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Cascade reaction engineering on Zirconia-supported mesoporous MFI zeolites with tunable Lewis-Brønsted acid sites: A case of the one-pot conversion of furfural to γ-valerolactone

Kyung Duk Kim,[1] Jaeheon Kim,[1] Wey Yang Teoh,[2] Jeong-Chul Kim,[1] Jun Huang,[3] Ryong Ryoo[1,4*]

[1]Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon 34141, Korea;

[2]School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

[3]Laboratory for Catalysis Engineering, School of Chemical and Biomolecular Engineering, Sydney Nano Institute, The University of Sydney, NSW 2006, Australia

[4]Department of Chemistry, KAIST, Daejeon, 34141, Republic of Korea;

[*] Corresponding author. Email: rryoo@kaist.ac.kr

Supporting information

Synthesis of zeolites

ZrO_2-MFI nanosponge (designated hereafter as MFI-NS)

MFI-NS was synthesized according to a process in the literature [1]. Briefly, $[C_{18}H_{37}\text{-}N^+(CH_3)_2\text{-}(CH_2)_6\text{-}N^+(CH_3)_2\text{-}C_6H_7][Br\text{-}]_2$ was used as an surfactant-directing agent (SDA) in this synthesis. aluminum sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$, 97%, Sigma-Aldrich] was used as the alumina source, aqueous sodium silicate solution (SiO_2 27.5 wt%, Si/Na = 1.75, Shinheung Chemical) as the silica source and commercial MFI zeolite (CBV-8014, Zeolyst) as the seed crystals. An aqueous solution of sodium silicate was added dropwise under magnetic stirring to an aqueous solution containing SDA and aluminum sulfate. Then, the resultant white gel was aged at 60 °C under magnetic stirring. After aging, the pH of the resultant gel was adjusted to approximately 10 by adding 10 wt% of a sulfuric acid aqueous solution dropwise under magnetic stirring. To the mixture, the commercial MFI zeolite amounting to 5 wt% of total silica was added as seed crystals, and the resultant mixture was subsequently aged for 1 d at 60 °C under magnetic stirring. The final gel composition at a molar ratio was 100 SiO_2/ n Al_2O_3/ 7.5 SDA/ 30 Na_2O/ 18 H_2SO_4/ 5000 H_2O, where n ranges from 0.284 to 1. The resulting zeolite powder was collected by filtration/drying and calcined at 550 ^oC. The calcined zeolites underwent ion exchange with NH_4^+ in an aqueous solution of 1 M NH_4NO_3 and were then calcined again in air at 550 ^oC to convert the exchanged NH_4^+ ions to H^+.

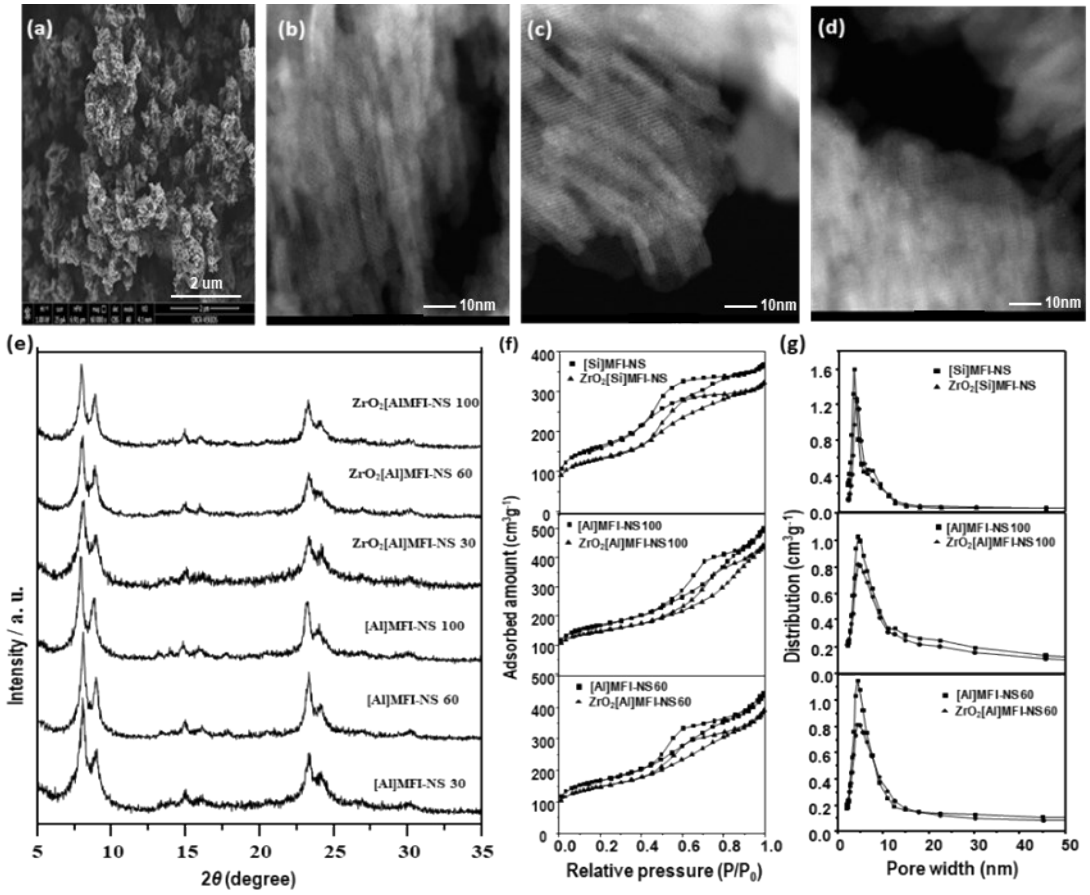
Bulk MFI zeolite

The bulk crystalline MFI zeolite was prepared using tetrapropylammonium hydroxide (TPAOH, 30 wt%, Junsei) as the structure-directing agent (SDA) [2]. Tetraethylorthosilicate (TEOS, 95%, Junsei) was used as the silica source and sodium aluminate was used as the

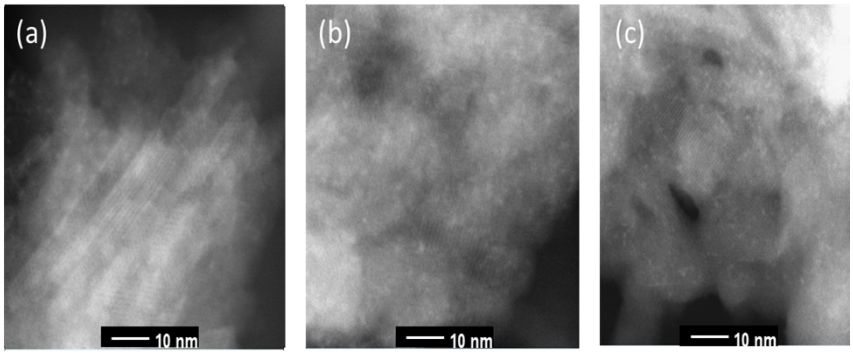
alumina source. In a typical synthesis, an amount of 0.20 g of sodium aluminate (53 wt% Al_2O_3, 41 wt% Na_2O, Sigma-Aldrich) was added to 85 ml of a 0.16 M aqueous solution of TPAOH with the resultant solution then stirred at 60 °C for 12 h. To this solution, 12.50 g of TEOS was added at once. The mixture was shaken vigorously by hand for 15 min and aged under magnetic stirring at room temperature for 12 h. The resultant clear solution had the following molar composition: 6 SiO_2/0.042 Al_2O_3/1 TPAOH/460 H_2O. The clear mixture was heated in a Teflon-lined autoclave at 170 °C for 2 d under static conditions.

Beta zeolite

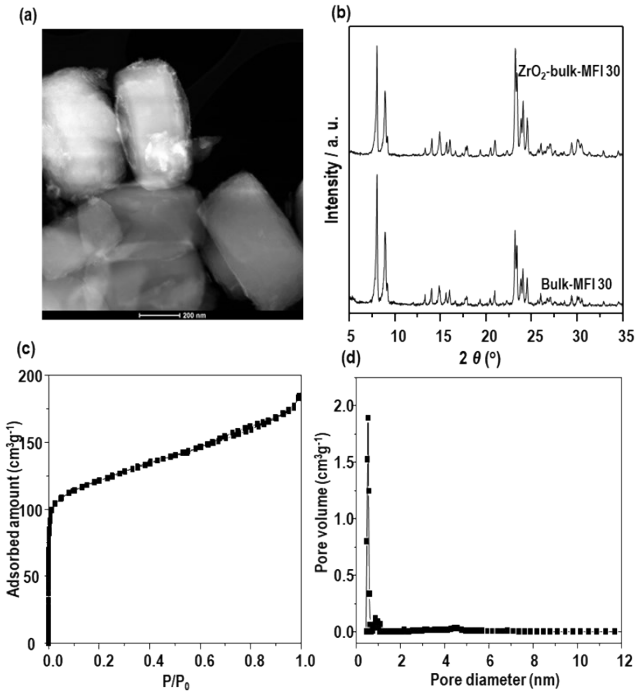
Al-Beta zeolite (Zeolyst CP814E, Si/Al =25) was used as a parent support. Partial dealumination was carried out by a treatment in a nitric acid solution (6.5 M HNO_3, 25 ^oC, 20 mL^{-g}) (60% aq. HNO_3, Sigma-Aldrich). After washing with deionized water and centrifugation, the resulting product was dried at 100^oC overnight. Thereafter, zirconium incorporation was accomplished by the process described above.



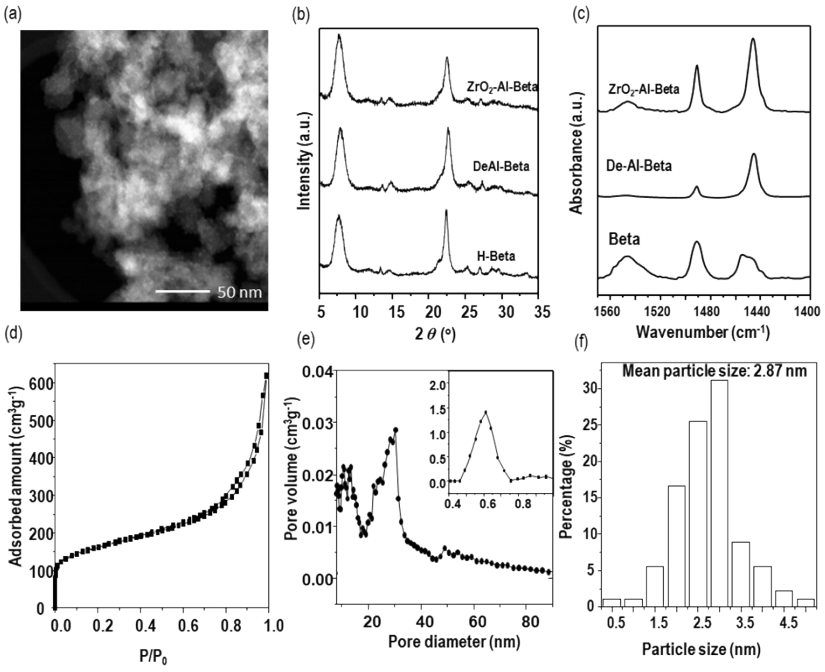
SFigure 1. a) SEM image of the MFI-NS zeolite, (b) STEM images of [Si]MFI-NS, (c) [Al]MFI-NS 60, (d) [Al]MFI-NS 100, (e) XRD pattern before/after loading of the ZrO_2 particles onto the zeolites, (f) Ar adsorption–desorption isotherm, and (g) pore size distribution of the MFI zeolite nanosponge



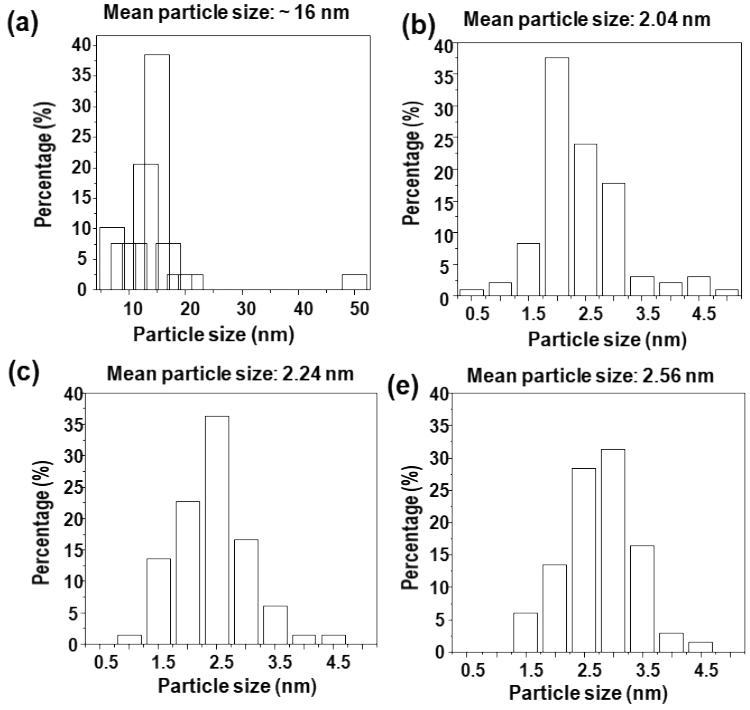
SFigure 2. STEM images of (a) ZrO_2-[Si]MFI-NS (b) ZrO_2-[Al]MFI-NS 60 and (c) ZrO_2-[Al]MFI-NS 100



SFigure 3 (a) STEM images of the Bulk MFI 30 zeolite, (b) XRD patterns before/after loading of the ZrO_2 particles, (c) Ar adsorption–desorption isotherm, and (d) pore size distribution of Bulk MFI 30

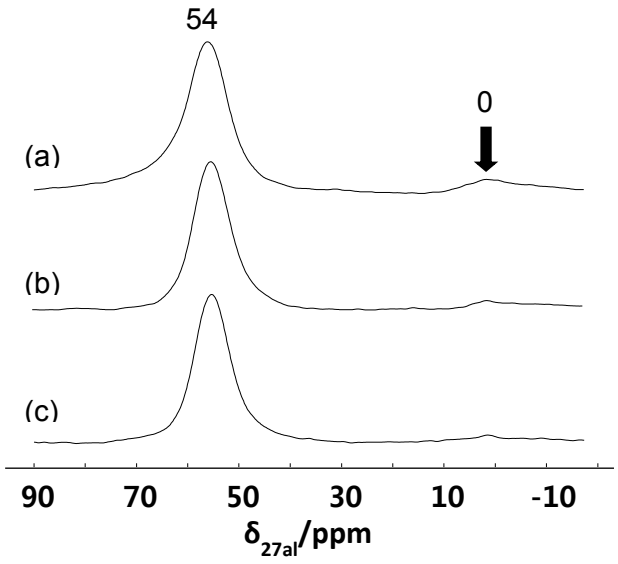


SFigure 4 (a) STEM image of the ZrO_2-Al-Beta zeolite, (b) XRD patterns and (c) Pyridine-FTIR spectra before/after loading of the ZrO_2 particles, (d) Ar adsorption–desorption isotherm, (e) pore size distribution and (f) Particle distribution and mean particle size over ZrO_2-Al-Beta



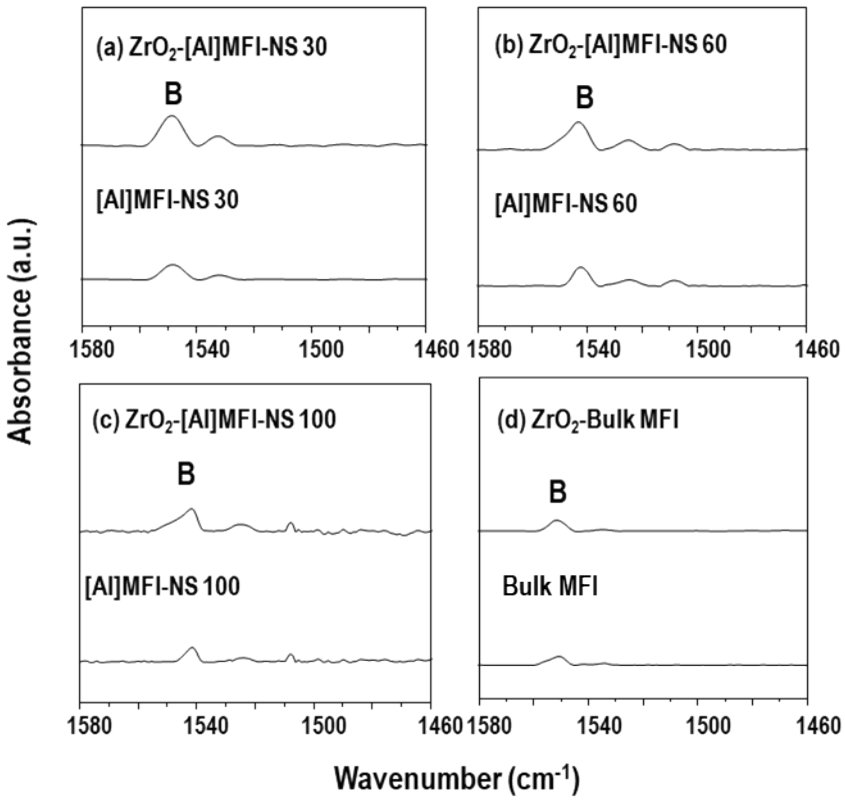
SFigure 5. Particle distribution and mean particle size over (a) ZrO_2-Bulk MFI 30, (b) ZrO_2-[Al]MFI-NS 30, (c) ZrO_2-[Al]MFI-60, and (d) ZrO_2-[Al]MFI-NS 100

The nanoparticle diameters were estimated using Digital Micrograph software distributed by Gatan via several TEM images showing more than 100 ZrO_2 particles overall.

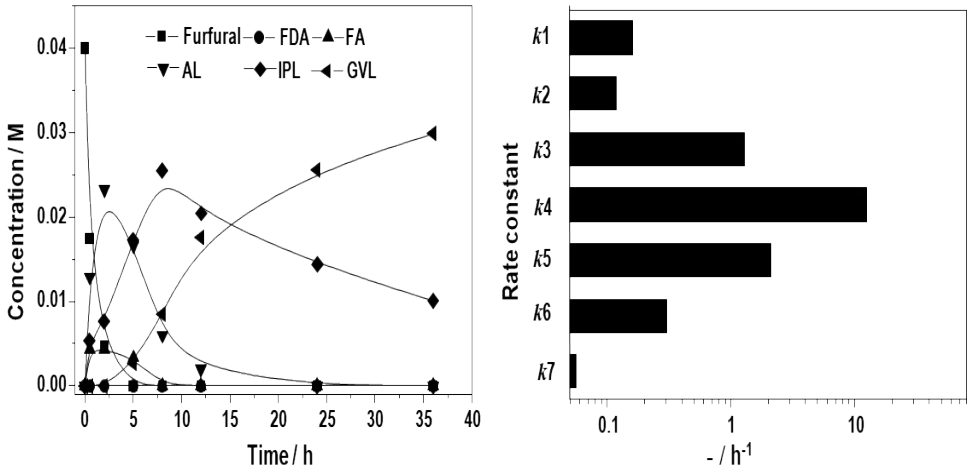


SFigure 6. ^{27}Al MAS NMR spectra of (a) [Al]MFI-NS 30, (b) [Al]MFI-NS 60, and (c) [Al]MFI-NS 100

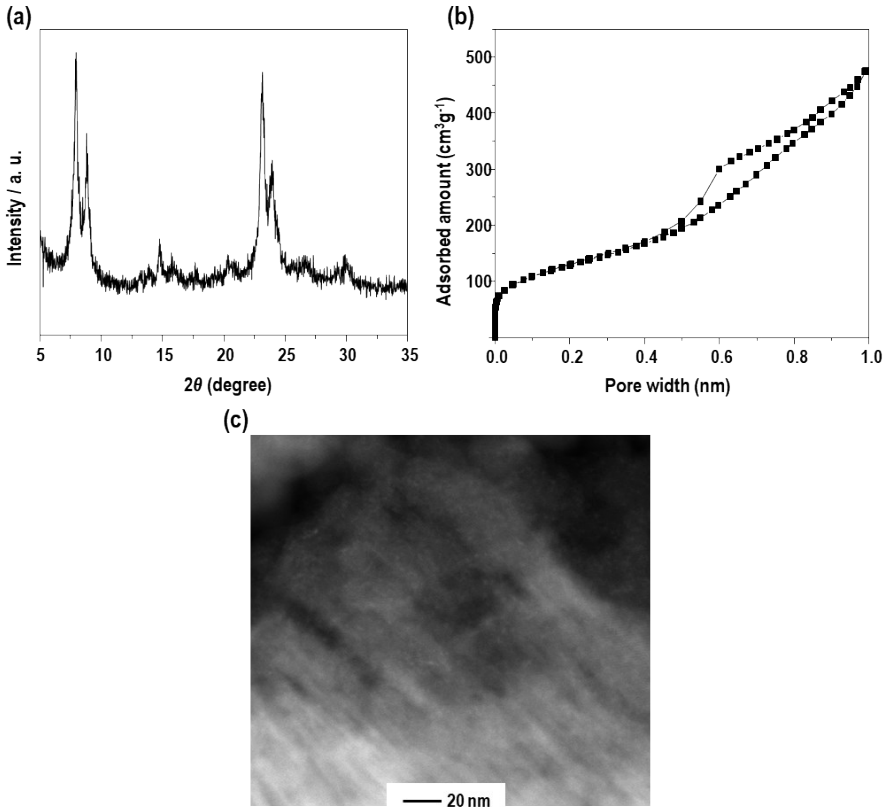
The main peak at 54 ppm is assigned to tetrahedrally coordinated aluminum (Al^{IV}) in the framework.. The weak peak shown at 0 ppm is due to the formation of octahedrally coordinated aluminum (Al^{VI}), an extra-framework as a function of the Lewis acid sites.



SFigure 7. 2,6-di-tertbutylpyridine-FTIR spectra of (a) ZrO_2-MFI-NS 30, (b) ZrO_2-MFI-NS 60 and (c) ZrO_2-MFI-NS 100 before and after deposition with ZrO_2, (d) ZrO_2-Bulk-MFI 30



SFigure 8. Kinetic plots of furfural, the product GVL and other intermediates (left) and the estimated pseudo-first order rate constants based on the mechanism in Scheme 1 (right) for ZrO_2-Al-Beta



SFigure 9 (a) XRD patterns, (c) Ar adsorption–desorption isotherm, and (d) STEM images of the ZrO_2-[Al]MFI-NS 30 after fourth recyclable reaction.

STable 1. Furfural conversion and product yields of large-scale catalytic reaction for ZrO_2[Al]MFI-NS 30

Catalyst	Furfural conversion (%)	Yield (mol%)				
		GVL	FA	AL	IPL	FDA
ZrO_2[Al]MFI-NS 30	100	78.4	0	0	21.6	

[a] Reaction condition: 170 ^{o}C, 36 h; 0.04 M furfural in a 1 : 50 molar ratio of furfural to 2-propanol solution (2-propanol as solvent and hydrogen donor),. catalysts loading 10 g_{catal} L^{-1}, 1 g of catalysts

STable 2. Furfural conversion and product yields of Nafion[a]

Catalyst	Furfural conversion (%)	Yield (mol%)				
		GVL	FA	AL	IPL	FDA
Nafion	30	0	0	0	0	30

[a] Reaction condition: 170 ^{o}C, 36 h; 0.04 M furfural in a 1 : 50 molar ratio of furfural to 2-propanol solution (2-propanol as solvent and hydrogen donor),. catalysts loading 10 g_{catal} L^{-1}

STable 3 Pseudo first-order reaction rate constants (ki) of the modelled overall reaction of furfural in 2-propanol over the prepared catalysts. See Scheme 1for the reaction steps.

Catalyst		ZrO_2 [Si]MFI-NS	ZrO_2 [Al] MFI-NS 30	ZrO_2 [Al] MFI-NS 60	ZrO_2 [Al] MFI-NS 100	ZrO_2 Bulk MFI 30	Physical mixture	ZrO_2-Al Beta
k_i/h^{-1}	1	0.10	0.10	0.12	0.17	0.62	0.14	0.16
	2	0.02	0.03	0.06	0.10	1.19	0.38	0.12
	3	0.61	2.90	1.97	1.79	0.02	0.08	1.27
	4	0.01	13.28	35.71	44.97	73.86	5.49	12.42
	5	0.00	0.02	0.01	0.51	0.06	0.01	2.10
	6	0.01	0.16	0.11	0.10	0.01	0.09	0.30
	7	0.01	0.12	0.11	0.08	0.00	0.12	0.06

1. Kim, J., J. Chun, and R. Ryoo, *MFI zeolite nanosheets with post-synthetic Ti grafting for catalytic epoxidation of bulky olefins using H2O2.* Chemical Communications, 2015. **51**(66): p. 13102-13105.
2. Kim, W. and R. Ryoo, *Probing the Catalytic Function of External Acid Sites Located on the MFI Nanosheet for Conversion of Methanol to Hydrocarbons.* Catalysis Letters, 2014. **144**(7): p. 1164-1169.