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for

Hydrothermal synthesis of boron-free Zr-MWW and Sn-MWW

zeolites as robust Lewis catalysts

Zhiguo Zhu,^a Yejun Guan,^b Haikuo Ma,^a Hao Xu,^{b*} Jin-gang Jiang,^b Hongying Lü^a

and Peng Wub*

^a Green Chemistry Centre, College of Chemistry and Chemical Engineering, Yantai University, 30 Qingquan Road, Yantai 264005, Shandong, China

^b Shanghai Key Laboratory of Green Chemistry and Chemical Process, School of Chemistry and Molecular Engineering, East China Normal University, North Zhongshan Rd. 3663, Shanghai 200062, China

E-mail address: pwu@chem.ecnu.edu.cn (P. Wu); hxu@chem.ecnu.edu.cn (H. Xu)

Experimental section

Materials. The chemicals were employed as purchased: hexamethyleneimine (HMI, 98 %, Aladdin), *N,N,N*-trimethyl-1-adamantammonium hydroxide (TMAdaOH, 25 %, Macklin), nitric acid (HNO₃, 65 %, Sinopharm Chemical Reagent Co., Ltd), potassium carbonate (K_2CO_3 , 99 %, Aladdin), tin chloride pentahydrate (SnCl₄·5 H₂O, 99 %, Aladdin), zirconium sulfate tetrahydrate (ZrSO₄·4 H₂O, AR, Macklin), fumed silica (SiO₂, Cabot Corporation), 2-adamantanone (98 %, Aladdin), cyclohexanone (99 %, Aladdin), 2-propanol (99.5 %, Macklin), hydrogen peroxide (H₂O₂, 30 %, Sinopharm Chemical Reagent Co., Ltd).

Hydrothermal synthesis of Zr-MWW zeolite. Zr-MWW zeolite was hydrothermally synthesized using TMAdaOH and HMI as co-structure-directing agents with the assistance of mineralization agent of K⁺. In a typical synthesis, HMI and K₂CO₃ were successively added in the TMAdaOH solution. After stirring for 10 min, ZrSO₄·4 H₂O was introduced into this mixture. Subsequently, the mixture was blended with fumed silica, giving rise to synthesis gel with the molar composition of 1.0 SiO₂ : 1/x ZrO₂ : 0.25 TMAdaOH : 0.31 HMI : 0.0375 K₂CO₃ : 44 H₂O (*x* represents the Si/Zr molar ratio). Aging for about 1 h, this gel was transferred into a PTFE-lined stainless steel autoclave and heat-treated at 423 K statically for 5 days. Afterwards, the as-synthesized lamellar precursor, denoted as Zr-MWW-*x*P, was obtained by filtration, washed with deionized water repeatedly, and drying at 373 K overnight. Zr-MWW-*x*P was directly calcined at 823 K for 6 h to afford Zr-MWW-*x*-C. On the other hand, to remove residual K⁺ and extra-framework Zr ions, Zr-MWW-*x*P was refluxed in a 2 mol/L HNO₃

solution with a liquid-to-solid weight ratio of 50 for 6 h, giving the acid-treated sample named Zr-MWW-*x*-A. Then, a subsequent calcination at 823 K for 6 h was performed on Zr-MWW-*x*-A to remove residual organics and further to form 3-dimensional framework, which was designed as Zr-MWW-*x*-AC.

Hydrothermal synthesis of Sn-MWW zeolite and control materials. The synthesis procedure for Sn-MWW zeolite was similar to that of Zr-MWW zeolite except that $SnCl_4 \cdot 5 H_2O$ was used as the stannum source.

For control experiment, Ti-MWW and Al-MWW were hydrothermally synthesized following well-established procedures reported previously.^{1,2} Siliceous MWW zeolite (Si-MWW or ITQ-1) was also synthesized according to the same procedure of Zr-MWW without adding metal source and K₂CO₃ into the synthesis gel. Impregnated ZrO₂/Si-MWW (SnO₂/Si-MWW) samples with a Si/Zr (Si/Sn) molar ratio of 100 were also prepared by stirring the mixture of Si-MWW and ZrSO₄·4H₂O (SnCl₄·5H₂O) with the liquid-to-solid weight ratio of 30 at room temperature for 3 h followed by drying at 353 K for 6 h and further calcination at 823 K for 6 h. Boron-containing Zr-MWW (denoted as Zr-B-MWW) and Sn-MWW (denoted as Sn-B-MWW) zeolites were hydrothermally synthesized with Si/metal molar ratio of 100 in the gels using boric acid and potassium hydroxide as crystallization-supporting agent and alkali source, respectively, according to the literatures reported previously.^{3,4} Similarly, an acid treatment before calcination was performed to remove K⁺ and extra-framework metal ions. Based on ICP analysis, the Si/Zr and Si/B molar ratio of Zr-B-MWW zeolite after the acid-calcination treatment were 119 and 59, respectively. The Si/Sn and Si/B molar ratio of Sn-B-MWW zeolite after the acid-calcination treatment were 125 and 65, respectively.

Characterizations

The X-ray diffraction (XRD) patterns were obtained from 2 to 35° on a Rigaku Smart Lab3 X-ray diffractometer with Cu-Ka radiation ($\lambda = 1.5405$ Å) at voltage and current of 35 kV and 25 mA, respectively. Scanning electron microscopy (SEM) images were recorded on a Zeiss Sigma 500 microscopy. The N2 adsorption-desorption isotherms were performed on a BELSORP-MAX instrument measured at 77 K after the sample was evacuated at 573 K for 5 h. The Si, Zr, and Sn contents were determined using inductively coupled plasma atomic emission spectrometer on a Thermo IRIS Intrepid II XSP. UV-visible (UV-vis) diffuse reflectance spectra were carried out on a TU-1901 spectrophotometer with the reference of BaSO₄. FT-IR spectra were measured on a Shimadzu IRAffinity-1S FT-IR spectrometer with a resolution of 4 cm⁻¹. After the zeolite material was compressed into a self-supported wafer, the wafer was then set in a quartz cell and sealed with CaF2 windows. The cell was connected to a vacuum system. The sample was dehydrated at 773 K for 2 h to remove any water in the material. Subsequently, the pyridine adsorption was realized by exposing the wafer to pyridine vapor at room temperature for 1 h. The FT-IR spectra were collected after the sample adsorbed pyridine was maintained at a specific temperature for 1 h. The thermogravimetric (TG) were took on a METTLER TOLEDO TGA/SDTA851e apparatus from room temperature to 1073 K with air atmosphere. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo K-Alpha equipped with a monochromatized aluminum X-ray source. The binding energies were calibrated with the C 1s peak at 284.8 eV. The ¹³C NMR spectra were measured on a VARIAN VNMRS 400WB NMR spectrometer with a 7.5 mm T3HX probe at 100.54 MHz and a spinning rate of 5 kHz.

Catalytic reactions

The catalytic performance was assessed in a 25 mL flask linked to a water condenser with appropriate stirring. In a typical run for the MPV reaction, cyclohexanone (1 mmol), 2-propanol (60 mmol), tetradecane (0.2 g, internal standard), and catalyst (75 mg) were stirred in the flask at 373 K for desired time. In the conversion of 2adamantanone, the flask was charged with 2-adamantanone (2 mmol), H_2O_2 (30 %, 4 mmol), chlorobenzene (10 mL), and catalyst (50 mg). The reaction mixture was kept at 363 K for desired time. Thereafter, for all reactions, the reaction system was immediately cooled down with the ice bath, centrifuged to remove the catalyst, and quantitatively analyzed employing a gas chromatograph (FuLi 9750, FID detector; HP-5 capillary column, 30 m). These organics were distinguished by a GC-MS instrument (Agilent-6890GC/5973MS).

Results and discussion

Table S1 Textural properties of metallosilicates with MWW structure

Samula	Si/metal ratio		Pore volume (cm ³ g ⁻¹)		$SSA^d (m^2 g^{-1})$	
Sample	Gel	Product ^a	$V_{micro}{}^{b}$	V _{ext} ^c	S_{BET}^{e}	$S_{ext}{}^{b}$
Zr-MWW-100P	100	102	-	-	-	-
Zr-MWW-100-AC	100	113	0.14	0.04	492	95
Zr-MWW-150P	150	148	-	-	-	-
Zr-MWW-150-AC	150	161	0.15	0.04	500	93
Sn-MWW-100P	100	101	-	-	-	-
Sn-MWW-100-AC	100	115	0.13	0.06	496	119
Sn-MWW-150P	150	151	-	-	-	-
Sn-MWW-150-AC	150	166	0.14	0.06	503	122

^{*a*} Determined by ICP analysis.

^{*b*} Calculated by *t*-plot method.

 c V_{ext} = V_{total} (calculated by BET method) – V_{micro}.

^dSSA, specific surface area, determined by N₂ adsorption at 77 K.

^{*e*} Calculated by BET method.

As shown in Table S1, the metal content in the precursor was approximately equal to that in the synthetic gels. After the acid treatment and further calcination, the increase of Si/metal molar ratio was observed, indicating partial loss of metal species. The micropore volume and specific surface area for both Zr-MWW and Sn-MWW zeolites were about 0.14 cm³ g⁻¹ and 495 m² g⁻¹, respectively, indicative of a high crystallinity. The external surface area and external volume of Sn-MWW-100-AC and Sn-MWW-150-AC were higher as compared to those of Zr-MWW-100-AC and Zr-MWW-150-AC zeolite perhaps due to the disordered arrangement of MWW layers as discussed in Fig. 1 and Fig. S10.

Sampla	Mass co	ontent (%)	C/N (mol/mol)	
	Ν	С		
Zr-MWW-100P	1.81	17.83	11.49	
Zr-MWW-100-A	1.20	7.82	7.60	

Table S2 Chemical composition of Zr-MWW-100 zeolite

CN elemental analysis was also performed to study the chemical composition of Zr-MWW-100 zeolite. The as-synthesized Zr-MWW-100P possessed C/N molar ratio of 11.49, suggesting that the organics including about 80 % TMAdaOH (C/N = 13) and 20 % HMI (C/N = 6) were occluded in MWW zeolite. After acid treatment, the C/N molar ratio varied from 11.49 to 7.6, which was very close to that of HMI. It had been reported that bulky TMAdaOH and HMI existed in interlayer region and intralayer 10membered ring for MWW zeolite precursor, respectively.⁵ It was inferred that most TMAdaOH organics were easily eliminated during the process of acid treatment.

	+	OH	Catalyst 373 K	ОН +	<u>+</u> (
	Cat		Conversion Selectivity (%)				TOF ^c
No.	No.	51/101*	(%)	cyclohexanol	alkene	others	(h ⁻¹)
1	Si-MWW (ITQ-1)	-	0	-	-	-	0
2	ZrO ₂ /Si-MWW	100	0	-	-	-	0
3	SnO ₂ /Si-MWW	100	0	-	-	-	0
4	Zr-B-MWW	119	89.3	96.2	0.5	3.3	9.6
5	Zr-MWW-100-AC	113	96.3	99.0	0.6	0.4	10.7
6	Zr-MWW-150-AC	161	61.1	99.4	0.3	0.3	9.8
7	Sn-B-MWW	125	72.5	91.3	0.7	8.0	7.6
8	Sn-MWW-100-AC	115	81.8	98.6	0.9	0.5	9.3
9	Sn-MWW-150-AC	166	45.0	99.1	0.6	0.3	7.3
10	Al-MWW	51	23.5	98.7	0.8	0.5	3.2
11	Ti-MWW	55	6.7	98.3	1.2	0.5	0.4

Table S3 Selective reduction of cyclohexanone with 2-propanol over different catalysts^a

^a Reaction conditions: cat., 75 mg; cyclohexanone, 1 mmol; 2-propanol, 60 mmol; temp., 373

K; time, 8 h.

^b Analyzed by ICP.

^c Moles of cyclohexanol formed hourly per mole of active sites in catalyst.

 Table S4 Baeyer-Villiger oxidation of 2-adamantanone with aqueous hydrogen peroxide over

 different catalysts^a

	+ H ₂ O ₂	Cat. 363 K	+ H ₂ O	
No.	Cat.	Si/M ^b	Conversion (%)	TOF^c (h^{-1})
1	Si-MWW	-	0	0
2	ZrO ₂ /Si-MWW	100	0.8	1.3
3	SnO ₂ /Si-MWW	100	1.2	1.9
4	Zr-B-MWW	119	35.4	63.9
5	Zr-MWW-100-AC	113	46.6	84.2
6	Zr-MWW-150-AC	161	38.2	98.4
7	Sn-B-MWW	125	51.5	94.7
8	Sn-MWW-100-AC	115	63.0	115.9
9	Sn-MWW-150-AC	166	48.7	129.3

^a Reaction conditions: cat, 25 mg; 2-adamantanone, 2 mmol; H₂O₂ (30 wt %), 4 mmol; chlorobenzene, 10 mL; temp., 363 K; time, 3 h.

^b Analyzed by ICP.

^c Moles of lactone formed hourly per mole of active sites in catalyst.

Zr-MWW and Sn-MWW zeolites were also applied to the Baeyer-Villiger oxidation of 2-adamantanone with aqueous hydrogen peroxide as oxidant. The selectivity of corresponding lactone was all close to 100 %. As shown in Table S4, when siliceous Si-MWW, Zr-impregnated ZrO₂/Si-MWW, and Sn-impregnated SnO₂/Si-MWW were utilized as catalysts, respectively, this reaction hardly proceeded (Nos. 1–3). A sharp increase of catalytic activities was observed with the addition of Sn-MWW or Zr-MWW catalyst, implying that the isolated metal species within zeolite framework may be the catalytic active sites. The catalytic performance of boron-free Zr-MWW-100-AC (conversion, 46.6 %; TOF, 84.2 h⁻¹) and Sn-MWW-100-AC (conversion, 63.0 %; TOF, 115.9 h⁻¹) zeolites were superior to those of boron-containing Zr-B-MWW (conversion, 35.4 %; TOF, 63.9 h⁻¹) and Sn-B-MWW (conversion, 51.5 %; TOF, 94.7 h⁻¹) zeolites under comparable Zr or Sn contents, which was probably ascribed to the weak acidity derived from the boron species in zeolite framework.⁶ Besides, with the metal contents increasing, the conversion was also enhanced. The catalytic activity of Sn-MWW was superior to that of Zr-MWW with comparable metal content.



Fig. S1 XRD patterns of as-made (a) Zr-MWW-100 and (b) Sn-MWW-100 without addition of K_2CO_3 into synthesis gel.

Zr-MWW and Sn-MWW zeolites could not be successfully synthesized without adding alkali metal ions such as K^+ into synthetic gels. This phenomenon indicated that the alkali metal ions were essential for the crystallization of MWW-type metallosilicates structure in particular containing large-sized heteroatoms. Alkalis metal ions in the synthesis gels was related to the silica dissolution, serving as mineralizers and stabilizing the negatively charged silica network at high pH.^{7,8}



Fig. S2 XRD patterns of as-made (a) Zr-MWW-100 and (b) Sn-MWW-100 with addition of Na_2CO_3 into synthetic gel.

As shown in Fig. S2, Zr-MWW and Sn-MWW zeolites were also smoothly obtained with addition of Na_2CO_3 into synthetic gel.



Fig. S3 ¹³C MAS NMR spectra of HMI-directed B-MWW (a), Zr-MWW-100P synthesized using TMAda⁺ and HMI (b), and TMAda⁺-directed Zr-free ITQ-1 silicate (c).

¹³C MAS NMR spectra were adopted to investigate the existing state of organic structure-directing agents (OSDA) of TMAda⁺ and HMI for the as-synthesized Zr-MWW zeolite (Fig. S3). As-made B-MWW zeolite hydrothermally synthesized with the OSDA of HMI exhibited chemical shift at 26.4 and 47.8 ppm, attributed to HMI molecule.⁵ C signals at 30.5, 34.7, 35.9, 47.9, and 73.8 ppm, associated with TMAda⁺ molecule,⁵ were obviously observed for Zr-free MWW zeolite (ITQ-1) synthesized using TMAda⁺ alone. Two bands indicated by arrows (Fig. S3c) was probably derived from the partial decomposition of the TMAda⁺. As-synthesized Zr-MWW-100P sample demonstrated evident resonance bands contributed by both TMAda⁺ and HMI, indicating that TMAda⁺ and HMI co-existed within Zr-MWW zeolite and their structures were preserved well in crystallization process.



Fig. S4 XRD patterns of (A) Zr-MWW and (B) Sn-MWW as-synthesized with Si/Sn ratio of 150 (a), 100 (b), 50 (c), and 30 (d).



Fig. S5 SEM images of Zr-MWW-50P (a), Zr-MWW-100P (b), Sn-MWW-50P (c), and Sn-MWW-100P (d).

Sn-MWW-100P and Zr-MWW-100P possessed a typical plate-like morphology, which was similar to Ti-MWW zeolite reported previously.¹ Nonetheless, numerous sponge-like substances adhering to plate, probably assigned to amorphous phase, were observed for Zr-MWW-50P and Sn-MWW-50P with a relatively high metal content in synthetic gels.



Fig. S6 UV-vis spectra of different samples. (A) Zr-MWW-100-AC (a) and Zr-MWW-150-AC (b); (B) Sn-MWW-100-AC (a) and Sn-MWW-150-AC (b).

The Zr and Sn species in MWW zeolite mainly existed in tetrahedrally coordination states after acid-calcination treatment.



Fig. S7 (A) Zr 3d XPS spectra of dehydrated Zr-MWW-100-AC (a) and Zr-MWW-150-AC (b); (B) Sn 3d XPS spectra of dehydrated Sn-MWW-100-AC (a) and Sn-MWW-150-AC (b).

XPS spectroscopy is an effective method for identifying the coordinate states of transition metal ions in metallosilicates.^{9,10} Fig. S7 shows Zr and Sn 3d XPS spectra of dehydrated Zr-MWW and Sn-MWW samples, respectively. Both Zr-MWW-100-AC and Zr-MWW-150-AC zeolites exhibited two bands at approximate 183.0 (Zr $3d_{5/2}$) and 185.4 eV (Zr $3d_{3/2}$), associated with tetrahedrally coordinated Zr species in the zeolite framework.⁹ Sn-MWW-100-AC and Sn-MWW-150-AC samples demonstrated signals centered at 487.7 ($3d_{5/2}$) and 496.2 eV ($3d_{3/2}$), indicative of the Sn species in zeolite framework.¹⁰ Additionally, no evident signals related to extra-framework metal species were found in these spectra. These results suggested that Zr or Sn ions were isomorphously substituted in the MWW-type zeolite framework.



Fig. S8 FT-IR spectra of (A) Zr-MWW-100-AC and (B) Sn-MWW-100-AC at room temperature (a) and after the evacuation at 823 K for 2 h (b).



Fig. S9 TG curves of as-made (a) and further acid treated (b) Zr-MWW-100 (A) and Sn-MWW-100 (B).

The weight loss below 450 K was attributed to physically adsorbed water, while that ranging from 450 to 1050 K was mainly caused by the organics removal.⁴ The assynthesized Zr-MWW-100P and Sn-MWW-100P precursor demonstrated 19.7 and 18.3 % weight loss of organics, respectively. After acid treatment, the weight loss of organics decreased (Zr-MWW-100A, 17.1 %; Sn-MWW-100A, 13.4 %) in comparison with precursor, indicating partial elimination of organics occluded in zeolite via acid treatment.



Fig. S10 XRD patterns of boron-containing Zr-B-MWW (a) and Sn-B-MWW (b) zeolites after acid-calcination treatment.

As shown in Fig. S10, both boron-containing Zr-B-MWW (Fig. S10a) and boron-free Zr-MWW (Fig. 2Ac) zeolites possessed 3-dimensional MWW topology structure. The structure of MCM-56 or SSZ-70 analogues was observed for boron-free Sn-MWW (Fig. 2Bc), indicating disordered arrangement of MWW layers, which was different from that of boron-containing Zr-B-MWW with typical 3-dimensional MWW topology structure.



Fig. S11 (A) Dependence of conversion (a) and selectivity (b) on strength of Lewis acid in MPV reaction of cyclohexanone. (B) Dependence of conversion (a) and selectivity (b) on strength of Lewis acid in B-V oxidation of 2-adamantanone. (C) Dependence of conversion (a) and selectivity (b) on the density/strength value in MPV reaction of cyclohexanone. (D) Dependence of conversion (a) and selectivity (b) on density of Lewis acid in B-V oxidation.

As shown in Fig. S11, no obvious correlation between conversion and strength was observed. With respect to MPV reaction, with the density/strength value increased, the conversion of cyclohexanone enhanced, indicating that the catalytic activity was affected by both density and strength of Lewis acid. With regard to B-V oxidation, the conversion of 2-adamantanone increased linearly with the enhancement of Lewis acid density, indicative of close relationship between catalytic activity and density of Lewis acid.

Notes and references

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