# Copper-exchanged large-port and small-port mordenite (MOR) for methane-to-methanol conversion

*Elemental Analysis*

Copper (Cu), aluminum (Al), and silicon (Si) content was determined using SpectraAA 220FS atomic absorption spectrometer. 10 mg of dried zeolite was digested in 2 ml of concentrated hydrofluoric acid and 3 ml of concentrated nitric acid overnight and then diluted to 50ml with deionized water. Copper, aluminum, and silicon calibration curves were prepared from standard solutions.

*Gas physisorption*

Zeolite samples were pretreated by heating under vacuum to 250° C overnight. The samples evaluated by nitrogen physisorption on Micromeritics Tristar II 3020 instrument

*Methane to methanol reaction testing*

Zeolite samples were sieved to 150-250 μm. Approximately 0.5 grams of samples were loaded into stainless steel autoclave (Premex Reactor Ag).  Samples were activated (ramp rate of 10 k/min) at 723 K under pure $O_2$ flow for 1 hour with approximately 25mL/min.  Prior to reaction, the system was purged for 15 minutes in pure helium. Pure methane was then introduced at 1 bar into the reactor and kept for 30 minutes.

*Methanol Quantification*

Methanol was extracted off-line by adding 2 ml of deionized water to yield an aqueous suspension that was stirred for 30 minutes. The sample was then filtered, and analysis was performed on the filtered liquid with a gas chromatograph (Agilent 6890GC equipped with an FID detector). Butanol was added as an external standard after filtration but prior to GC analysis. Calibration curves were obtained with different mixture of methanol and butanol in water. For a second extraction, the filter cake was re-suspended in 2 ml of deionized water and stirred for 30 minutes.

*Toluene adsorption setup*
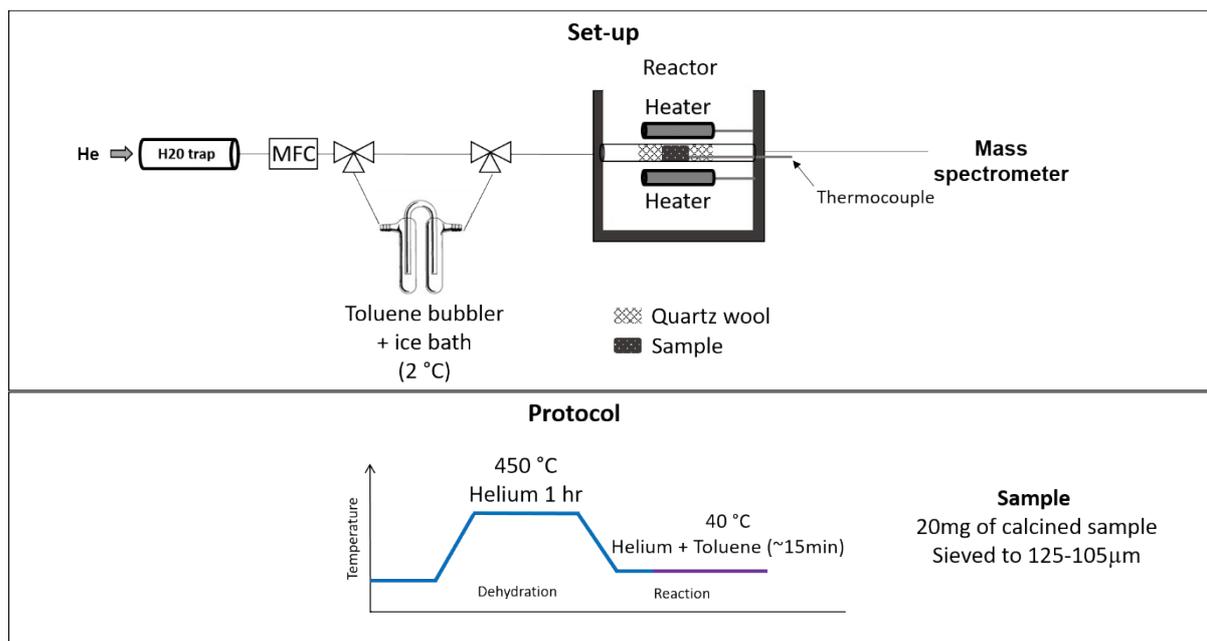
Figure 1: Diagram of toluene adsorption setup and the temperature profile protocol

*Toluene adsorption calculations*

The toluene adsorption capacity, $q_{toluene}$ *[g-toluene/g-zeolite]*, of each sample was calculated by numerical integration of a breakthrough curve of toluene in a helium carrier gas flowing through a known mass of dry zeolite sample, as defined in Eq. 1.

$$q_{toluene} = \frac{M_{toluene}}{m_{sorbent}} \int_{t=0}^{t_\infty} (x_{toluene,in} - x_{toluene,out}) N_{He} dt$$

(1)

Here, $M_{toluene}$ *[g-toluene/mol-toluene]* is the molar mass of toluene, $m_{sorbent}$ *[g-zeolite]* is the dry mass of the zeolite sample, $x_{toluene,in}$ and $x_{toluene,out}$ *[mol-toluene/mol-gas]* are molar concentrations of toluene in the inlet and outlet gas streams respectively, and $N_{He}$ *[mol-gas/s]* is the molar flowrate of the carrier gas helium during the breakthrough experiment.

The inlet carrier gas flowrate was set by mass flow controller. The carrier gas was saturated with toluene by passing through a toluene bubbler held at 2°C by an ice bath. The saturation pressure of toluene $P_{sat,toluene}(T)$ at that temperature was calculated using the Antoine equation parameters fitted by NIST[S1] from the data of Besley and Bottomley[S2] in the temperature range 273.15-297.89 K. The resulting molar concentration of toluene in the inlet gas was determined using an ideal gas assumption for the highly dilute He-toluene mixture by $x_{toluene,in} = P_{sat,toluene}(T)/P_{system}$. This molar concentration was also used as the calibration basis for the mass spectrometer signal which was used to detect the rising toluene concentration in the outlet gas, $x_{toluene,out}$. The numerical integration was performed in Excel.

S1    NIST Chemistry Webbook, https://webbook.nist.gov/, (accessed 5 February 2021).
S2    L. M. Besley and G. A. Bottomley, *J. Chem. Thermodyn.*, 1974, **6**, 577–580.