catalysts

Supplementary Material: Nanosheet MFI zeolites for gas phase glycerol dehydration to acrolein

Jianfeng Shan[1,2,†], Zhikai Li[1,†], Shanhui Zhu[1,*], Huan Liu[1,2], Junfen Li[1], Jianguo Wang[1], and Weibin Fan[1,*]

S1. Experimental details

The organic surfactant $C_{18\text{-}6\text{-}6}Br_2$ was synthesized as follows: 0.03 mol 1-bromodocosane (TCI) and 0.30 mol N,N,N',N'-tetramethyl-1,6-diaminohexane (Aldrich) were dissolved in 300 mL toluene/acetonitrile mixture (1:1 volume ratio) and reacted under electromagnetic stirring at 70 °C for 10 h. After cooling to room temperature, the resulting mixture was filtered, washed with diethylether, and dried at 60 °C in a vacuum oven. The obtained product (0.03 mol) was mixed with 100 mL acetonitrile, and then 9.9 g (0.06 mol) 1-bromohexane (Aldrich) was added with 10 h reflux. After cooling to room temperature, the product was filtered, washed with diethylether, and dried in a vacuum oven at 60 °C. Subsequently, the nanosheet MFI zeolites were synthesized under hydrothermal conditions using the above template. Deionized water, H_2SO_4, NaOH, $Al_2(SO_4)_3{\cdot}18H_2O$, $C_{18\text{-}6\text{-}6}Br_2$ and tetraethylorthosilicate (TEOS) were mixed to get a gel with a composition of 30 Na_2O: x Al_2O_3: 100 SiO_2: 10 $C_{18\text{-}6\text{-}6}Br_2$: 18 H_2SO_4: 4,000 H_2O. The crystallization process was performed in a Teflon-lined stainless-steel autoclave at 150 °C for 5 days under autogenous pressure with the autoclave setting to tumbling at 15 r.p.m [1,2]. After that, the solid products were separated by centrifugation, washed 3 times with deionized water and dried at 100 °C overnight. To remove the template, the obtained zeolites were calcined in air at 550 °C for 5 h. Nanosheet MFI zeolites with Si/Al molar ratios as 30, 50, 100 (the atomic ratio of silicon to aluminum in the synthesis gel) were synthesized by changing the Al content as x = 1.65, 1 and 0.5. For the conventional MFI zeolites, sodium aluminate ($NaAlO_2$), NaOH, TPAOH and silica sol (40 wt.% SiO_2, 4 wt.% Na_2O) were added into deionized water in sequence with constant stirring, and then a certain amount of silicalite-1 seeds were added. The obtained gels were transferred into Teflon-lined stainless-steel autoclaves and crystallized at 170 °C for 48 h. The solid products were then separated, washed, dried and calcined with the same procedure in the synthesis of nanosheet MFI zeolites. To get H-form zeolites, all the zeolites obtained above were ion-exchanged with 1 M NH_4NO_3 solution at 80 °C two times over 8 h. After ion-exchange, the zeolites were washed and dried, followed by calcination at 550 °C for 5 h. Before use, H-form zeolite powders were pressed, crushed and sieved to 20–40 mesh.

S2. Figures and Tables

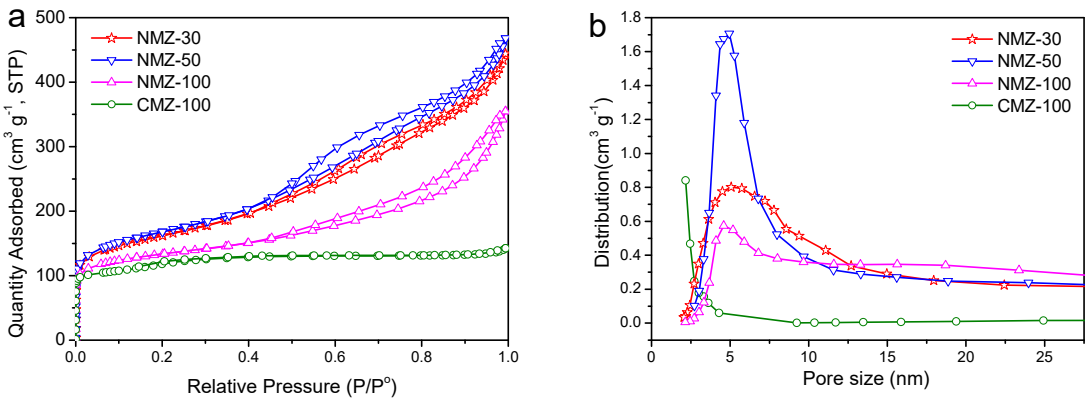

Figure S1. (a) N_2 adsorption-desorption isotherms at −195.8 °C and (b) pore size distribution.

Table S1. Overall acidic properties of different zeolite catalysts.

Sample	Acidity by NH_3-TPD[a] (μmol g^{-1})			Acidity by Py-IR (μmol g^{-1})			
	total	weak	strong	total	Brønsted	Lewis	B/L
NMZ-30	412	215	197	384	238	146	1.63
NMZ-50	279	97	182	260	182	78	2.33
NMZ-100	178	44	134	116	83	33	2.51
CMZ-50	295	109	186	258	179	79	2.27
CMZ-100	189	50	139	104	74	30	2.47
CMZ-150	148	35	113	72	52	20	2.60

[a]Quantities of weak and strong acid sites determined at peaks in 120–250 and 250–550 °C by NH_3-TPD, respectively.

Table S2. Summary of the infrared band assignments.

Mode	Frequency (cm^{-1})	Adsorbed species	Ref.
νC=O	1728	Acrolein and acetol	3,4
νC=C	1671	Acrolein	3,4
δCH_2	1462	Glycerol	5
δOH	1410	Glycerol	5
δCH	1345	Glycerol	5

Table S3. Coke content of used catalysts and coresponding coke deposition rate.

Sample	TOS (h)	Coke content[a] (%)	Coke deposition rate[b] (g_{coke} g_{cat}^{-1} h^{-1})
NMZ-30	24	28.8	$16.8*10^{-3}$
NMZ-100	24	17.4	$8.8*10^{-3}$
CMZ-100	10	10.2	$11.4*10^{-3}$
CMZ-150	9	8.0	$9.7*10^{-3}$

[a]Coke contents were calculated from TG profiles of used catalysts (the catalysts were collected after glycerol conversion decreased to about 80%).

[b]Coke deposition rate was calculated with the following formula:

Coke deposition rate= 1/(1-Coke content)×Coke content/TOS

References

1. Choi, M.; Na, K.; Kim, J.; Sakamoto, Y.; Terasaki, O.; Ryoo, R. Stable single-unit-cell nanosheets of zeolite MFI as active and long-lived catalysts. Nature **2009**, 461, 246-249.
2. Na, K.; Choi, M.; Park, W.; Sakamoto, Y.; Terasaki, O.; Ryoo, R. Pillared MFI zeolite nanosheets of a single-unit-cell thickness. J. Am. Chem. Soc. **2010**, 132, 4169-4177.
3. Yi, X.D.; Zhang, X.B.; Weng, W.Z.; Wan, H.L. Studies on the reaction pathways for the selective oxidation of propane to acrolein over MoPO/SiO2 catalyst by IR spectroscopy. J. Mol. Catal. A: Chem. **2007**, 277, 202-209.
4. Ravenelle, R.M.; Copeland, J.R.; Pelt, A.H.V.; Crittenden, J.C.; Sievers, C. Stability of Pt/gamma-Al2O3 Catalysts in Model Biomass Solutions. Top Catal. **2012**, 55, 162-174.
5. Copeland, J.R.; Foo, G.S.; Harrison, L.A.; Sievers, C. In situ ATR-IR study on aqueous phase reforming reactions of glycerol over a Pt/gamma-Al2O3 catalyst. Catal. Today **2013**, 205, 49-59.