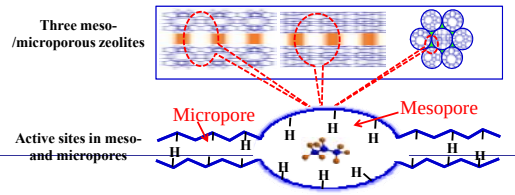
Synthesis and Mechanistic Characterization of Meso-/microporous MWW and MFI Zeolites

Dongxia Liu

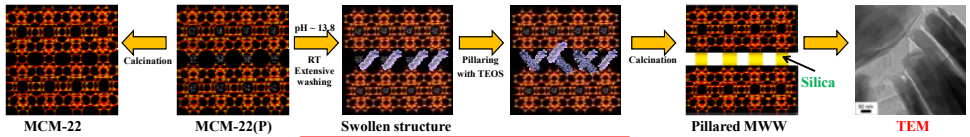
Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD, 20742

Overview: *Three meso-/microporous zeolites (pillared MWW, pillared MFI, and 3DOm-i MFI) were synthesized and their catalytic behavior was studied using ethanol dehydration, monomolecular conversion of propane, and alkylation of benzyl alcohol with mesitylene as probe reactions. The rate and apparent activation energy of the catalytic ethanol and propane probe reactions in zeolites possessing dual micro- and mesoporosity was comparable to conventional microporous analogues, implying that the catalytic behavior of Brønsted acid sites in meso-/microporous zeolites is preferentially dominated by the microporous environment possibly because it provides a better fit for adsorption of small alkane or alcohol reactant molecules. The apparent rate of the catalytic conversion of benzyl alcohol in meso/micro-porous zeolites was higher than that of the microporous zeolite materials, revealing the important role of the mesoporosity in space-demanding catalytic reactions.*



Synthesis and textural property characterizations

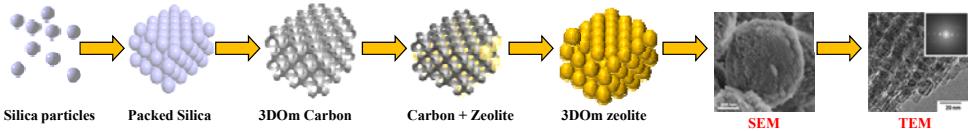
❑ Schematic illustration of synthesis of pillared MWW zeolite



[1] S. Maheshwari, et al., J. Am. Chem. Soc. ***2008****, 130, 1507.*

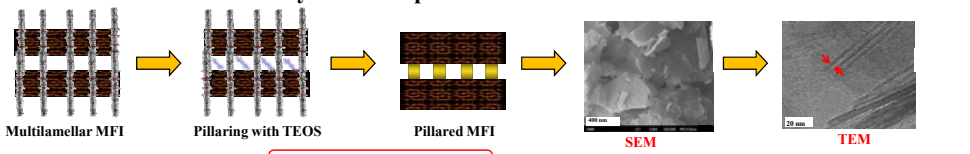
Hexamethyleneimine Cetyltrimethylammonium bromide

❑ Schematic illustration of synthesis of 3DOm-i MFI zeolite



[1] W. Fan, et al., Nat. Mater., ***2008****, 7, 984.*

❑ Schematic illustration of synthesis of pillared MFI zeolites

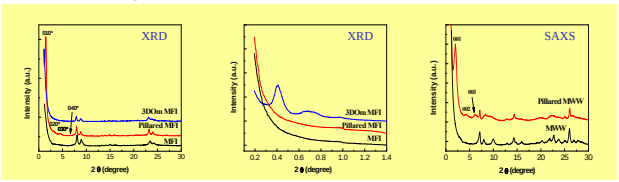


[1] K. Na, et al., J. Am. Chem. Soc. ***2010****, 132, 4169.*

$C_{22}H_{45}$-$N^+(CH_3)_2$-C_6H_{12}-$N^+(CH_3)_2$-C_6H_{13}

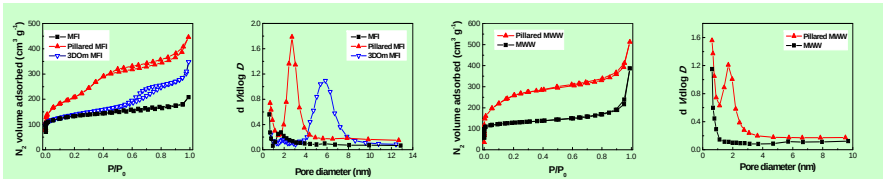
❑ Properties of meso-/microporous MWW and MFI zeolites

(a) XRD and SAXS patterns



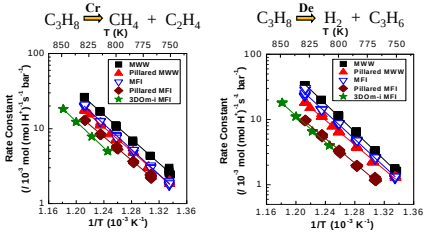
Zeolite	Cumulative pore vol (cc/g)	Micropore vol (cc/g)	Mesopore size (nm)	Si/Al ratio	Brønsted acid sites (mmol/g)
MWW	0.20	0.13	-	15	0.55
Pillared MWW	0.38	0.12	1.8	20	0.32
MFI	0.20	0.13	-	43	0.41
3DOm-i MFI	0.28	0.12	6.0	64	0.20
Pillared MFI	0.31	0.11	2.8	71	0.22

(b) N_2 isotherms and pore size distribution



Catalytic behaviour of Brønsted acid sites

❑ Propane cracking (Cr) and dehydration (De) reactions (~3kPa reactant pressure, less than 2% conversion)



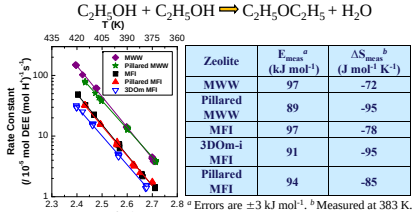
Zeolite	E_{meas} (kJ mol^{-1}) Cr[a]	E_{meas} (kJ mol^{-1}) De[b]	k_{meas} (x10^3) @773 K (mol (mol H$^+$)$^{-1}$s^{-1}bar^{-1}) Cr	k_{meas} (x10^3) @773 K (mol (mol H$^+$)$^{-1}$s^{-1}bar^{-1}) De	Cr/De ratio
MWW	160	202	5.8	4.8	1.2
Pillared MWW	159	180	3.9	3.1	1.3
MFI	164	200	3.8	3.5	1.1
3DOm-i MFI	160	186	1.9	1.2	1.6
Pillared MFI	155	183	3.0	1.7	1.7

[a] Errors are ±7 kJ mol^{-1}. [b] Errors are ±8 kJ mol^{-1}.

* Similar E_{meas} and k_{meas} indicate similar catalytic behavior across zeolites with different meso-/microporosity.

❑ Ethanol dehydration reaction and base titration

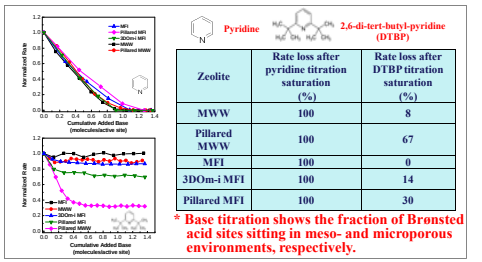
(369 K-418 K, ~3 kPa reactant pressure, less than 2% conversion)



Zeolite	E_{meas}[a] (kJ mol^{-1})	ΔS_{meas}[b] (J mol^{-1} K^{-1})
MWW	97	-72
Pillared MWW	89	-95
MFI	97	-78
3DOm-i MFI	91	-95
Pillared MFI	94	-85

[a] Errors are ±3 kJ mol^{-1}. [b] Measured at 383 K.

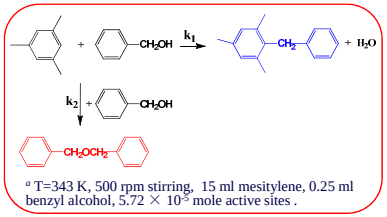
* Similar E_{meas} and ΔS_{meas} indicate similar catalytic behavior across different meso/microporous zeolites.



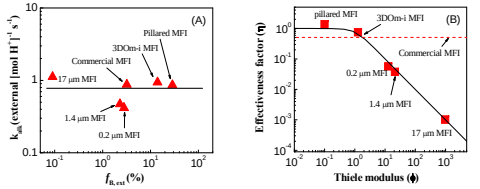
Zeolite	Rate loss after pyridine titration saturation (%)	Rate loss after DTBP titration saturation (%)
MWW	100	8
Pillared MWW	100	67
MFI	100	0
3DOm-i MFI	100	14
Pillared MFI	100	30

* Base titration shows the fraction of Brønsted acid sites sitting in meso- and microporous environments, respectively.

❑ Catalytic conversion of benzyl alcohol in mesitylene over MFI zeolites



[a] T=343 K, 500 rpm stirring, 15 ml mesitylene, 0.25 ml benzyl alcohol, 5.72 × 10^{-5} mole active sites .



(A) External alkylation (B) Internal etherification

* External alkylation rate constant is invarient with zeolite crystallite sizes;
Intenral etherification rate scales with crystalliete sizes consistent with Thiele concept.

1. Liu, D.; Bhan, A.; Tsapatsis, M.; Hashimi, S. A. ACS Catalysis, 2011, 1, 7-17.
2. Zhang, X.; Liu, D.; Bhan; A.; Tsapatsis, M.; et al., Science, in press.