

Specific Microwave Effect on Sn- and Ti-MFI Zeolites Synthesis

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Experimental Section

1. Reagents

Tetrapropylammonium hydroxide (TPAOH, 25 wt.%) was purchased from YiXing Dahua Chemical Co., Ltd. Tetraethylorthosilicate (TEOS) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Tin (IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) and Tetrabutyl titanate (TBOT, $\geq 98\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2. Synthesis of Sn- and Ti-MFI zeolites

A certain amount of 25 wt.% aqueous solution of TPAOH was added in water, followed by addition of TEOS. After the mixture aging for 10 h, then the desired amount of Sn or Ti source was added to the silica sol. After continuously stirring for 12 h, a homogeneous solution was achieved. For Sn-MFI and Ti-MFI, the final solution with a composition are $0.025\text{SnO}_2/\text{SiO}_2/0.45\text{TPAOH}/35\text{H}_2\text{O}$ and $x\text{TiO}_2/\text{SiO}_2/0.45\text{TPAOH}/35\text{H}_2\text{O}$ ($x = 0.025, 0.075$). Then 4 ml initial gel was transferred into a borosilicate glass (Pyrex) or silicon carbide (SiC) vessel placed in a microwave reactor (Monowave 300, Anton Paar) and crystallized at 80 °C for 90 min and 130 ~ 170 °C for different time. The solid product was centrifuged, washed extensively with deionized water for several times, and then dried at 60 °C overnight. Finally, all of the samples were calcined at 550 °C for 6 h in air.

Generally, the synthesis time was set no more than 210 min (upper time: 240 min) every time. Then the reactor would be cooled and re-heated during synthesis. Despite the fact, we still guaranteed the comparative trial remaining highly parallel. For example, the ramping time of reaction system in Pyrex and SiC vessels are basically the same whether in low or high temperature zone. When drop 170 °C to room temperature, the cooling times basically maintained within 3 min.

3. Characterizations.

Dynamic light scattering (DLS) measurement was used to monitor the particle growth during all the syntheses. Malvern Zetasizer Nano-ZS90 instrument with a detector collecting scattered light at 90° was used to estimate the variation of average particle size and size distribution with respect to time. All the light scattering measurements were carried out at 25 °C by using diluted mother liquors. Dilutions were continued until the reproducible size results obtained. Each measurement was repeated at least nine times. The X-ray diffraction (XRD) patterns were taken on a Persee XD-2 X-ray diffractometer using Cu K α radiation operated at 40 KV and 30 mA. The crystallinity was calculated by the formula of (peak area in the range of $2\theta = 8.0-10.0$ and $23.0-25.0^\circ$ of the product prepared in SiC vessel)/(peak area in the range

of $2\theta = 8.0-10.0$ and $23.0-25.0^\circ$ of the product prepared in Pyrex vessel). The morphologies of the as-synthesized samples were taken on Hitachi S-4800 field emission scanning electron microscope (FESEM). The diffuse reflectance (DR) UV-Vis spectra were collected on a Shimadzu UV-2450 spectrophotometer using BaSO_4 as the reference. The element compositions were conducted on energy dispersive X-ray (EDX) data. X-ray photoelectron spectroscopy (XPS) was collected on Thermo Scientific ESCALAB 250Xi scanning X-ray microprobe using Al $K\alpha$ radiation focused to a spot size of $500\ \mu\text{m}$ and an electron analyser pass energy of $20\ \text{eV}$ for narrow range scans. All binding energies were calibrated using contaminant carbon ($\text{C}1\text{s} = 284.6\ \text{eV}$). Temperature-programmed reduction by hydrogen (H_2 -TPR) was performed on Micromeritics AutoChem 2920 instrument. All the samples were pretreated at $550\ ^\circ\text{C}$ in Ar for 1 h and cooled to $50\ ^\circ\text{C}$. Then samples were heated at $10\ ^\circ\text{C}\cdot\text{min}^{-1}$ under a $30\ \text{mL}\cdot\text{min}^{-1}$ of 5% H_2/Ar mixture gas flow. Argon sorption isotherms were measured by a Quantachrome Autosorb iQ2 instrument at 87K. The total surface area was obtained by application of Brunauer–Emmett–Teller (BET) equation. The external surface area and micropore volume were calculated by using the t-plot method. The pore size distribution was estimated with the nonlocalized density function theory (NLDFT) method, adopting cylindrical siliceous zeolite pores. The acidity of these catalysts was investigated by potentiometric titration with *n*-butylamine. Briefly, a catalyst was first dried in flowing air at 723 K for 2 h to desorb the adsorbed moisture. Then, about 100 mg of dried catalyst was dispersed in 50 mL of acetonitrile. After being agitated for 1.5 h, the suspension was titrated by 0.01012 mol/L *n*-butylamine solution in acetonitrile with a ZDJ-5 automatic titrator (Lei-Ci Device Works, Shanghai).

4. Catalytic reactions

4.1 MPV reaction

The Meerwein-Ponndorf-Verley (MPV) reduction of furfural was carried out under microwave irradiation (PreeKem NOVA-2S). Briefly, 1 mmol of furfural was dissolved in 100 mmol of isopropanol, and then 100 mg of catalyst (Sn-MFI) was added. After the reaction mixture solution was dispersed uniformly by ultrasonic treatment, it was put in the microwave reactor at $100\ ^\circ\text{C}$ with magnetic stirring. After 1-5 h, the products were collected and analyzed by gas chromatography (GC, Shimadzu GC-2010 plus equipped with DM-FFAP capillary column ($30\ \text{m} \times 0.25\ \text{mm} \times 0.25\ \mu\text{m}$) and FID detector). The quantification of each reactant and product was obtained from the corresponding response factor and peak area. Furfural conversion and *i*-propyl-furfuryl ether (PFE) selectivity were calculated as follows:

$$\text{Furfural conversion} = \left[1 - \frac{\text{Mole of furfural in the products}}{\text{Initial mole of furfural}} \right] \times 100\%$$

$$\text{PFE selectivity} = \left[\frac{\text{Mole of PFE in the products}}{\text{Mole of converted furfural}} \right] \times 100\%$$

4.2 Ring-opening of epoxide reaction.

The ring-opening of epoxide reaction was carried out under microwave irradiation (PreeKem NOVA-2S). Briefly, 1 mmol of styrene oxide was dissolved in 60 mmol of methanol, and then 20 mg of catalyst (Ti-MFI) was added. After the reaction mixture solution was dispersed uniformly by ultrasonic treatment, it was put in the microwave reactor at 80 °C with magnetic stirring. After 20-120 min, the products were collected and analyzed by gas chromatography (GC, Shimadzu GC-2010 plus equipped with DM-FFAP capillary column (30 m × 0.25 mm × 0.25 μm) and FID detector). The quantification of each reactant and product was obtained from the corresponding response factor and peak area. Phenyl acetaldehyde conversion and 2-Methoxy-2-phenylethanol selectivity were calculated as follows:

$$\text{styrene oxide conversion} = \left[1 - \frac{\text{Mole of styrene oxide in the products}}{\text{Initial mole of styrene oxide}} \right] \times 100\%$$

$$\begin{aligned} \text{2 - Methoxy - 2 - phenylethanol selectivity} \\ = \left[\frac{\text{Mole of 2 - Methoxy - 2 - phenylethanol in the products}}{\text{Mole of converted styrene oxide}} \right] \times 100\% \end{aligned}$$

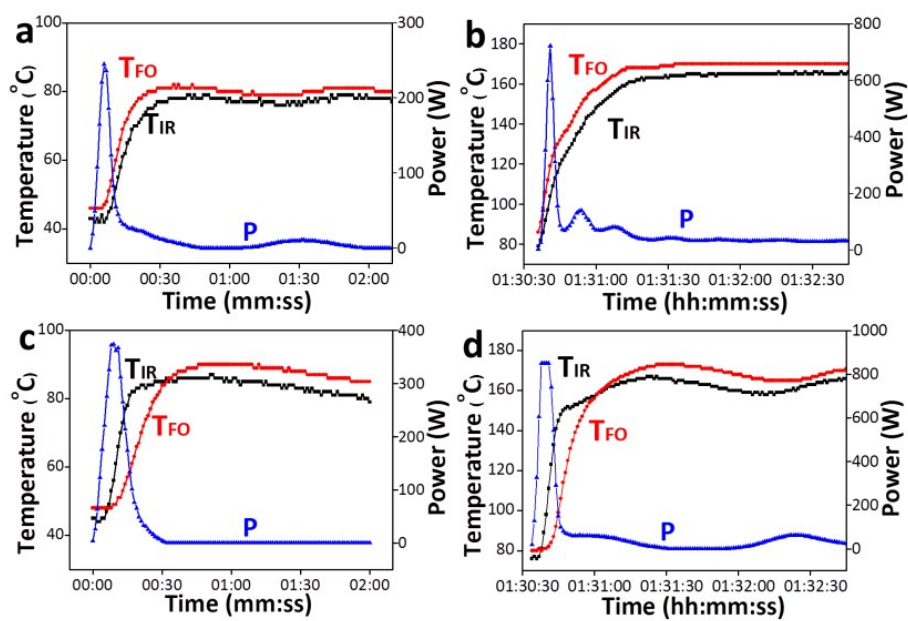


Fig. S1 Temperature (T_{IR} , T_{FO}) and power (P) profiles in the ramping phase recorded for the reaction system for Sn-MFI in the Pyrex (a: 80 °C, b: 170 °C) and SiC vessel (c: 80 °C, d: 170 °C), respectively, heated with microwave under sealed-vessel conditions in the Monowave 300 reactor.

Table S1 Ramping time of reaction system of Ti-MFI zeolites under microwave irradiation from room temperature to 80 °C, from 80 °C to 170 °C and from room temperature to 170 °C, respectively. The initial gel composition is 0.075TiO₂:SiO₂:0.32TPAOH:40H₂O.

	Pyrex	SiC	Pyrex	SiC	Pyrex	SiC
	32 (+2	30	48 (+7	41	43 (+5	38
)	28)	35)	39
	26 (-	24	43 (+8	34	42 (+3	39
t (RT	2)	31	t (80 °C	39	t (RT	34
-80 °C)	23 (-	23	-170 °C)	42(+8)	-170 °C)	42 (+3
/s	1)	26	/s	46(+7)	/s	38
	30 (-	21	40(+5)	29	42 (+8	38
	1)	25	39(+3)	37)	35
	28 (+5	23	38(+9)	34	45 (+7	35
)		36(-1))	
	26 (+0		38 (+4		43 (+5	
)))	
	24 (+3				40 (+2	
))	
	23 (-				40 (+5	
	2))	
	25 (+2				44 (+9	
))	
Average /s	26 (+0	26	41 (+5	36	42 (+5	37
)))	

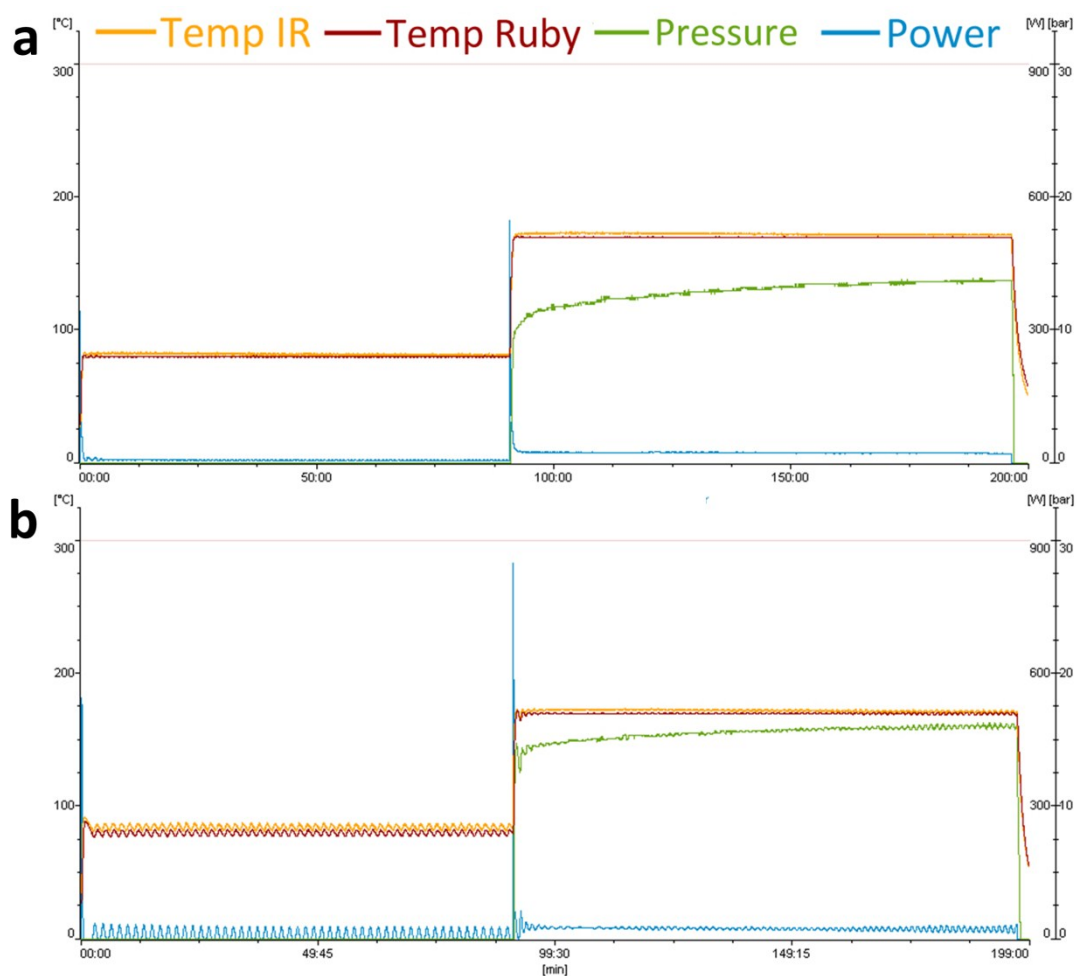


Fig. S2 Temperature (T), pressure (p), and power (P) profiles recorded for the reaction solution (4 ml) for Ti-MFI in the Pyrex (a) or SiC vessel (b), respectively, heated with microwaves under sealed-vessel conditions in the Monowave 300 reactor.

As shown in Fig. S2, the temperature, pressure and power profiles present the microwave reactor run in temperature mode. Also, it can be seen that, in ramping, holding and cooling stages, no matter which kind of the reaction vessel used, the calculate temperature is reliably measured by FO probe with an accuracy of ± 2.0 °C. Actually in most cases, the temperature recorded by IR sensor and FO probe are very similar.

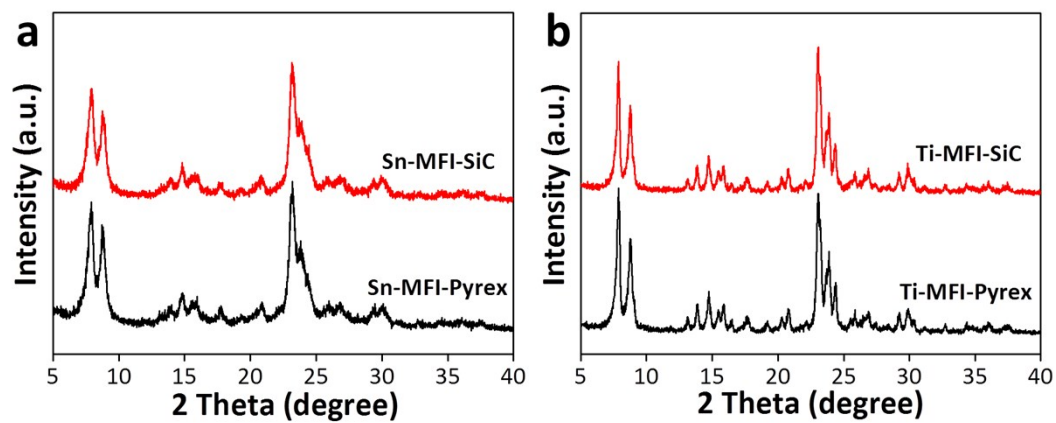


Fig. S3 XRD patterns of (a) Sn-MFI and (b) Ti-MFI zeolites prepared in Pyrex and SiC systems under microwave irradiation.

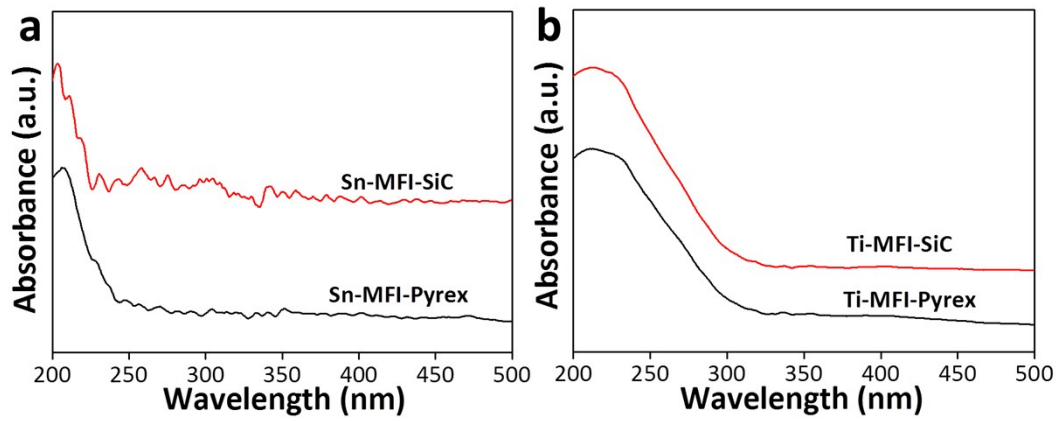


Fig. S4 DR UV-Vis spectra of (a) Sn-MFI and (b) Ti-MFI zeolites prepared in Pyrex and SiC systems under microwave irradiation.

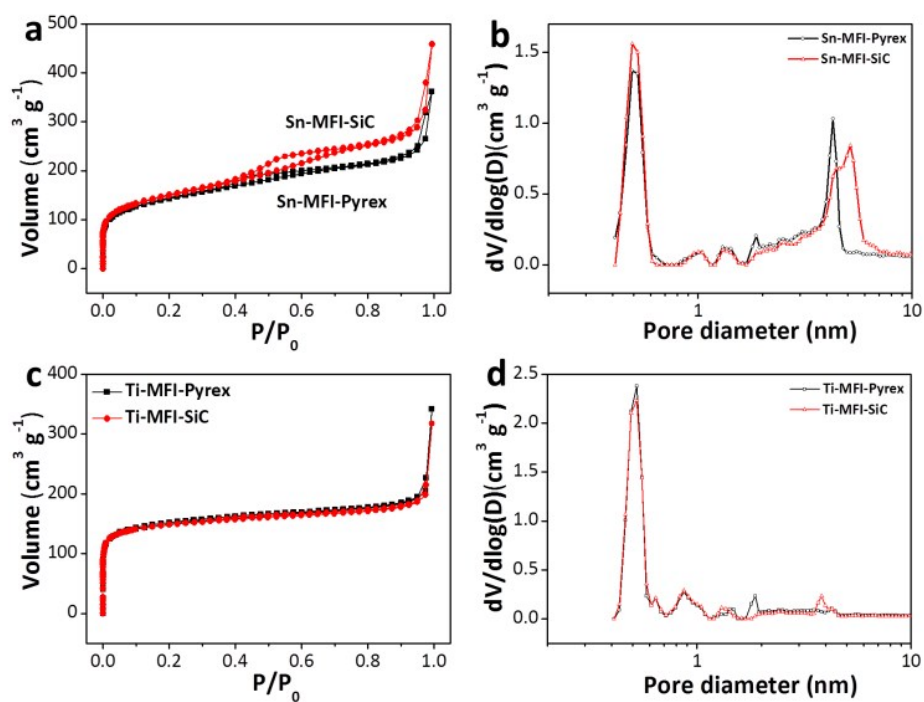


Fig. S5 (a) (c) Argon sorption/desorption isotherms, and (b) (d) NLDFT pore size distribution curves of Sn-MFI (a) (b) and Ti-MFI (c) (d) catalysts.

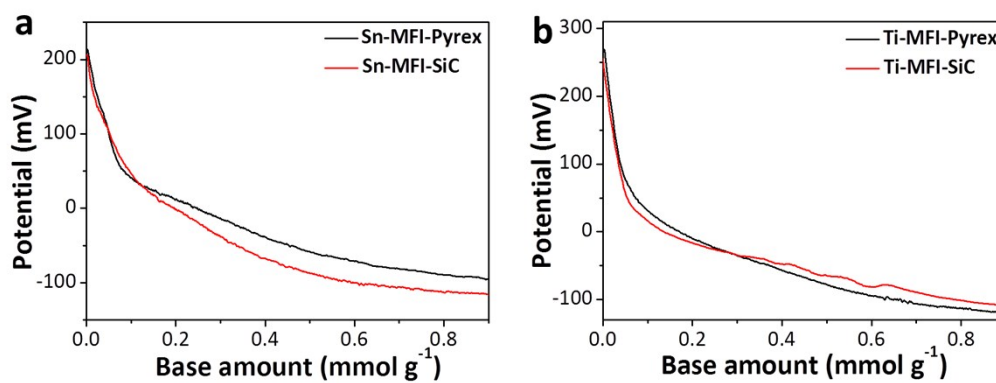


Fig. S6 Potentiometric titration curves with n-butylamine of (a) Sn-MFI-Pyrex and Sn-MFI-SiC; (b) Ti-MFI-Pyrex and Ti-MFI-SiC catalysts.

Table S2 Textural properties of Sn-MFI-Pyrex, Sn-MFI-SiC and Ti-MFI-Pyrex, Ti-MFI-SiC catalysts, as well as their initial electrode potentials and total acid amounts calculated by their potentiometric titration curves with n-Butylamine.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^a	S_{micro} ($\text{m}^2 \text{g}^{-1}$) ^b	S_{ext} ($\text{m}^2 \text{g}^{-1}$) ^b	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	E_i (mV) ^c	amount of total strong acid (mmol g^{-1}) ^d
Sn-MFI-Pyrex	450	223	227	0.09	214	0.050
Sn-MFI-SiC	470	195	275	0.07	206	0.051
Ti-MFI-Pyrex	496	420	76	0.16	269	0.038
Ti-MFI-SiC	494	426	68	0.16	256	0.035

a. Determined by the BET equation; b. Determined by the t-plot method; c. Initial electrode potential; d. Total amount of strong acid calculated from the titration amount of n-butylamine at $E \geq 100$ mV.