Synthesis of Hierarchical Sn-MFI as Lewis Acid Catalysts for Isomerization of Cellulosic Sugars

Hong Je Cho, Paul Dornath, and Wei Fan[*]

Department of Chemical Engineering, University of Massachusetts Amherst,
686 North Pleasant St., Amherst, MA   01003

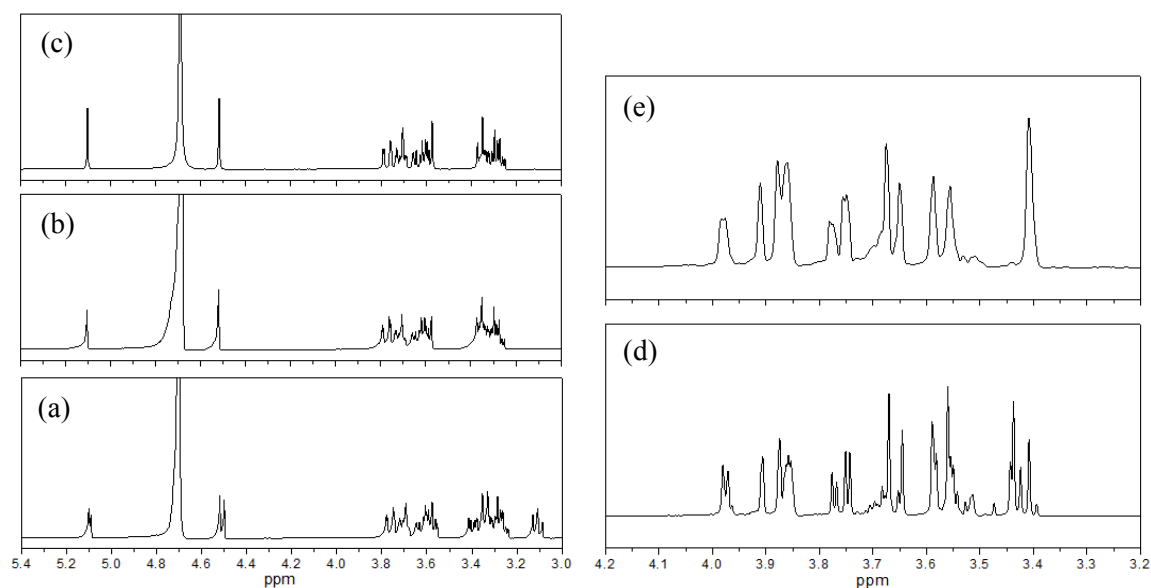[*] To whom correspondence should be addressed. E-mail: wfan@ecs.umass.edu

Figure S1. ^{1}H NMR spectra of (a) unlabeled glucose, (b) labeled glucose-D2, (c) glucose fraction obtained after the reaction of labeled glucose-D2 with 3DOm-i Sn-MFI, (d) unlabeled fructose and (e) fructose fraction obtained after the reaction of labeled glucose with 3DOm-i Sn-MFI. Reaction conditions are as follows: 2 g of 10 wt % labeled glucose-D2 in water, 0.1 g of 3DOm-i Sn-MFI, 50 h and 95 °C. In the spectra for glucose, the signal at 3.1 ppm, which is assigned to the hydrogen atom in the C-2 position (Figure S1a), was not seen in the labeled glucose-D2 (Figure S1b) as well as the glucose obtained after the reaction (Figure S1c). This reveals that the deuterium atom is still located at the C-2 position after the reaction. In the case of spectra for fructose, the peaks between 3.35 and 3.5 ppm, which correspond to two hydrogen atoms at the C-1 position (Figure S1d), become a single peak in the spectrum of fructose after the reaction of labeled glucose-D2 in Figure S1e. This is a strong indication that the deuterium atom located in the C-2 position of labeled glucose-D2 has moved to the C-1 position of fructose during the isomerization, consistent with earlier literature.[1,2]
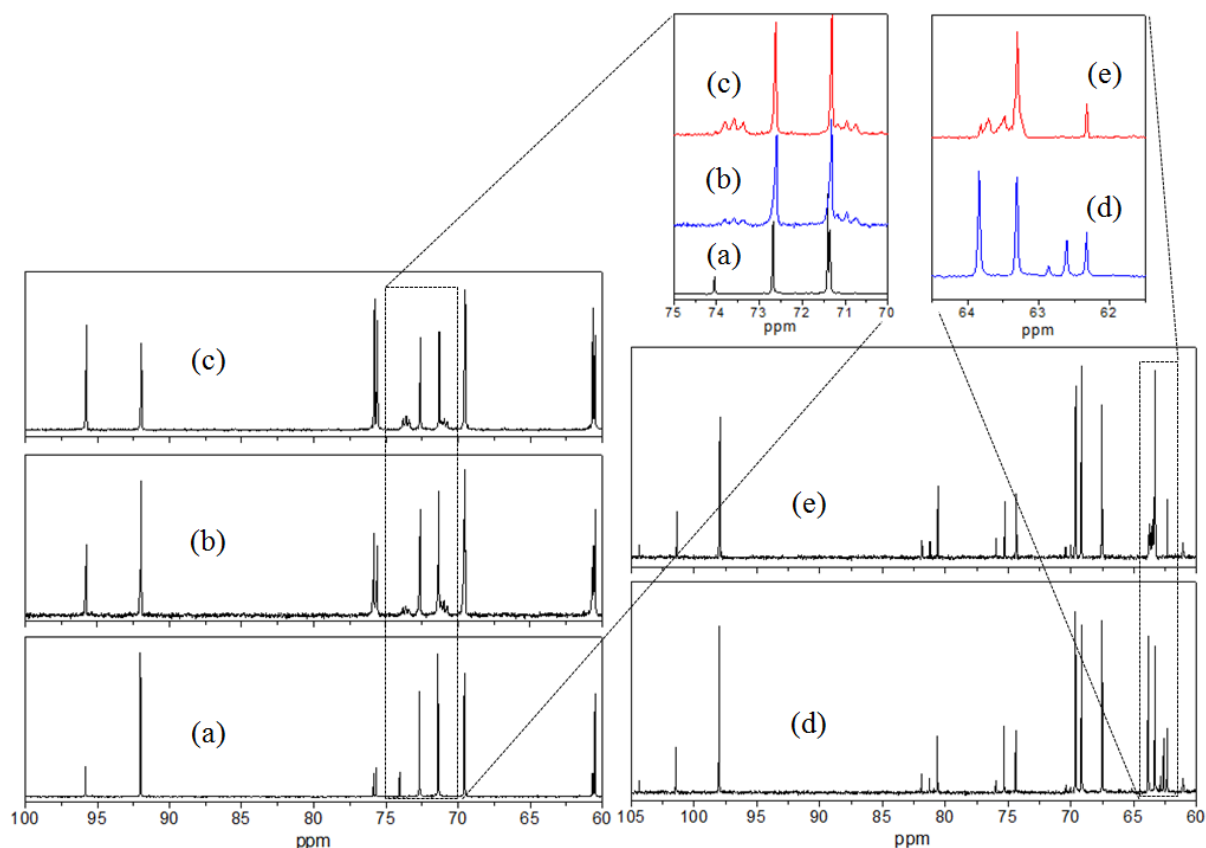
Figure S2. ^{13}C NMR spectra of (a) unlabeled glucose, (b) labeled glucose-D2, (c) glucose fraction obtained after the reaction of labeled glucose-D2 with 3DOm-i Sn-MFI, (d) unlabeled fructose and (e) fructose fraction obtained after the reaction of labeled glucose with 3DOm-i Sn-MFI. Reaction conditions are as follows: 2 g of 10 wt % labeled glucose-D2 in water, 0.1 g of 3DOm-i Sn-MFI, 50 h and 95 °C. ^{13}C NMR spectrum of unlabeled glucose reveals resonances at 74.1 and 71.3 ppm, assigned to the C-2 positions of β-pyranose and α-pyranose, and their low-intensity triplets indicate the presence of deuterium atoms (Figure S2a and b).[1,2] After the glucose-D2 reaction, analysis of ^{13}C NMR shows that glucose-D2 remains unchanged (Figure S2b and c). But, the fructose product formed from reaction of glucose-D2 has significant differences compared to an unlabeled fructose standard (Figure S2d and e). Specifically, resonances at 63.8 and 62.6 ppm that arise from the C-1 positions of β-pyranose and β-furanose, respectively,[1,2] appear as low-intensity triplets in the fructose fraction after the reaction. These results confirm that deuterium atoms are bonded to fructose C-1 carbon atoms, consistent with earlier literature.[2]
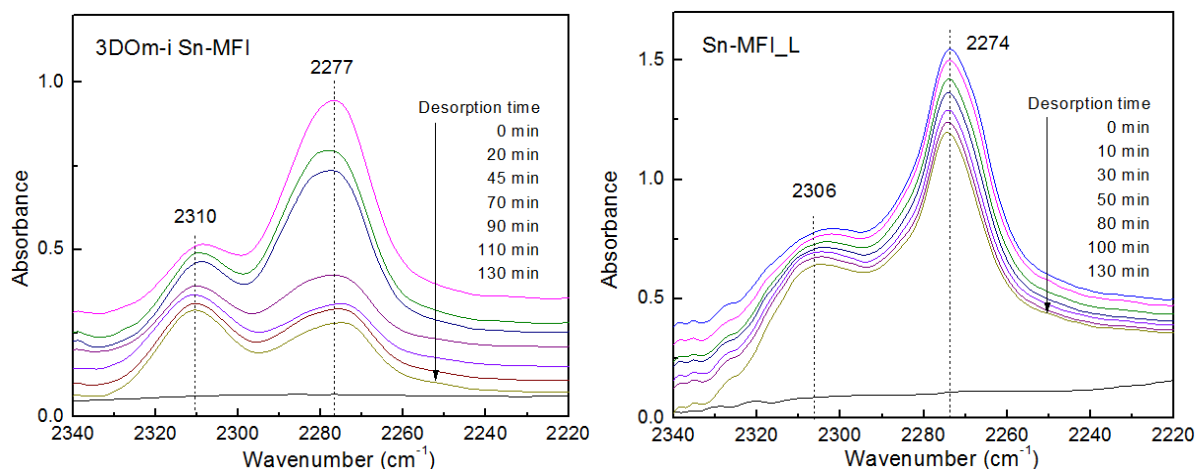
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Figure S3. FT-IR spectra of 3DOm-i Sn-MFI and Sn-MFI_L catalysts using deuterated acetonitrile (CD$_3$CN) as a probe molecule. The sample was degassed at 550 °C for 1 h under the flow of He to remove adsorbed water. After that, small aliquots of CD$_3$CN were subsequently exposed to the sample at room temperature, and then the excess acetonitrile was removed from the solid by flowing He. Desorption of CD$_3$CN was carried out under vacuum conditions at the same temperature. FT-IR spectra were collected on the samples for specific periods of desorption time.
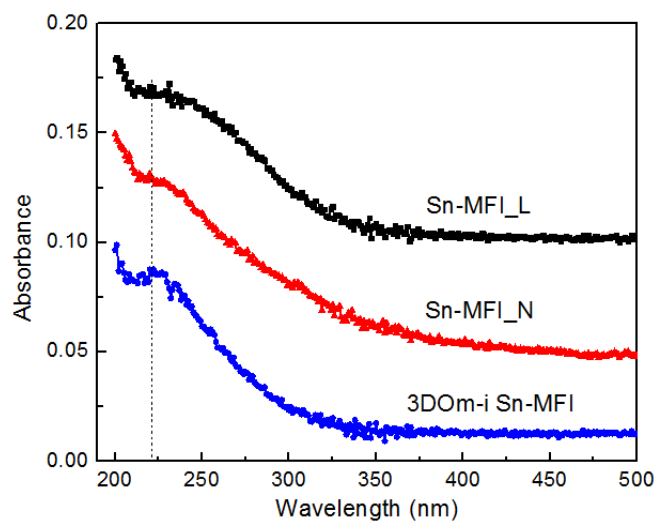
Figure S4. Diffuse reflectance UV-Vis (DR-UV) spectra of the Sn-MFI catalysts. The UV-Vis signal at around 200-205 nm is in good agreement with tetrahedrally coordinated Sn as suggested in the previous studies.[3-6] An absorption at ~220 nm can be assigned to charge transitions from O^{2-} to Sn^{4+} in tetrahedral coordination.[3] All samples exhibited no band at 280 nm which arises from Sn-O-Sn type of species.
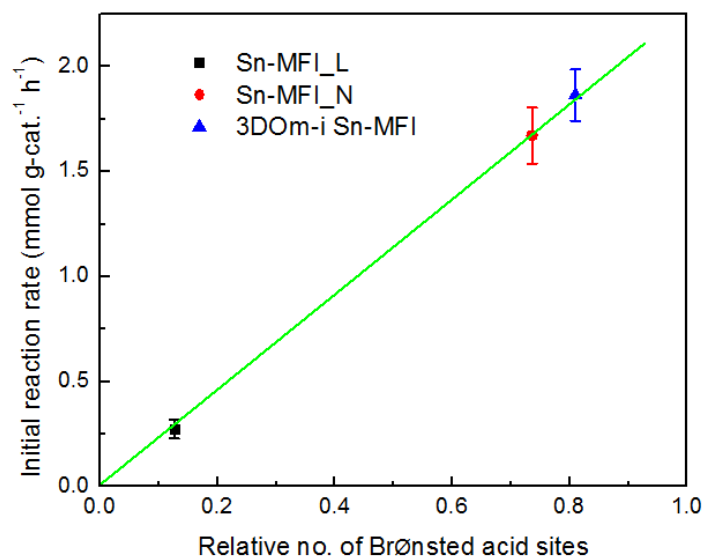
Figure S5. Plots of initial reaction rates against relative number of Brønsted acid sites for the conversion of DHA into ML. Initial reaction rates (mmoles of product divided by grams of catalyst per reaction time) are evaluated when the product yield lies between 5% and 20%. Reaction conditions are as follows: 0.3125 mmol DHA, 1 g methanol (MeOH), DHA to Sn molar ratio of 127 : 1, and 70 °C. Due to the different types of silanol groups in these materials, it is challenging to directly quantify the concentration of silanol groups. Furthermore, since the dehydration reaction from DHA to PA is catalyzed by Brønsted acid, we decided to measure the concentration of Brønsted acid sites in the samples and correlate them to the reaction rates. Using pyridine FT-IR spectra in Figure 3b and Sn concentration, relative number of Brønsted acid sites for each catalyst was obtained. At first, peak areas at 1455 cm^{-1} (Lewis acid sites) and 1546 cm^{-1} (Brønsted acid sites) in Figure 3b were calculated. The peak area at 1455 cm^{-1} is proportional to Sn content. Based on the peak area for Sn-MFI_L at 1455 cm^{-1}, relative number of Brønsted acid sites was calculated by normalization. Initial reaction rates were plotted in terms of relative number of Brønsted acid sites. The result clearly indicates that dehydration of DHA to PA is linearly correlated to the number of Brønsted acid sites.
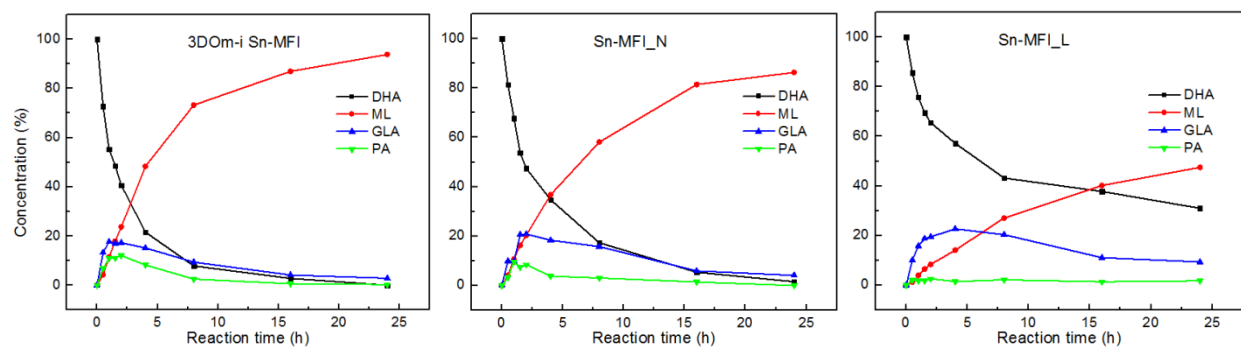
Figure S6. Product distributions for the conversion of dihydroxyacetone (DHA) into methyl lactate (ML) over Sn-MFI catalysts. Reaction conditions are as follows: 0.3125 mmol DHA, 1 g methanol (MeOH), DHA to Sn molar ratio of 127 : 1, and 70 °C.

Figure S7. Plots of $-ln(1-x)$ against a reaction time where x is the product yield for the conversion of pyruvaldehyde (PA) into methyl lactate (ML) over Sn-MFI catalysts. Reaction conditions are as follows: 0.3125 mmol PA, 1 g 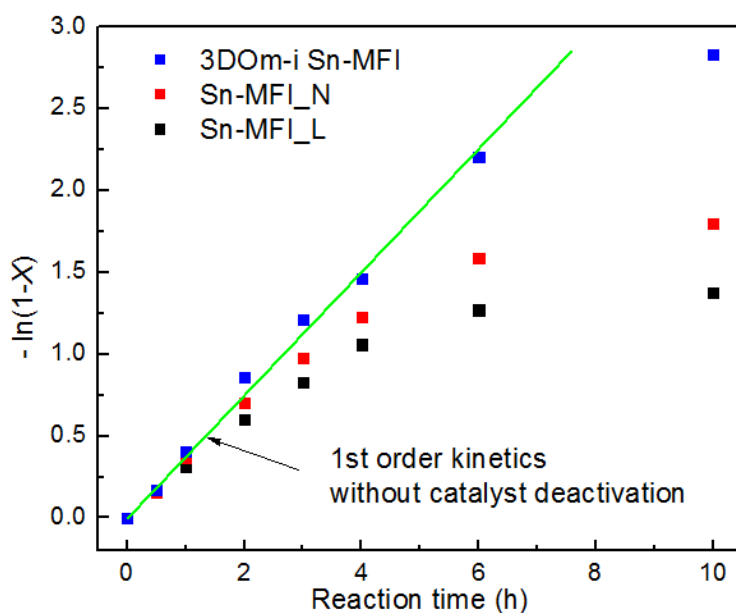methanol (MeOH), PA to Sn molar ratio of 127 : 1, and 70 °C. In a constant-volume batch reactor, this reaction can be approximated as pseudo-first order in the limiting reactant PA, giving a straight line (green) in the figure. In the three catalysts, the reaction over 3DOm-i Sn-MFI is in good agreement with the pseudo-first order reaction kinetic. The discrepancy shown in the Sn-MFI_N and Sn-MFI_L samples clearly implies the catalyst deactivation.
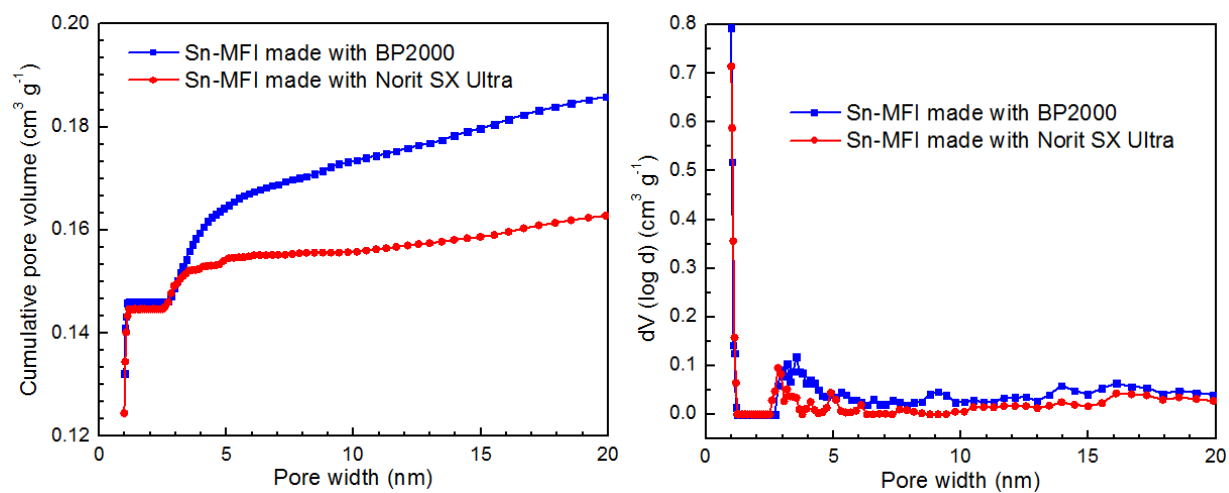
Figure S8. Cumulative pore volumes (left) and pore size distributions (right) using NLDFT of hierarchical Sn-MFI zeolites made with BP2000 and Norit SX Ultra, respectively, derived from nitrogen adsorption-desorption isotherms. Pore size distribution and cumulative pore volumes were calculated by using NLDFT (nonlocal density functional theory) adsorption model which describes N_2 adsorbed in cylindrical pores (AsiQwin 1.02, Quantachrome).
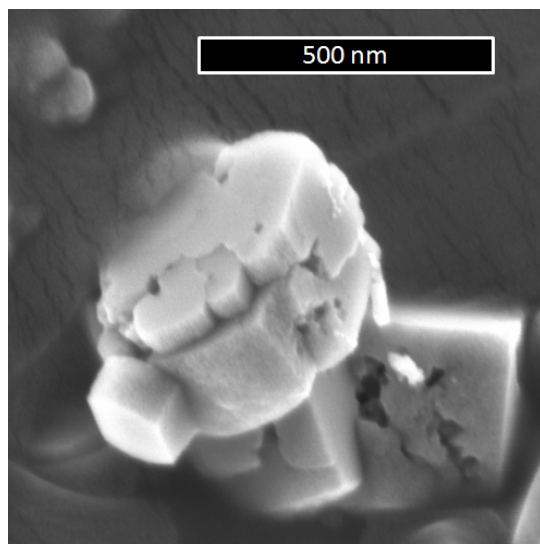
Figure S9. A SEM image of hierarchical Sn-MFI made with BP2000.

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