

## Synthesis and Characterization of Sn, Ge, and Zr Isomorphous Substituted MFI Nanosheets for Glucose Isomerization to Fructose

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Various metals including Sn, Ge, and Zr have been successfully incorporated into the MFI nanosheets via a one-pot synthesis. The as-synthesized zeolites exhibit high external surface area and mesopore volume without large metal oxides aggregated on zeolite surfaces. Interestingly, the successful introduction of heteroatoms in MFI nanosheets can be confirmed by shifted XRD peaks corresponding to the unit cell expansion due to the replacement of metals into the framework. In addition, the UV-

## Introduction

Zeolites are microporous crystalline aluminosilicate materials demonstrating many outstanding properties, in particular high thermal/hydrothermal stability and adjustable acidity, eventually resulting in using them as solid supports and catalysts.<sup>[1]</sup> Among them, the MFI is one of the most promising zeolite types, which has been extensively utilized in different catalytic applications in petrochemical industries because of their widerange catalytic properties and their appropriate medium porous structures of 10 membered rings, which are suitable for various chemical reactions.<sup>[2]</sup>

However, a conventional zeolite, containing a sole microporous structure, exhibits some drawbacks with regard to the diffusion limitation inside the zeolite network. This results in the pore-blockage, and therefore bulky molecules cannot penetrate easily to active sites located in micropores, eventually leading to the fast deactivation of catalysts. To overcome these problems, over the past decade, the hierarchical zeolites with additional mesopores and/or macropores have been developed intensively.<sup>[3]</sup> Typically, they have been synthesized via both post-synthesis methods (desilication and dealumination) and templating methods.<sup>[4]</sup> It was confirmed that the additional mesopores and/or macropores facilitate the molecular trans-

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Vis absorbance spectra reveal that at the suitable metal loading the incorporated tetrahedral coordination of metal species in the zeolite framework has been obtained. To illustrate the benefits of the prepared catalysts, the glucose isomerization to fructose was carried out in a water/dioxane system. Obviously, the SnMFI-NS samples, containing the high dispersion of metal isomorphous species demonstrate the outstanding catalytic behavior in term of fructose selectivity (>85%).

portation and reduce the coke deposition, resulting in an improved catalytic lifetime.  $^{\rm [5]}$ 

Moreover, zeolite catalysts have been modified with various metals to adjust the appropriate acid strength and active sites. In general, some metals, such as iron (Fe), zinc (Zn), and gallium (Ga) were loaded on zeolites obtained via simple ion-exchange and impregnation methods to reduce their acid strength.<sup>[6]</sup> However, the metal species obtained from each loading method are different and appropriate for different catalytic reactions. In addition, another alternative approach to incorporate the metal in a zeolite is the isomorphous substitution of zeolite frameworks with tetravalent metal ions, such as germanium (Ge), tin (Sn), titanium (Ti), and zirconium (Zr), which can substitute into the zeolite framework.<sup>[7]</sup> For example, these metals can act as Lewis acid sites demonstrating the acid strength in the order of  $Si \ll Ge < Ti < Sn < Zr$ , and they are appropriate for various catalytic applications, especially in biomass conversion.<sup>[8]</sup>

Indeed, over the past decades, researchers have studied the characteristic properties of the heteroatom-substituted zeolite frameworks to gain insights into their structural analysis and their catalytic behavior.<sup>[9]</sup> For example, the germanium (Ge), which has similar properties to silicon, is one of the most interesting elements, which has been widely used to design metal-isomorphously substituted zeolites.<sup>[7b,10]</sup> The conventional Ge-ZSM-5 was successfully synthesized by direct synthesis, and XAS results could confirm the presence of tetrahedral Ge in the zeolite framework.<sup>[7b]</sup> In addition, other metals such as zirconium (Zr) and tin (Sn) incorporated in zeolites, well-known active sites for biomass conversion, such isomerization,<sup>[11]</sup> dehydration,<sup>[12]</sup> hydrogenation,<sup>[13]</sup> as hydroxylation,<sup>[14]</sup> oxidation,<sup>[15]</sup> and epoxidation,<sup>[16]</sup> have been studied for some catalytic applications. For example, Song Song, et al. described the incorporation of Zr in a mesoporous Beta zeolite framework for the conversion of biomass-derived



furfural to γ-valerolactone. Its hierarchically micro-mesoporous structure is crucial to facilitate molecular transport in a zeolite network.<sup>[17]</sup> Moreover, hierarchical Sn-MFI nanosheets with the different Si/Sn ratio of 75, 186, and 223 have been manufactured by a one-pot synthesis. The designed materials could provide the high yield of fructose and lactulose obtained from glucose and lactose conversion, respectively.<sup>[9b]</sup> Although there are some related literatures describing about the development of isomorphous substitution of metals in hierarchical zeolite frameworks, their catalytic applications, especially in biomass conversion, are still in the early stage of development.

In this contribution, we report the fabrication and structural analysis of the isomorphous substitution of various metals including germanium (Ge), zirconium (Zr), and tin (Sn) into zeolite frameworks with hierarchical structures. In addition, the analysis of active sites has been achieved by various numerous techniques, such as X-ray powder diffraction (XRD), scanning electron microscopy (SEM), together with energy dispersive Xray spectrometry (EDS), transmission electron microscopy (TEM), UV-Vis spectroscopy, and X-ray photoelectron spectroscopy (XPS) to confirm the isomorphous structure of metals species. In addition, various metals-isomorphous substituted zeolites have been applied in glucose isomerization to examine the effect of isomorphous substitution on the catalytic activity.

## **Results and Discussion**

# Synthesis of metal-isomorphously substituted zeolites with hierarchical structures

To obtain various metal-isomorphously (Ge, Zr, and Sn) substituted hierarchical MFI nanosheets (NS), Scheme 1 demon-

strates the related synthesis procedure in which the quaternary ammonium cation, TBAOH, was applied as a hierarchical structure-directing agent (SDA) to direct both the microporous structure and the self-assembly of zeolite nanosheets in the presence of metal precursors. To confirm the crystalline structure, the XRD patterns of all the prepared catalysts with different metal contents exhibit high crystallinity with the characteristic peaks of MFI framework appeared at  $2\theta$  of 7.8, 8.7, 23.1, and 23.8°, attributing to the plane indices of (101), (111), (501), and (303), respectively, without the interference of other crystalline phases (Figures 1 and S1).<sup>[18]</sup> Obviously, there is no significant change of the relative crystallinity when increasing the metal content in the range of 0.1 to 0.7 wt.%. These observations demonstrate that the crystalline structure can be preserved in the presence of metals, which might be located inside the zeolite framework. In addition, to confirm the incorporation of metals into the zeolite framework, the magnified XRD patterns in the  $2\theta$  range of 7.0 to  $10.0^{\circ}$ demonstrate that almost all the synthesized samples with the metal incorporation exhibit their XRD characteristic peak (at  $2\theta$ around 8°), shifting approximately 0.05 to 0.1° with respect to the non-metal loaded silicalite-1 nanosheets (SiNS). Interestingly, this shifting peak is more obvious with increasing of metal loading. The reason of XRD peak shifting to lower  $2\theta$ relates to the expansion of unit cell due to the metal substitution in the zeolite framework as shown in Figure 1.<sup>[19]</sup> This could be explained from Bragg's Law equation in which dspacing and  $2\theta$  are inversely proportional to each other. It is therefore reasonable to confirm the presence of isomorphous substitution of metals in zeolite frameworks.

To investigate the morphologies of the as-synthesized samples, SEM and TEM images are demonstrated as shown in Figures 2, S2, and S3. The SEM images of all metal substituted



Scheme 1. Illustration of preparation scheme demonstrating the synthesis of various metal-substituted MFI silicalite-1 nanosheets.





Figure 1. (A, C, E) XRD patterns and (B, D, F) magnified XRD patterns in the  $2\theta$  range of 7.0 to  $10.0^{\circ}$  of: (a) SiNS, (b) 0.18%GeMFI-NS, (c) 0.33%GeMFI-NS, (d) 0.53%GeMFI-NS, (e) 0.14%ZrMFI-NS, (f) 0.33% ZrMFI-NS, (g) 0.73%ZrMFI-NS, (h) 0.17%SnMFI-NS, (i) 0.31%SnMFI-NS, and (j) 0.59%SnMFI-NS.

MFI nanosheets illustrate the identical raspberry-like morphology with the nanoparticles-stacking structure with the particle size distribution in the range of 80 to 150 nm (Figure S4). The particle sizes of GeMFI-NS samples are relatively smaller than those of SnMFI-NS and ZrMFI-NS samples. For example, the particle sizes of the 0.53%GeMFI-NS, the 0.73%ZrMFI-NS, and the 0.59%SnMFI-NS samples are approximately  $85 \pm 12$ ,  $152 \pm 26$ , and  $118 \pm 18$  nm, respectively. Moreover, the sheet thickness of all samples is in the range of 5 to 7 nm (Figure S5).

Additionally, to investigate in term of the metal distribution, SEM-EDS images illustrate high metal dispersion over the entire area of zeolite surfaces (Figure 2(d–f), and S6). As expected, TEM images of all samples clearly explain nanosheet morphology without the aggregation of metal oxides on the external surface of zeolites. These observations indicate that metal species are highly dispersed in the zeolite framework.<sup>[19b]</sup>

To reveal the textural properties of synthesized zeolites, the nitrogen adsorption-desorption isotherms are shown in Figure 3, Table 1, and Table S1. All the synthesized samples with

hierarchical structures demonstrate the integrated type I and IV isotherms containing the high adsorption at low relative pressure and the hysteresis loops at 0.9 to 1.0 of P/P<sub>0</sub>. These results confirm the presence of both microporous structure due to a typical zeolite feature of MFI and a hierarchical structure of nanosheets, eventually leading to an increased external surface area and external pore volume compared with the conventional silicalite-1. For example, the specific surface area  $(S_{BET})$  and external pore volume ( $V_{ext}$ ) of the 0.53%GeMFI-NS, the 0.73% ZrMFI-NS, and the 0.59%SnMFI-NS samples are 570, 486, and 562  $m^2 g^{-1}$ , and 1.16, 1.09, and 0.84  $cm^3 g^{-1}$ , respectively, while the 0.53 %SnMFI-CON possesses 404  $m^2g^{-1}$  of  $S_{\text{BET}}$  and  $0.13\ \text{cm}^3\text{g}^{-1}$  of  $V_{\text{ext}}$ . Interestingly, when the Sn content of SnMFI-NS is increased from 0.17 to 0.59 wt.%, the  $S_{BET}$  area and micropore volume ( $V_{micro}$ ) are enhanced from 510 to 562 m<sup>2</sup>g<sup>-1</sup> and from 0.11 to 0.14 cm<sup>3</sup>g<sup>-1</sup>, respectively. This could be attributed to the smaller particle size and sheet thickness, which were obtained when increasing the Sn content as can be seen in SEM, TEM images, and particle size distribution results, while





Figure 2. (a–c) SEM images, (d–f) EDS images of corresponding metals (Ge, Zr, and Sn), and (g–i) TEM images of (a, d, g) 0.53 %GeMFI-NS, (b, e, h) 0.73 %ZrMFI-NS, and (c, f, i) 0.59 %SnMFI-NS.



Figure 3. (A) Nitrogen adsorption-desorption isotherms and (B) NLDFT pore size distribution over different catalysts: (a) 0.17%SnMFI-NS, (b) 0.31%SnMFI-NS, (c) 0.59%SnMFI-NS, (d) 0.53%GeMFI-NS, (e) 0.73%ZrMFI-NS, and (f) 0.53%SnMFI-CON.

Table 1. Textural properties of the prepared catalysts measured by N2 physisorption.							
Catalysts	Surface area [m <sup>2</sup> g <sup>-1</sup> ]			Pore volume [cm <sup>3</sup> g <sup>-1</sup> ]			V <sub>ext/total</sub> <sup>[g]</sup>
	S <sub>BET</sub> <sup>[a]</sup>	S <sub>micro</sub> <sup>[b]</sup>	S <sub>ext</sub> <sup>[c]</sup>	$V_{total}^{[d]}$	V <sub>micro</sub> <sup>[e]</sup>	$V_{ext}^{[f]}$	
0.17%SnMFI-NS	510	276	235	1.09	0.11	0.97	0.89
0.31%SnMFI-NS	534	295	240	0.97	0.13	0.84	0.86
0.59%SnMFI-NS	562	318	244	0.98	0.14	0.84	0.85
0.53 %GeMFI-NS	570	323	247	1.29	0.14	1.16	0.89
0.73%ZrMFI-NS	486	298	189	1.21	0.12	1.09	0.90

[a]  $S_{BET}$ : specific surface determined by BET. [b]  $S_{micro}$ : micropore surface area. [c]  $S_{ext}$ : external surface area. [d]  $V_{total}$ : total pore volume. [e]  $V_{micro}$ : micropore volume. [f]  $V_{ext}$ : external pore volume ( $V_{ext} = V_{total} - V_{micro}$ ). [g] Fraction of mesopore and macropore volume (external volume).



their relative crystallinity was decreased. In addition, the NLDFT and BJH pore size distributions (PSD) of the metal isomorphous substituted MFI nanosheets demonstrate that they contain both micropores and mesopores (Figure 3 and S7). In contrast, the 0.53%SnMFI-CON contains a single characteristic of a microporous structure. From these observations, it can be concluded that the hierarchical samples greatly enhance external surface area due to the interparticle voids of nanolayers.

To study the acid properties,<sup>[15a,20]</sup> the NH<sub>3</sub>-TPD profiles are displayed in Figure S8 and Table S2. All catalysts exhibit two distinct peaks, which can be assigned to weak acid sites appeared at the temperature of 100 to 300°C, and the peak at the higher temperature ranging from 300 to 700 °C, containing various species of medium and strong acid sites. The results illustrate that the 0.18%GeMFI-NS, the 0.33%GeMFI-NS, and the 0.53 %GeMFI-NS contain the similar total acid amount, which is in the range of 135–148  $\mu$ mol g<sup>-1</sup>. For ZrMFI-NS catalysts, the 0.14%ZrMFI-NS, the 0.34%ZrMFI-NS, and the 0.73%ZrMFI-NS illustrate the total acid amount of 141, 171, and 142  $\mu$ molg<sup>-1</sup>, respectively. Intriguingly, the low acid amount of 142  $\mu$ mol g<sup>-1</sup> was obtained when the highest percentage of Zr was introduced to the zeolite (0.73 wt.%). This phenomenon might be attributed to the presence of higher portion of zirconium oxide than the tetrahedrally coordinated Zr, which clearly indicates that the acid density is not only greatly affected by metal amount but also the metal species and dispersion. In addition, SnMFI-NS catalysts possess the total acid density of 141, 160, and 181  $\mu$ mol g<sup>-1</sup> for the 0.17%SnMFI-NS, the 0.31% SnMFI-NS, and the 0.59%SnMFI-NS, respectively, which slightly increased when increasing the metal content. However, the 0.53 % SnMFI-CON exhibits only 125  $\mu$ molg<sup>-1</sup> of the total acid densities calculated from the characteristic peak at the temperature ranging from 100 to 600 °C. This could also be attributed to the low dispersion of metal on the conventional support, which would affect its acidity.<sup>[21]</sup>

Moreover, FTIR spectroscopy of pyridine adsorption was applied to characterize Lewis acid property of the metal isomorphously substituted MFI nanosheets as shown in Figure S9. It clearly shows that the synthesized samples (0.59% SnMFI-NS, 0.53%GeMFI-NS, 0.73%ZrMFI-NS, and 0.53%SnMFI-CON) possess the characteristic band at 1447 cm<sup>-1</sup>, belonging to Lewis acid sites but there is no characteristic peak at 1545 cm<sup>-1</sup> of Bronsted acid sites.<sup>[22]</sup> Furthermore, there are some characteristic peaks at 1597 and 1613 cm<sup>-1</sup>, which might be related to H-bonded pyridine on surface silanol groups.<sup>[23]</sup> These observations indicate that the synthesized samples mainly contain the Lewis acid sites, which are typically considered as active species for glucose isomerization.

As stated above, the different acid densities of the synthesized metal-isomorphous substituted zeolites would derive from different metal species and dispersion. In order to further confirm the isomorphous substitution of metals in the zeolite framework, all of the prepared samples were also characterized by UV-Vis spectroscopy to observe the metal species (Figure S10). Prior to the measurement, catalysts were pretreated at 300 °C for 12 h under vacuum to remove moisture and impurity. It was found that the 0.73 %ZrMFI-NS catalyst

obviously exhibits the main characteristic peaks at approximately 200 nm, which could refer to the LMCT, ligand-to-metal charge transfer from oxygen framework to Zr<sup>4+ [24]</sup> indicating the incorporation of Zr into the zeolite framework with a minor contribution of bulk ZrO<sub>2</sub> at approximately 250 to 300 nm, corresponding to octahedral coordination of ZrO<sub>2</sub> species.<sup>[24b,25]</sup> It should be noted that the Zr loading on a zeolite demonstrates the main characteristic of Zr in tetrahedral form. These observations confirm the Zr isomorphous substitution in the zeolite framework for the prepared samples obtained via a one-pot synthesis method. Moreover, the SnMFI-NS catalysts also exhibit characteristic peaks at approximately 220 nm, which is attributed to the  $O^{2-}$  to  $Sn^{4+}$  charge transfer of isolated tetrahedral coordination in the framework and characteristic peaks in the range of 250 to 400 nm, which could be referred to charge transfer of the Sn-O-Sn located outside the framework structure or SnO2.[26] To further investigate, the 0.17%SnMFI-NS, which contains the lowest Sn loading content exhibits predominantly the tetrahedral Sn. However, when increasing the Sn content, the 0.31%SnMFI-NS and the 0.59% SnMFI-NS demonstrate the combination of SnO<sub>2</sub> together with tetrahedral species. Moreover, Tauc plots were applied to demonstrate the shifted extract edge energy of the samples obtained from a one-pot synthesis and an impregnation method (Figure S11 and Table S3).<sup>[15a,27]</sup> Compared with the sample obtained from the impregnation method (0.50%Sn(imp) MFI), which mainly composes of bulk octahedral tin species, the higher edge energy is observed (5.62 and 4.45 eV for SnMFI-NS and 0.50%Sn(imp)MFI, respectively). It can be concluded that Sn has also been isomorphously substituted into the zeolite framework by a one-pot hydrothermal synthesis when using small metal loading.

To further confirm the oxidation states of metal species in zeolite, XPS spectroscopy measurement was performed as shown in Figure 4. For the 0.53%GeMFI-NS, as shown in Figure 4(A), the Ge species is overlapped with O2 s. However, for the deconvoluted peaks, it was found that there are two Ge species appeared at the binding energies of 32.6 eV and 29.3 eV, attributing to the Ge<sup>4+</sup> species and Ge<sup>0</sup>, respectively.<sup>[28]</sup> For the 0.73 %ZrMFI-NS sample, it contains two different species of Zr as can be seen by the unique characteristic peaks at the binding energies of 183.1 eV and 185.3 eV, attributing to 3d<sub>5/2</sub>, and  $3d_{3/2}$ , respectively, contributing to the tetrahedrally coordinated Zr in zeolite framework and other peaks appear at the lower binding energies of 182.5 eV and 184.8 eV, which could be Zr-O species of bulk ZrO2.<sup>[29]</sup> The higher binding energy of tetrahedral coordination of Zr with respect to bulk ZrO<sub>2</sub> could be described due to higher positive charge of Zr in the framework compared with the Zr located in extra framework.<sup>[30]</sup> For SnMFI-NS catalysts, the 0.17%SnMFI-NS, the 0.31%SnMFI-NS, and the 0.59%SnMFI-NS exhibit three main characteristic peaks at the binding energies approximately 484.5, 486.5, and 487.4 eV (3d<sub>5/2</sub>), which can be described as metallic Sn, SnO<sub>2</sub>, and tetrahedrally coordinated Sn species, respectively.[19b] However, the main characteristics are in tetrahedrally coordinated Sn species as shown in Table S4 demonstrating the ratio of tetrahedrally coordinated Sn species (487.4 eV) to SnO<sub>2</sub>





Figure 4. XPS spectra of (A) 0.53 % GeMFI-NS (B) 0.73 % ZrMFI-NS (C) 0.17 % SnMFI-NS, (D) 0.31 % SnMFI-NS, and (E) 0.59 % SnMFI-NS.

species (486.5 eV) above 1. In addition, this ratio is slightly decreased with an increase in Sn content. Moreover, the 0.53% SnMFI-CON exhibits the lower ratio of tetrahedrally coordinated Sn to SnO<sub>2</sub> species as shown in Figure S12 and Table S4 with respect to SnMFI-NS with the similar metal content. Therefore, these observations confirm that all the prepared samples contain both tetrahedrally and octahedrally coordinated Sn species. Indeed, both types of Sn sites, including tetrahedral and extra-framework SnO<sub>2</sub> species can convert glucose to fructose in aqueous media.<sup>[31]</sup>

#### Catalytic testing for glucose isomerization to fructose

To demonstrate the beneficial effect of the metal isomorphously substituted zeolites with hierarchical structures, the glucose isomerization to fructose using water (5 wt.%)/dioxane system as a solvent was chosen as a model reaction. Indeed, it has been known that dioxane is a cost-effective solvent for continuous HMF production from fructose, which is the major product from glucose isomerization. Thus, using dioxane as a solvent is an alternative choice, which could facilitate the next step of reaction for HMF production. In addition, by using the mixed solvent with water, it can enhance the fructose yield.<sup>[30]</sup> Generally, glucose isomerization to fructose using Lewis acid catalysts can be occurred via 1,2 intramolecular hydride transfer following the previous works on both tetrahedral and extraframework SnO<sub>2</sub> species.<sup>[31,32]</sup> In this work, the metals isomorphously substituted MFI catalysts were tested in glucose isomerization at 90 °C for 12 h using 1 wt.% of glucose in 15 ml of water (5 wt.%)/dioxane. For the control experiment, it was found that the reaction cannot proceed in the absence of a

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catalyst (Figure 5 and Table S5). For GeMFI-NS samples, they exhibit guite low performance in glucose conversion, and it is similar to what has been observed in the case of bare SiNS catalyst. For example, with increasing the Ge loading content to 0.53 wt.%, the glucose conversion and the fructose selectivity are built up to only 18.6% and 21.7%, respectively (Figure 5). This could be attributed to the equivalent acid amount of all the GeMFI-NS samples (135–148  $\mu$ mol g<sup>-1</sup>) compared with the SiNS (70  $\mu$ mol g<sup>-1</sup>)<sup>[33]</sup> as shown in Table S2. In addition, Lewis acid strength of Ge has been considered as guite similar as Si.<sup>[8b]</sup> For the ZrMFI-NS cases, the 0.14%ZrMFI-NS exhibits moderate glucose conversion and fructose selectivity of 26.7% and 35.8%, respectively. This might relate to the high portion of tetrahedrally coordinated Zr species. However, when increasing the amount of Zr to 0.73 wt.%, the relatively low catalytic activity could be observed with the glucose conversion and fructose selectivity of 6.4% and 36.3%, respectively, because it composes of higher fraction of ZnO<sub>2</sub> species (Figure 4). For SnMFI-NS catalysts, the sample with a low amount of Sn catalyst (0.17%SnMFI-NS) performs a very low catalytic activity of 3.7% of glucose conversion with 63.6% of fructose selectivity. These observations relate to low Lewis acid amount of the tetrahedrally coordinated Sn (Figure S9 and Table S2). By increasing the Sn content, SnMFI-NS catalysts exhibit a higher catalytic activity. Interestingly, the 0.59%SnMFI-NS performs the highest glucose conversion and fructose selectivity of 31.4% and 87.1% with the yield almost 30%, respectively, attributing to the highest number of strong acid sites (Figure S9 and Table S2), which are the most selective species for glucose isomerization.<sup>[33]</sup> Moreover, in this case the catalytic activity advances toward the equilibrium conversion of glucose, which is 56% with high fructose selectivity.[11a,34] Compared to a





Figure 5. (A) Fructose selectivity (red bar), glucose conversion (black bar) and equilibrium conversion (green line), and (B) fructose yield (blue bar) over different catalysts: (a) blank, (b) SiNS, (c) 0.18%GeMFI-NS, (d) 0.33%GeMFI-NS, (e) 0.53%GeMFI-NS, (f) 0.14%ZrMFI-NS, (g) 0.33% ZrMFI-NS, (h) 0.73%ZrMFI-NS, (i) 0.17%SnMFI-NS, (j) 0.31%SnMFI-NS, (k) 0.59%SnMFI-NS, and (l) 0.53%SnMFI-CON. (Reaction condition: a 0.3 g of catalyst, 1 wt.% glucose in water (5 wt.%)/ dioxane at 90°C for 12 h of reaction time)

conventional zeolite, the 0.53%SnMFI-CON exhibits a very low glucose conversion at 3.8% with fructose selectivity of 86.8%, which could be attributed to the low amount of strong acid site, resulting in low catalytic performance in glucose isomerization. Moreover, the conventional silicalite-1 containing a sole microporous structure with 0.55 nm of microporous channel could not facilitate the glucose transportation to the active sites, resulting in the low catalytic activity. Indeed, the kinetic diameter of glucose is approximately 0.85 nm, which is larger than zeolite micropores.<sup>[35]</sup> However, the catalytic activity is significantly improved when applying the SnMFI-NS containing hierarchical structures. These observations confirm that the reaction is probably proceeded on external surface of the zeolite especially between nanosheet layers.

## Conclusion

In this work, various metal-isomorphous substituted MFI nanosheets were successfully synthesized, including GeMFI-NS, ZrMFI-NS, and SnMFI-NS using a one-pot hydrothermal method. Based on various characterization results, it was confirmed that the isomorphous substitution into the zeolite framework has been achieved. XRD spectra clearly illustrate the characteristic peak shifting to lower 2 $\theta$  degrees approximately 0.05 to 0.1°, confirming the larger unit cell of metal-isomorphous framework with respect to the unmodified zeolite. SEM and TEM images as well as SEM-EDS mapping analysis reveal the nanosheet structure with high dispersion of metals. Moreover, UV-Vis and XPS spectra can confirm the presence of tetrahedral framework of metals substituted in a zeolite structure as the main characteristic. Intriguingly, these isomorphous substituted catalysts have been tested in glucose isomerization, in which the 0.59%SnMFI-NS performs the highest glucose conversion and fructose selectivity of 31.4% and 87.1%, respectively, attributing to the highest amount of strong acid sites of Sn tetrahedral coordination. This work reveals the benefit of the metal isomorphous substitution of Sn, Ge, and Zr into the MFI zeolite

framework together with the nanosheet structure of zeolite catalysts utilizing glucose isomerization. It opens up a potential route to further study metal substituted zeolites for many applications in the future.

### **Experimental Section**

#### **Catalyst preparation**

Silicalite-1 nanosheets (SiNS) and metals substituted MFI nanosheets were manufactured via a one-pot hydrothermal method.[2a] Typically, a 4.34 g of TEOS (tetraethyl orthosilicate) as a silica source taken from Sigma-Aldrich was mixed with a metal source including germanium oxide (Alfa Aesar, 99.999% metals basis), zirconyl (IV) nitrate solution (ACROS Organics, 99.5%) or tin (IV) chloride pentahydrate (Sigma-Aldrich, 98%) solution with varying the loading content of  $MO_x/SiO_2$  molar ratio ranging from 0 to 0.04. Subsequently, the prepared precursor was stirred with adding a 4.06 g of 40 wt.% of tetra(n-butyl)ammonium hydroxide in H<sub>2</sub>O (TBAOH, Leonid) as a structure-directing agent (SDA). After that, a sodium hydroxide solution, a 0.01 g of NaOH (Carlo Erba) in H<sub>2</sub>O, was added under vigorous stirring, then stirred continuously for 12 h to the above-mentioned mixture. The total amount of H<sub>2</sub>O is 1.32 g. The obtained precursor was then kept in the autoclave at 130  $^\circ\text{C}$  for 2 days. After that, the synthesized compound was washed with DI water to get rid of the excess basic fragments, dried at 100 °C, and calcined to remove the template at 550 °C for 6 h. The prepared zeolites are named as x% GeMFI-NS, x%ZrMFI-NS, and x%SnMFI-NS for Ge, Zr, and Sn incorporated in MFI framework, respectively, where x refers to metal content in wt.%.

In addition, to compare with the bulk zeolite, the isomorphous substitution of Sn in a conventional silicalite-1 was obtained by a hydrothermal method. Firstly, the mixture composed of tetraethyl orthosilicate (TEOS, 3.50 g), a 1 M tetrapropylammonium hydroxide in H<sub>2</sub>O (TPAOH, Sigma-Aldrich, 1.72 g), tin chloride, and DI water (10 g) was stirred for 10 min. The sodium hydroxide solution (a 0.07 g of NaOH in a 2.27 g of DI water) was mixed and stirred for 2 h with the previous mixture. Subsequently, it was transferred to the autoclave and heated at 180 °C for 3 days. After that, it was filtered until pH less than 7, dried overnight at 100 °C and calcined



to remove the template at  $550\,^\circ\text{C}$  for 6 h. The prepared sample is named as the 0.53\,\%SnMFI-CON.

#### Characterization

The X-ray powder diffraction (XRD) using D8 ADVANCE model of Bruker was applied to characterize the crystallinity of all samples using step sizes of 0.036° from 5 to 55° of 20. To characterize the elemental compositions, they were characterized using a wavelength dispersive X-Ray fluorescence spectroscopy (WDXRF) of S8 Tiger model, Bruker. Scanning electron microscope and energy dispersive X-ray spectrometer (SEM-EDS) were performed using JEOL JSM-7610F and transmission electron microscopy (TEM) images were obtained by a JEOL-JEM-ARM2000F to confirm the morphologies, particle size, and metal distribution of the samples. Nitrogen adsorption-desorption analysis was used to measure the textural properties of the synthesized samples at -196°C using a BELSORP-max model. Before the measurement, zeolites were performed under the vacuum-pretreatment at 300°C for 24 h. The specific surface area (S<sub>BFT</sub>) was estimated from Brunauer-Emmett-Teller (BET) theory. The total pore volume ( $V_{total}$ ) was acquired at P/  $P_0$  of 0.99. The micropore volume ( $V_{micro}$ ) was estimated using the *t*plot method. The pore size distribution was obtained from the Barrett-Joyner-Halenda (BJH) method. To measure acid properties and acid amount, ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD) was performed by BELCAT II model. The samples were heated at 500°C under He for 1 h before characterization. For charge transfer investigation, selected samples were analysed by ultraviolet-visible spectroscopy (UV-Vis) using PerkinElmer Lambda 1050 in the diffuse reflectance mode and they were pretreated at 300 °C for 12 h under vacuum before measurement. To investigate the metal species, the X-ray photoelectron spectroscopy (XPS) performed on JEOL JPS-9010 was operated by using Mg K $\alpha$  X-rays (1254.6 eV) for Sn and Zr samples and Al K $\alpha$  X-rays (1486.6 eV) for Ge sample. The standard Cls peak at 284.8 eV was used as a reference for charge correction.

#### **Catalytic testing**

The catalytic testing on glucose isomerization to fructose was carried out in a round-bottom flask equipped with a reflux condenser. A 1 wt.% of glucose solution was prepared in the solution mixture of water (5 wt.%) and dioxane solvent (15 ml). A 0.3 g of a catalyst was dispersed into the solution, which was heated to 90 °C for 12 h. The liquid samples were analysed using Shimadzu HPLC (LC-40) with SH1011 Shodex sugar column with 0.5 mM  $H_2SO_4$  in water as the mobile phase. The glucose conversion, product selectivity, and product yield are described below:

$$Glucose \ conversion \ (\%) = \frac{mole \ of \ converted \ glucose}{mole \ of \ initial \ glucose} \times 100$$

Product selectivity 
$$(\%) = \frac{\text{mole of desired product}}{\text{mole of converted glucose}} \times 100$$

Product yield (%) =

$$\frac{glucose \ conversion \ (\%) \times product \ selectivity \ (\%)}{100}$$

In addition, the mass balance was determined based on the amount of detectable products and reactant calculated from GC chromatogram results and it was in the range of  $93.56 \pm 5.20$ %.

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## **Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** glucose isomerization • hierarchical zeolites • isomorphous substitution • MFI zeolites • zeolite nanosheets

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## **FULL PAPERS**

Sn, Ge and Zr isomorphously substituted MFI zeolites with hierarchical structures have been fabricated. The MFI nanosheets with appropriate amounts of Sn could significantly improve the catalytic activity in glucose conversion to fructose due to the major contribution of tetrahedrally coordinated Sn in the framework together with hierarchical structures, eventually facilitating molecular transportation of bulky molecules to active sites.



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Synthesis and Characterization of Sn, Ge, and Zr Isomorphous Substituted MFI Nanosheets for Glucose Isomerization to Fructose