Supplementary information

Facile and fast synthesis of highly active Lewis acid MWW zeolite from a pure silica ITQ-1

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Experimental

Materials and reagents

Hexamethyleneimine (HMI, 98 wt%, Shanghai Annaiji Chemical Reagent Co.), tetrapropylammonium hydroxide (TPAOH, 40 wt% in water, Shanghai Annaiji Chemical Reagent Co.), fumed silica (Cab-o-sil M5), boric acid (99.5 wt%, Tianjin Damao Chemical Reagent Factory), stannic chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, 99 wt%, Tianjin Damao Chemical Reagent Factory), ethanol (99 wt%, Tianjin Fuyu Fine Chemical Reagent Co.), D-glucose (99.5 wt%, Shanghai methanol-D4 (CD_3OD, 99.8 wt%, Shanghai Annaiji Chemical Reagent Co.), deuterium oxide (D_2O, 99 wt%, Shanghai Annaiji Chemical Reagent Co.), nitric acid (65～68 wt%, Xilong Scientific Co., Ltd.), sodium chloride (NaCl, 99 wt%, Tianjin Damao Chemical Reagent Factory), N,N,N-trimethyl-1-adamantammonium hydroxide (TMAdaOH, 25 wt% in water, Shanghai Annaiji Chemical Reagent Co.).

Synthesis of B-MWW.

In a typical synthesis, a solution was obtained by dissolving 0.62 g of boric acid into 30 g of deionized water. Subsequently, 3.00 g of fumed silica, 0.30 g of Si-MWW seeds and 3.52 g of HMI were added into the above solution. Then, the mixed gel was placed in an oil bath at 80 °C and stirred for evaporation to remove the water completely, and a near dry powder was obtained, denoted as mixture A (SiO_2: $0.2H_3BO_3$: 0.71HMI). Then mixture A was transferred into a small PTFE container, and the small container was placed in a PTFE lined stainless steel autoclave with a mixed solution B (2.25g of H_2O and 3.52g of HMI) at the bottom of the PTFE liner. After heated at 170 °C for 4 days under static conditions, the sample was filtered and washed with abundant deionized water until the pH was less than 8 and dried at 80 °C. The dried samples were calcined at 580 °C in a muffle furnace for 10 h to obtain B-MWW.

Synthesis of deB-MWW

The above synthesized B-MWW zeolite was deboronated by treatment with 6 mol/L nitric acid (1 g zeolite/30 mL HNO_3) in a round bottom flask under reflux for 24 h at 100 °C. The sample was centrifuged and washed with abundant deionized water until the pH reached 7 and finally dried at 80 °C overnight. The corresponding MWW zeolite was denoted as deB-MWW.

Synthesis of Sn-MWW (TPA)

As a typical run, 0.508 g of tetrapropylammonium hydroxide (TPAOH, 40 wt%) was mixed with 7.20 g of deionized water and 0.0175 g of $SnCl_4.5H_2O$ and stirred for 15 min. Then, pure silica ITQ-1 precursor (1.20 g) were added to the above solution and stirred for 2 h at room temperature. Then the final gel with the molar composition of SiO_2: 0.004 SnO_2: 0.05 TPAOH: $20H_2O$ was transferred to a PTFE lined stainless steel autoclave and heated at 170 °C for 48 h under static conditions. The sample was filtered and washed with abundant deionized water until the pH was less than 8 and dried at 80 °C.

Catalytic Test

Glucose isomerization reaction was carried out in stirred 20-mL thick-walled glass reactors (VWR) sealed with crimp tops (PTFE/silicone septum, VWR). All the reactants and products were analyzed by high performance liquid chromatography (HPLC) using a refractive index detector with a Bio-Rad Aminex HPX87C (300 x 7.8 mm) column (Phenomenex).

Table S1. Weight change during different growth stages for preparing of Sn-MWW-250

Treatment time	Weight (g)	
	Mother sample	Product
2 h	0.3	0.28
8 h	0.3	0.29
24 h	0.3	0.29
72 h	0.3	0.28

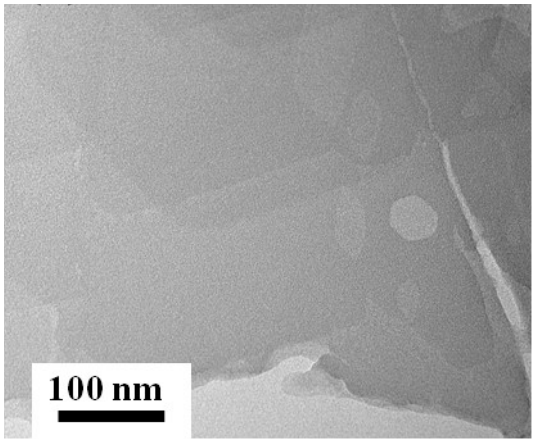


Fig. S1. TEM image of Sn-MWW-250.

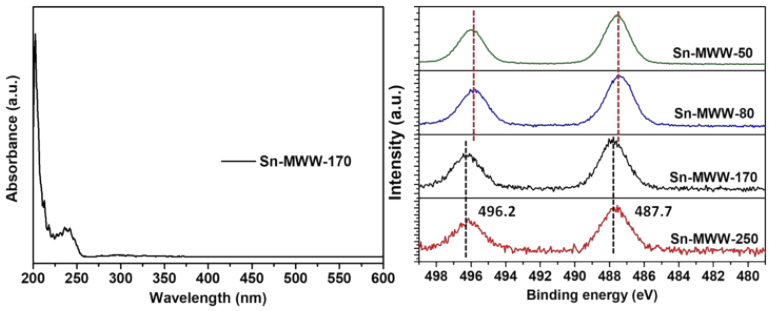


Fig. S2. (a) UV–vis spectrum of Sn-MWW-170 and (b) XPS spectra of Sn-MWW-50, Sn-MWW-80, Sn-MWW-170 and Sn-MWW-250.

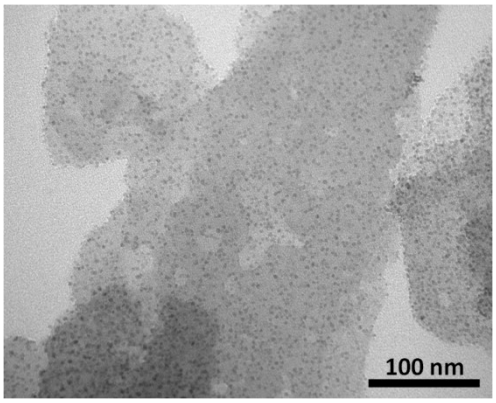


Fig. S3. TEM image of Sn-MWW-50.

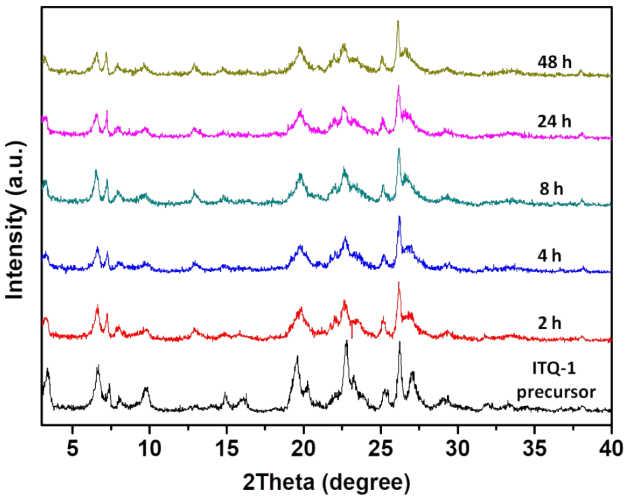


Fig. S4. XRD patterns of ITQ-1 precursor and products at different growth time (2-48 h), SDA/Si=1.0, SDA=HMI, ITQ-1 precursor as mother sample.

Table S2. The pH of the secondary growth solution (TPAOH and HMI)

SDA(HMI)/Si	pH	SDA(TPAOH)/Si	pH
0.2	**11.94**	**0.05**	**12.60**
0.4	**12.09**	**0.2**	**13.36**
1.0	**12.18**	**0.4**	**13.68**

The pH of the solution is measured at room temperature.

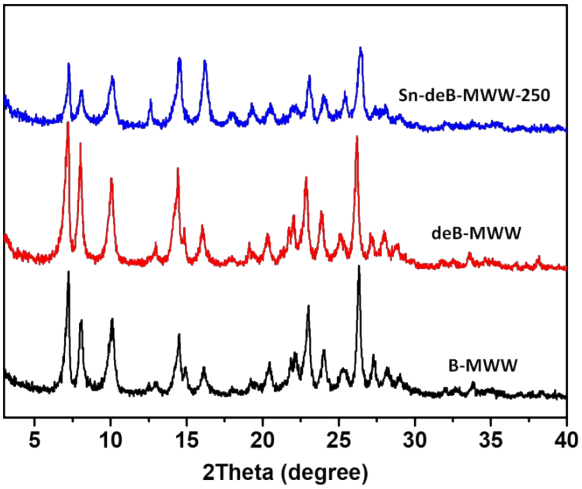


Fig. S5. XRD patterns of Sn-deB-MWW-250, deB-MWW and B-MWW samples.

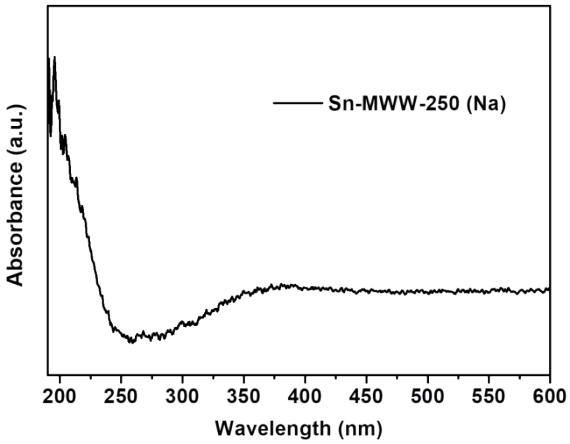
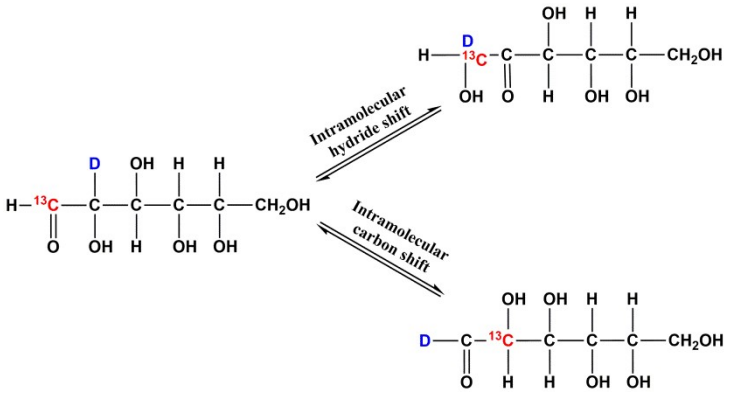


Fig. S6. UV−vis spectrum of Sn-MWW-250 (Na) sample.



Scheme S1. Reaction routes for isomerization of glucose.