73 nm of stokes diameter) (Lew et al., 2012). To improve the catalytic activity of MFI zeolite, Dapsens et al. performed the desilication process using NaOH to generate the hierarchical pore structure of Sn-MFI zeolite. In this work, the two methods of the hierarchical formation of Sn-MFI zeolite were investigated, i.e., the conventional alkaline treatment of Sn-MFI and the alkaline assisted stannation of silicalite-1. Generation of 5-20 nm of mesopore could enhance glucose conversion. However, the higher catalytic activity was demonstrated for the catalyst prepared with the latter method due to the better utilisation of Sn which located in the mesopore surface (Dapsens et al., 2014).

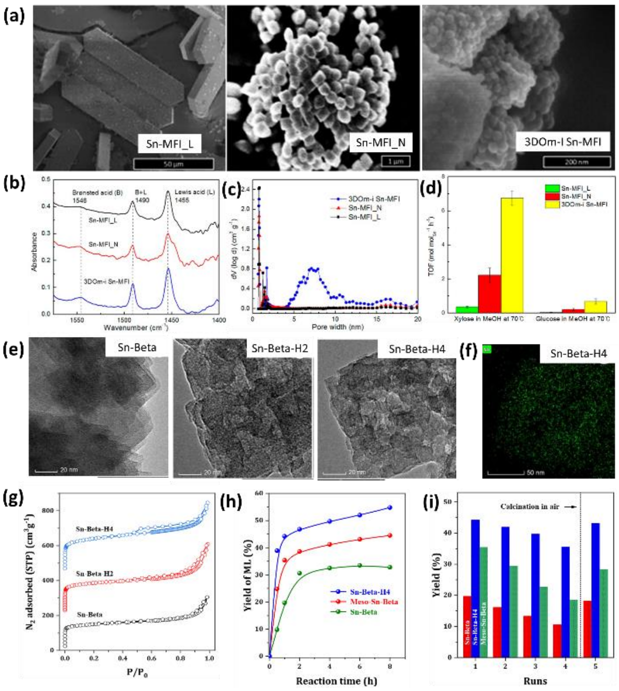

Figure 1. (a) TEM Images (b) Pyridine-FTIR Spectra (c) NLDFT Pore-size distribution (d) Initial catalytic activity of conventional (Sn-MFI_L), nano-sized (Sn-MFI_N), and hierarchical (3DOm-i Sn-MFI) zeolite. Reproduced with permission (Cho et al., 2014), Copyright 2014 ACS Catalysis. (e) TEM image of conventional (Sn-Beta) and hierarchical beta zeolite that synthesized with 0.64 g PDADMAC (Sn-Beta-H2) and 1.28 g of PDADMAC (Sn-Beta-H4). The hierarchical zeolite that synthesized by post-treatment using acid-base was coded as (Meso-Sn-Beta) (f) Elemental maps of Sn-Beta-H4 sample corresponding to Sn distribution in zeolite crystals (g) N_2 adsorption-desorption isotherms (h) Conversion of glucose to methyl lactate (ML) (i) Recyclability of the catalyst. Reproduced with permission (Tang et al., 2020), Copyright 2020 ACS Paragon plus environment.

Another approach to creating a hierarchical structure of MFI zeolite for isomerization of triose sugar, dihydroxyacetone (DHA), was reported by Cho et al. The three-dimensionally ordered mesoporous (3DOm-i) in Sn-MFI zeolite was constructed by seeded growth method using a 3DOm carbon template. For comparison, the nano-sized (Sn-MFI_N) and the conventional (Sn-MFI_L) zeolite samples were also used. The typical morphology of these three samples was depicted in Fig. 1a. The highest conversion of cellulosic sugars was achieved for 3DOm-I Sn-MFI. It was related to the abundance of 4-11 nm mesopore and the weak of Bronsted acid (Fig. 1b-c), facilitating Pyruvaldehyde (PA) formation as an intermediate through a dehydration reaction. Moreover, the activity was 20 times higher than conventional in xylose conversion (Fig. 1d). However, this catalyst showed the diffusional limitation in glucose isomerization associated with the large kinetic diameter of glucose molecules (Cho et al., 2014). In another work, they applied the hierarchical hydrophobic Sn-BEA zeolite to isomerize the glucose and the bulkier cellulosic sugars like lactose. They concluded that the catalyst's hydrophobicity and mass transport property were crucial to improving the catalytic activity (Cho et al., 2019).

Slightly similar to Dapsens's approach, Liu et al. applied the post-synthetic treatment followed by the isomorphous substitution method to produce the hierarchical structure of Sn-BEA zeolite for glucose isomerization to fructose. Through this method, the content of Sn in BEA zeolite could be increased, resulting in the 66% glucose conversion (Liu et al., 2014). Furthermore, the use of another framework type of zeolite in glucose isomerization was reported by Graca et al. They utilized the basic site instead of the acid site of Y zeolite by impregnating the desilicated sample with Mg. The presence of Mg in zeolite could enhance the catalytic activity. By using the Na-form zeolite, only 3.4-6.6% conversion was produced. Moreover, the presence of mesopore in desilicated mg impregnated Y zeolite improved the glucose conversion from 28% to 51% with the 38% yield of fructose. It was related to the diffusion enhancement of glucose to the pore and the more accessible basic site through the mesoporous structure (Graca et al., 2018).

Yang et al. pointed out the importance of both the mesoporosity and the Lewis acid site in the multistep process of glucose conversion into methyl levulinate (MLE) over Sn-Al-BEA zeolite catalyst. The presence of Sn site was crucial to isomerize the glucose to fructose and negligible in dehydration reaction of fructose to MLE compared to Bronsted acid site, while the mesoporous facilitated the diffusion both of reactant and product (Yang et al., 2019). Tang et al. set up a series of experiments with the Sn-BEA zeolite catalyst to catalyze the same reaction but with different mesopore generation strategies. The hydrophobic and hierarchical samples (Sn-Beta-H4) were obtained by dealumination of silicious Sn-Beta followed by self-assembly with Sn precursor and PDADMAC (polydiallydimethylammonium chloride) in the presence of TEAOH (tetraethylammonium hydroxide) and fluoride through hydrothermal treatment. The effect of the PDADMAC amount as mesoporogen was also evaluated.

Fig. 1e shows the TEM images of the conventional and hierarchical Sn-Beta with different amounts of PDADMAC. The abundance amount of mesopore was obvious in hierarchical and increased with the increase of PDADMAC amount. This result was supported with N_2 adsorption data (Fig. 1g). The hierarchical zeolite exhibits superior activity in methyl lactate (ML) production even if compared with the hierarchical sample obtained by conventional post-treatment (Meso-Sn-Beta) (Fig. 1h). Also, this catalyst was reusable and remain stable after 5 times used (Fig. 1i) (Tang et al., 2020). Very recently, Yang et al. has also used PDADMAC as mesoporogen followed by dealumination and solid-gas reaction with $SnCl_4$ vapor. 99% conversion of glucose with 42% selectivity to HMF product was obtained for hierarchical beta sample. This value was higher than the conventional one due to the presence of the intracrystalline mesopore, leading to the efficient diffusion of the molecule during the reaction (Yang et al., 2021).

Isomerization of Fatty Acid

Fatty acids, derived from vegetable oils and animal fats, have come up as a promising alternative for many applications in chemical industry, such as surfactants, biodegradable lubricants, biodiesel, etc. The synthesis approaches of branched saturated fatty acids consist of direct isomerization of linear saturated fatty acids and skeletal isomerization of unsaturated fatty acids followed by hydrogenation (Ha et al., 2009). Nowadays, the efforts to obtain branched fatty acids focus on using zeolite as a catalyst in skeletal isomerization reaction. Notwithstanding, the limited channel of the micropores in zeolite impede the accessibility of product and result in catalyst deactivation. Zeolite L, mordenite, pentacyl, and beta showed some activities yet coke formation still became the problem (Ha et al., 2009; Ngo et al., 2007).

Zhang and Zhang reveals the role of mesopores in HBeta zeolites. To be noted, zeolite beta could have structural defects and mesopores which depend on the manufacturing process. The results showed HBeta, with the high activities, has a large number of mesopores. So, it can be concluded that the mesopores are the main point that can increase the effectiveness of fatty acid isomerization. It is due to the most accessible acid sites inside the mesopores (Zhang and Zhang, 2007).

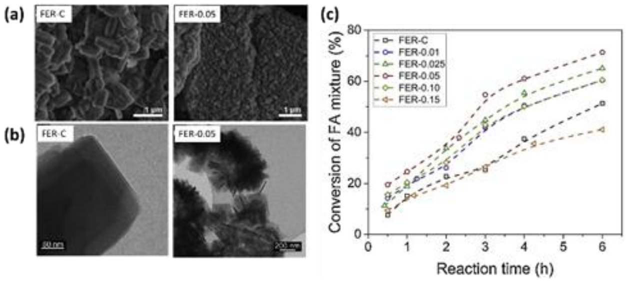

Figure 2. (a) SEM images and (b) TEM images of conventional FER zeolite (FER-C) and hierarchical FER zeolite with the range of NMP substitution for C_{16}dMImz is 0.05mol, (c) Catalytic conversion of fatty acid mixture over zeolite FER; FER-C represent the zeolite FER conventional and FER-x, x represent the range of NMP substitution for C_{16}dMImz. Reproduced with permission (Bolshakov et al., 2020), Copyright 2020 Elsevier.

Bolshakov et al. realized hierarchical FER zeolite for fatty acid mixture isomerization, which contain about 90wt% oleic acid. They applied the one-pot (bottom-up) method to synthesize hierarchical FER zeolite via FAU transformation using N-methylpyrrolidine (NMP) and 1,2-dimethyl-3-hexadecyl-1H-imidazol-3-ium bromide (C_{16}dMImz) as nano and mesoscale SDAs, respectively. The samples with C_{16}dMImz substituted by NMP denoted as FER-x, which x showed the mol ratio. The use of FAU regarding its effectiveness as a silica-alumina precursor for FER zeolite. The SEM images (Fig. 2a) show that the conventional FER zeolite has an agglomeration of sheets with size of 0.5-0.7 µm. The substitution of NMP with C_{16}dMImz causes the decrease of the crystal size in a- and b-direction, as depicted in Fig. 2b. From this work, the optimal catalyst, i.e., FER-0.05 which have the higher effective acidity, high mesoporous area, large external surface area, and good accessibility than conventional FER zeolite, shows the conversion up to 71% after 6 h (Fig. 2c) (Bolshakov et al., 2020).

Recently, Kersten et al. investigated hierarchical ZSM-5 zeolite for the solventless isomerization of fatty acids compared to FER zeolite. The hierarchical ZMS-5 zeolite obtains by using post-synthetic treatments via the top-down method, i.e., alkaline treatment with NaOH, then followed by an acid wash using HCl. The additional mesopores take a role in facilitating the reagent and products to and from the acid sites of zeolite. The results show the conversion of fatty acid using hierarchical ZSM-5 zeolite of >90%, five times higher than conventional ZSM-5 and 1.3 times higher than FER zeolite. Furthermore, the average yield of branched fatty acid using hierarchical ZSM-5 zeolite is almost 69%, higher than FER zeolite. It is matter to emphasize that the accessibility of the Brønsted acid sites are the main key in the isomerization reaction. So, the introduction of hierarchical ZSM-5 zeolite for the realization of branched fatty acids could be a tremendous alternative for industry; although there are material losses, it could cover by the lowest price of ZSM-5 compared with FER zeolite (Kersten et al., 2021).

Conclusion and Outlook

The use of hierarchical zeolite in the isomerization of biomass has demonstrated superior activity due to the mass transfer enhancement. There have been many strategies to synthesize the hierarchical zeolite, either bottom-up or top-down approach. Furthermore, the combination of these two methods was also applied. However, it has to be noted that additional mesopore is not the only determinator regarding the catalytic performance. Other properties such as acidity and hydrophobicity have also been considered. In a typical isomerization reaction of cellulosic sugars, the zeolite is usually modified with Sn atoms to generate the Lewis acid site. Also, the use of a basic site was reported. It is different from the fatty acid, where the Brønsted acid was employed. Despite the catalyst properties, other factors which have to be noticed are the reactant and the type of solvent used. Regarding the progress, the catalytic evaluation of other zeolite framework types or zeolite synthesized with greener strategies has to be more explored. Moreover, the detailed mechanism of each reaction is also a crucial part to investigate. Finally, the upscaling research of this topic will significantly impact the sustainability goal of economic and environmental perspectives.

Conflict of Interest

We have no conflict to declare.

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