Supporting Information for:

Insights into Size Effects of Pt/Al_2O_3 Catalysts on Hydrogen Production from Methylcyclohexane Dehydrogenation

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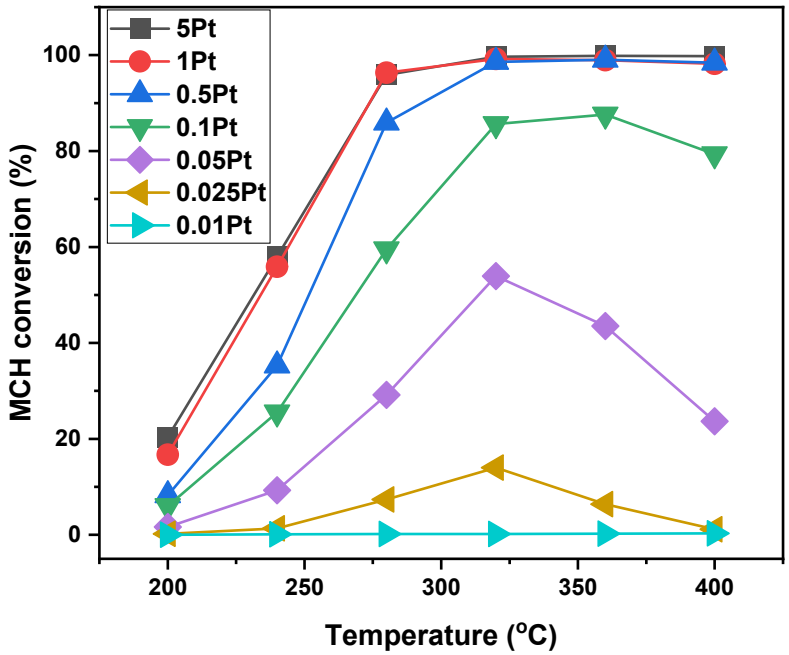


Figure S1. MCH conversion over Pt/Al_2O_3 catalysts with different Pt loadings. Reaction conditions: 6.5 mL/min Ar and 0.006 mL/min MCH (14kPa MCH) injected using a syringe pump; 30 mg catalyst was used in each experiment.

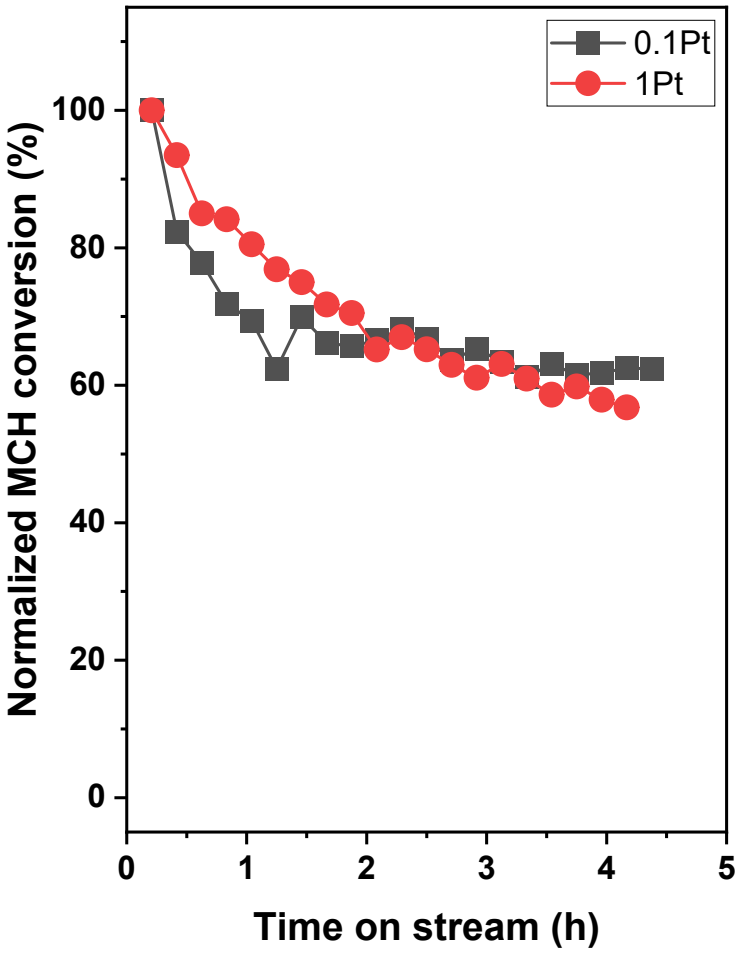
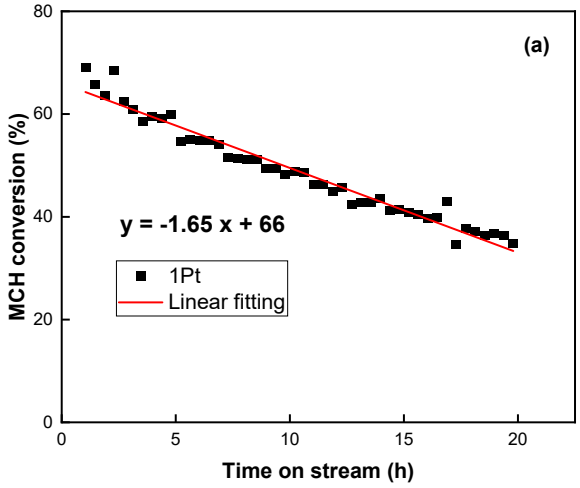
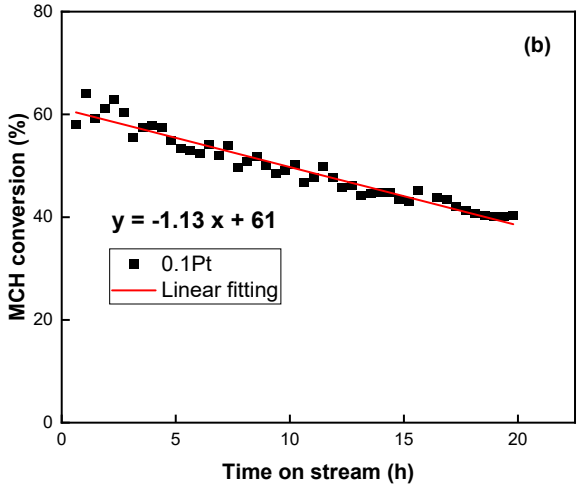


Figure S2. MCH dehydrogenation over 0.1Pt and 1Pt samples at 200 °C with both MCH and toluene in the feed at ratio of 6:1. Experiment conditions: 0.006 mL/min MCH injected using a syringe pump with Ar carrier gas flow rate at 6.5 mL/min.


(a)
MCH conversion (%)
Time on stream (h)
y = -1.65 x + 66
1Pt
Linear fitting


(b)
MCH conversion (%)
Time on stream (h)
y = -1.13 x + 61
0.1Pt
Linear fitting

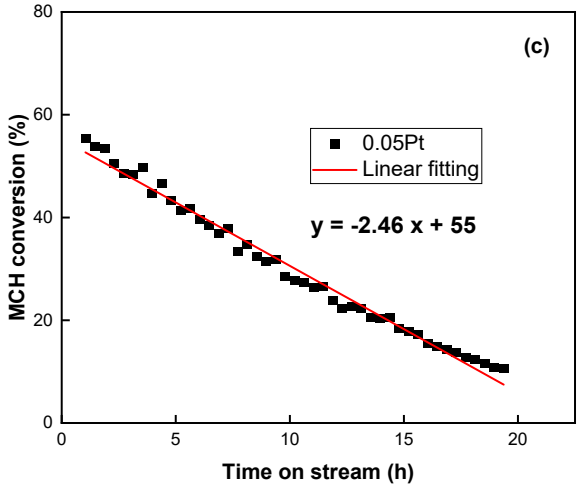

(c)
MCH conversion (%)
Time on stream (h)
0.05Pt
Linear fitting
y = -2.46 x + 55

Figure S3. Linear fitting of the MCH conversion over 1Pt (a), 0.1P (b) and 0.05Pt (c) samples during a 20h MCH dehydrogenation test at 320 °C (Figure 6 in the manuscript). The amount of catalysts used for the reaction: 30 mg 0.1Pt sample, 60 mg 0.05Pt sample, and 3mg 1Pt sample mixed with 27 mg quartz sand. Reaction conditions: 6.5 mL/min Ar and 0.006 mL/min MCH injected using a syringe pump.

Estimation of mass and heat transfer limitation

To accurately evaluate the catalytic performance of Pt/Al_2O_3 catalysts, it is essential to ensure that the catalyst is free of heat transfer limitation and mass transfer limitation. MCH dehydrogenation is a highly endothermic reaction, and given the small amount of catalyst in this study and the long time wait at each temperature (at least 1hour), the heat transfer limitation should be minimal.

The mass transfer limitation can be categorized into internal mass transfer limitation and external mass transfer limitation, which are evaluated using Weisz-Prater Modulus and effectiveness factor, respectively. These two coefficients are calculated using the open-source method developed by Purdue University (link: https://engineering.purdue.edu/~catalyst/gradientcheck/grad_index.html). The parameters required in this method are listed as follows:

(1) quartz reactor diameter is 4 mm.

(2) 30 mg catalyst is used in each reaction with the catalyst bed length of 3 mm.

(3) Particle size of Pt/Al_2O_3 sample is estimated to be 0.1 mm (150 mesh) obtained from the vender. Surface area of catalyst is 120 m^2/g with a pore volume of 0.5 cm^3/g. The catalyst tortuosity

is estimated to be 3 according to the previous study on γ-Al_2O_3 (ref: doi.org/10.1016/j.micromeso.2017.04.010).

(3) Catalyst bed density is estimated at 750 kg/m^3 with a void fraction of 0.4.

(4) Enthalpy of MCH dehydrogenation is 204.8 kJ/mol (Ref: doi.org/10.3390/membranes11120955).

(5) Fluid viscosity.

The fluid viscosity of MCH and toluene at 473 K is estimated to be 1.2 x 10^{-5} (kg m^{-1} s^{-1})which is calculated via the open-source link (http://ddbonline.ddbst.de/VogelCalculation/VogelCalculationCGI.exe) on the basis of cyclohexane assuming that cyclohexane has similar viscosity as the MCH and toluene. Fluid viscosity of Ar gas is calculated based on the open-source link (https://www.engineeringtoolbox.com/gases-absolute-dynamic-viscosity-d_1888.html).

(6) Heat capacity

The heat capacity of MCH is 2280 J kg^{-1} K^{-1} at 473 K according to the open-source NIST document (https://webbook.nist.gov/cgi/cbook.cgi?ID=C108872&Mask=FFF). The heat capacity of toluene is assumed to be same as MCH at 2280 J kg^{-1} K^{-1} at 473 K, given their similar molecular weight and structure. The heat capacity of Ar is determined to be 520 J kg^{-1} K^{-1} at 473K based on open-source NIST document (https://webbook.nist.gov/cgi/cbook.cgi?ID=C7440371&Mask=1&Type=JANAFG&Table=on).

(7) Thermal conductivity:

The thermal conductivity of MCH is determined to be 0.03 W m^{-1} K^{-1} at 473 K (based on the data at 450 K from ref (doi.org/10.1021/je800255r) and the thermal conductivity of toluene is assumed to be the same as MCH, given their similar molecular weight and structure. The thermal

conductivity of Ar is determined to be 0.0268 W m^{-1} K^{-1} (based on the data at 500 K in the open source data profile https://www.engineersedge.com/heat_transfer/thermal-conductivity-gases.htm).

With these parameters and reaction rate at 0.1 mol MCH (kg-cat · s)$^{-1}$, the WP number is calculated to be 0.12, which is lower than 0.3, indicating that internal mass transfer limitation can be excluded. The effectiveness factor is calculated to be 0.93 (>0.9), indicating the external mass transfer can also be excluded. Note that the maximum reaction rate in our study is 0.01 mol MCH (kg-cat · s)$^{-1}$, much less than 0.1 mol MCH (kg-cat · s)$^{-1}$ used in the calculation. Hence, the mass transfer limitation is anticipated to be smaller than that determined in this calculation, and can be ignored in this study.