Electronic Supporting Information

Hydroisomerization of n-Hexadecane: Remarkable Selectivity of Mesoporous Silica Post-Synthetically Modified with Aluminum

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Catalyst synthesis

Mesoporous silica and zeolite synthesis. Mesostructured cellular foam (MCF-17) type SiO_2 with an average pore size of 26.5 nm was synthesized by the method previously reported in the literature.[1] In a typical synthesis, triblock copolymer Pluoronic P123 (Sigma-Aldrich) is first dissolved in 2 M HCl solution after which 1,3,5-trimethylbenzene (TMB, Sigma-Aldrich) was added under stirring. After constant stirring the solution rigorously for 2 hours at 40 ºC, tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich) was added and the solution was stirred for additional 20 hours. Then NH_4F was added to the solution, and the solution was incubated for 24 hours at 100 ºC without stirring. The white suspension was then filtered and washed several times with hot deionized water, and dried in oven at 80 ºC. Finally, the mesoporous silica was calcined at 550 ºC for 6 hours in air to remove organic species.

For the synthesis of Santa Barbara Amorphous (SBA-15) type silica, same synthesis procedure for MCF-17 was followed, except the addition of the swelling agent 1,3,5-trimethylbenzene (TMB).[2] The average pore size of 6.4 nm was obtained as characterized by N_2 physisorption at 77 K.

Self-pillared pentasil (SPP) type microporous silica was synthesized according to the procedure reported recently.[3] First, an aqueous solution of tetra(n-butyl)phosphonium hydroxide (40% by weight, Sigma-Aldrich) was added dropwise into tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich) solution in a 100 mL round bottom flask under constant stirring. Deionized water was then added and the mixture was stirred for 12 hours until a clear solution was obtained ($1SiO_2$ / 0.3TBPOH / $10H_2O$ / 4EtOH). The final solution was transferred to a 100 mL Teflon liner of a Parr Instrument autoclave bomb, sealed, and placed into a pre-heated oven held at 115 °C and aged for 40 hours. The product was washed with distilled water by repeated centrifugation and decanting of the supernatant. The final precipitate was dried at 80 °C for 12 hours and calcined at 550 ºC for 6 hours in air.

Mesoporous zeolites with framework types BEA and MFI were synthesized according to the procedure published previously.[4] For the synthesis of mesoporous BEA zeolite, sodium silicate (Na_2SiO_3, Sigma-Aldrich), aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$, Sigma-Aldrich), and organic structure-directing agent (SDA) were dissolved in sodium hydroxide solution (NaOH, Sigma-Aldrich) to give a molar composition of $30Na_2O$ / $5Al_2O_3$ / $100SiO_2$ / 10SDA / $15H_2SO_4$ / $6000H_2O$. A cyclic diammonium type organic SDA was prepared via a procedure reported in the literature.[5] The solution was aged for 1 hour at room temperature, after which it was placed into a 23 mL Teflon liner of a Parr Instrument autoclave bomb and aged at 170 ºC for 1 day under constant stirring. The product was washed with distilled water by repeated centrifugation and decanting of the supernatant. The final precipitate was dried at 80 °C for 12 hours and calcined at 550 ºC for 6 hours in air.

For the synthesis of mesoporous MFI zeolite, sodium-silicate, $Al_2(SO_4)_3{\cdot}18H_2O$, NaOH, SDA, H_2SO_4 and distilled water were mixed to obtain a gel with composition of $30Na_2O$ / $1Al_2O_3$ / $100SiO_2$ / 10SDA / $24H_2SO_4$ / $4000H_2O$. After aging for 6 hours under magnetic stirring at 60 ^{o}C, the gel was hydrothermally treated at 150 ^{o}C for 4 days under constant stirring. The product was washed with distilled water by repeated centrifugation and decanting of the supernatant. The final precipitate was dried at 80 °C for 12 hours and calcined at 550 ºC for 6 hours in air.

Doping of silica with aluminum. All three types of silica were acidified via the same procedure. SiO_2 was first doped with aluminum through a grafting method, then ion-exchanged to give protonated aluminosilicate catalyst. In a typical synthesis, as-prepared SiO_2 was added to an ethanolic solution of anhydrous $AlCl_3$ and stirred for 24 hours at room temperature (RT), after which the sample was collected by rotary evaporation. The mole ratio of 10:1 for Si:Al was used in the synthesis. The aluminum doped SiO_2 was then dried in oven at 80 ºC and calcined at 550 ºC in air for 6 hours. The sample was then suspended in 1 M (in excess) of NH_4NO_3 solution for 4 hours at room temperature. After ion-exchanging the aluminum sites with NH_4^+, the solid sample was separated by centrifugation, washed several times with deionized water, and dried in oven at 80 ºC. The ion-exchanging and drying process was repeated 3 times to enable complete ammonification of the aluminum sites. Finally, the sample was calcined at 550 ºC for 6 hours to remove ammonia and generate protonated aluminum doped silica.

Platinum nanoparticle synthesis. Platinum nanoparticles were synthesized by a polyol synthesis technique and their size was controlled using poly(vinylpyrrolydone) (PVP) as a capping agent. For the synthesis of 3.0 nm, 5.5 nm, and 7.5 nm platinum nanoparticles similar procedure was followed. The size was tuned by refluxing the solutions for different time periods.

First, PVP (Sigma-Aldrich) and $H_2PtCl_6{\cdot}6H_2O$ (Sigma-Aldrich) were dissolved in 10 mL of ethylene glycol separately, mixed in 50 mL round bottom flask at room temperature under constant stirring, then aged in the pre-heated oil bath at 180 ºC for 10-30 minutes under argon gas atmosphere. The final suspension was naturally cooled to room temperature, mixed with excess amount of hexane to help nanoparticles separate by centrifugation, and washed with a solution composed of ethanol and acetone (volume ratio is about 1:3) for 3 times. Finally, platinum nanoparticles were re-dispersed and kept in ethanol.

For the synthesis of 1.5 nm platinum nanoparticles, NaOH was dissolved in ethylene glycol and mixed with $H_2PtCl_6{\cdot}6H_2O$ dissolved in ethylene glycol separately. Then, the solution was aged in the pre-heated oil bath at 160 ºC for 3 hours under argon gas atmosphere. The resulting nanoparticles were precipitated using 2.0 M HCl and re-dispersed in a 0.1 mM solution of PVP in ethanol.

Table S1. Physicochemical properties of aluminum modified silica and zeolite catalysts

Support	Mesopore size (nm)	Micropore size (nm)	Si/Al mole ratio[a]	Total Al[a] (mmole/g)	Pt/Al mole ratio[a] ($\times 10^{-2}$)
Pt/Al-SBA-15	6.4	N/A	13.4 ± 0.1	1.20 ± 0.01	2.39± 0.01
Pt/Al-MCF-17	26.5	N/A	14.0 ± 0.2	1.15 ± 0.02	2.32± 0.02
Pt/Al-SPP	6.5	0.5	10.6 ± 0.3	1.50 ± 0.04	1.47± 0.04
Pt/BEA	14.0	0.7	8.0 ± 0.1	1.97 ± 0.02	1.07± 0.02
Pt/MFI	11.0	0.5	36 ± 0.2	0.32 ± 0.01	7.53± 0.01

[a] Determined from elemental analysis (ICP-AES, Microanalytical Lab, University of California – Berkeley)

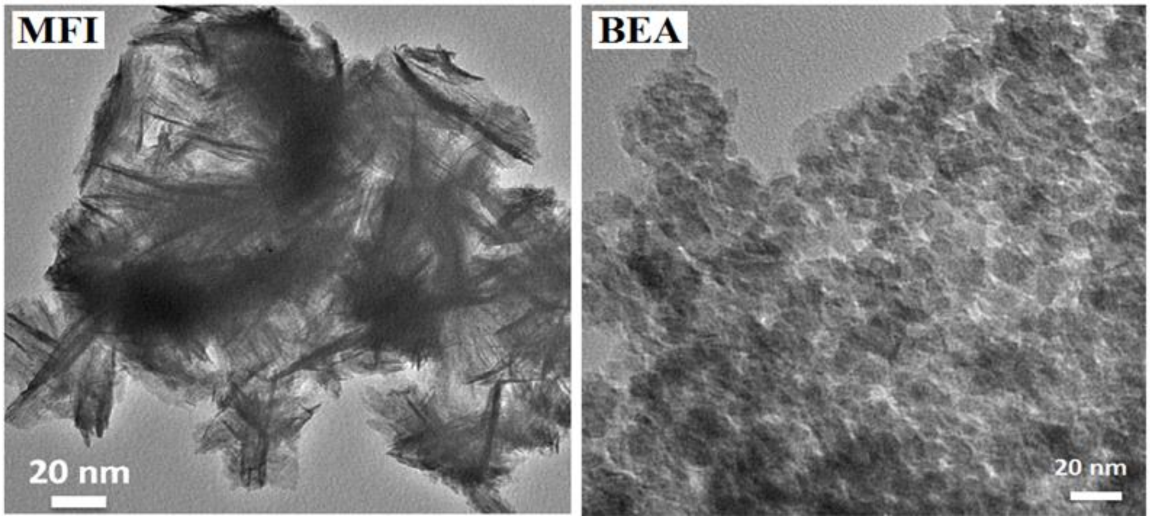

Figure S1. TEM images of mesoporous MFI (left) and BEA (right) zeolites. Physicochemical properties are given in Tables 1 and S1.

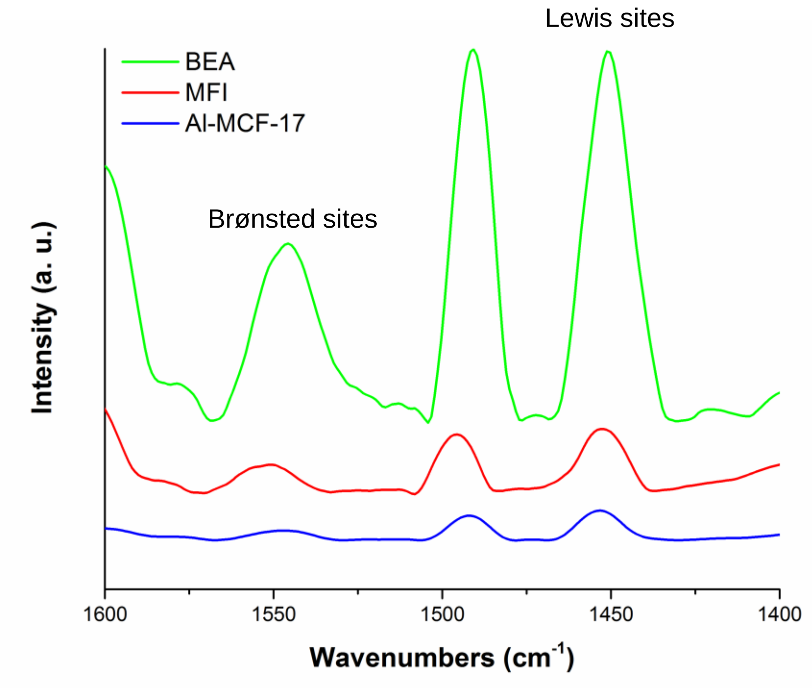

Figure S2. FT-IR spectra of pyridine molecules adsorbed on Brønsted and Lewis acid sites of mesoporous BEA and MFI zeolites and mesoporous Al-MCF-17. The amount of Brønsted and Lewis acid sites can be calculated by correlating the adsorbed pyridine molecules to the acid sites.

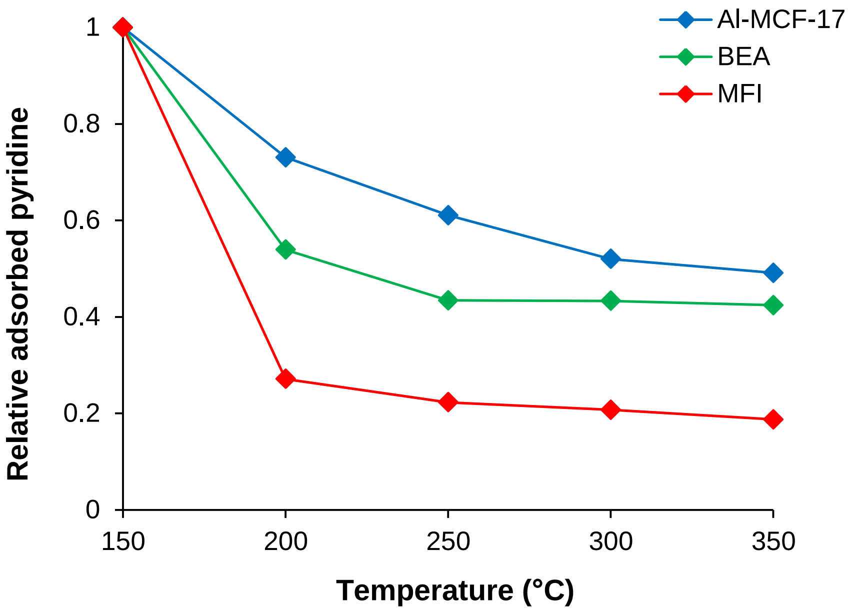

Figure S3. Amount of pyridine molecules adsorbed on Lewis acid sites of mesoporous Al-MCF, mesoporous BEA and MFI zeolites as a function temperature. More rapid desorption of pyridine molecules demonstrates weaker acidic sites. According to the plot, Al-MCF-17 has the strongest Lewis acid sites while MFI zeolite has the weakest Lewis acid sites.

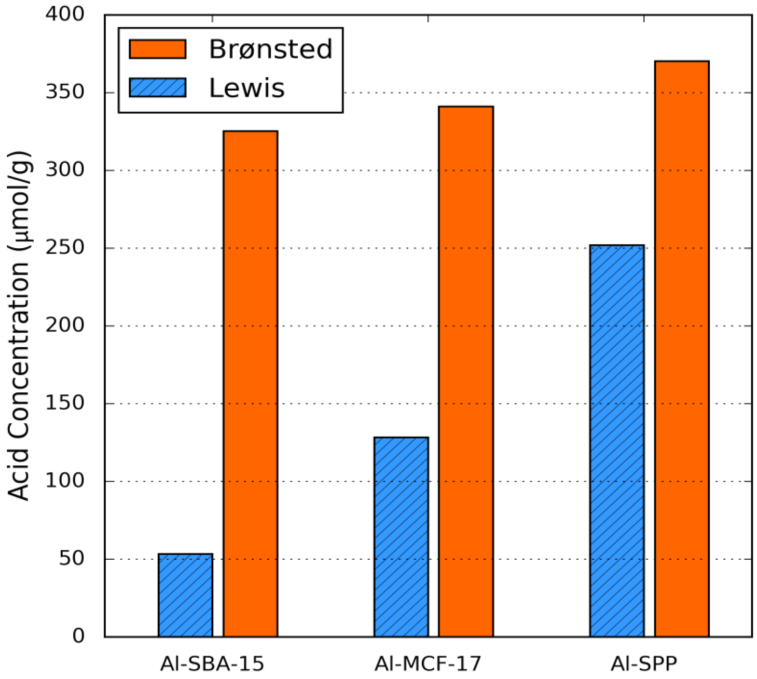

Figure S4. Total Brønsted and Lewis acid site concentration for three different aluminum modified silica supports. The acid sites were quantified by titrating the sites with pyridine and analyzing the corresponding IR bands.

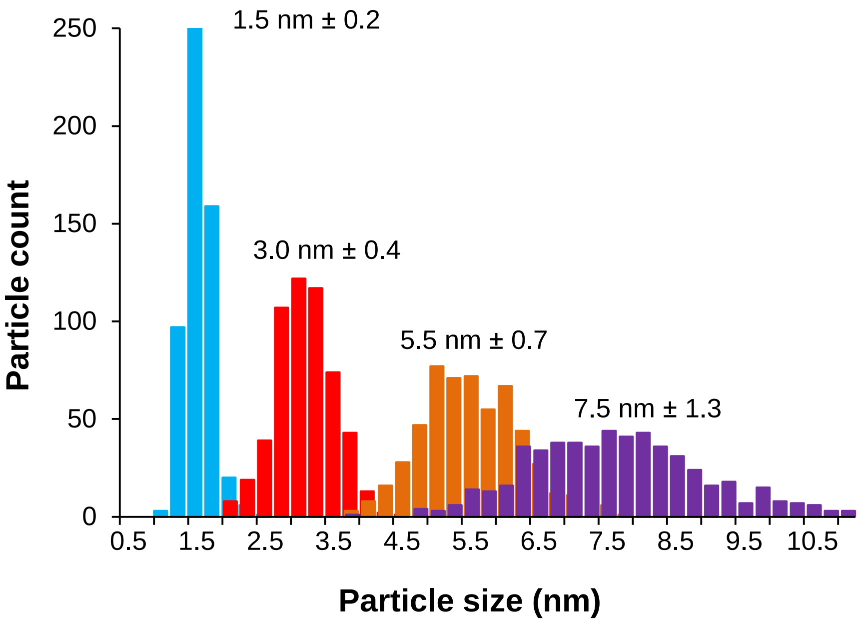

Figure S5. Average particle sizes and size distributions of platinum nanoparticles characterized by TEM. The platinum nanoparticles were synthesized by a polyol technique, in which the size of the particles was controlled by a capping agent, polyvinylpyrrolidone (PVP).

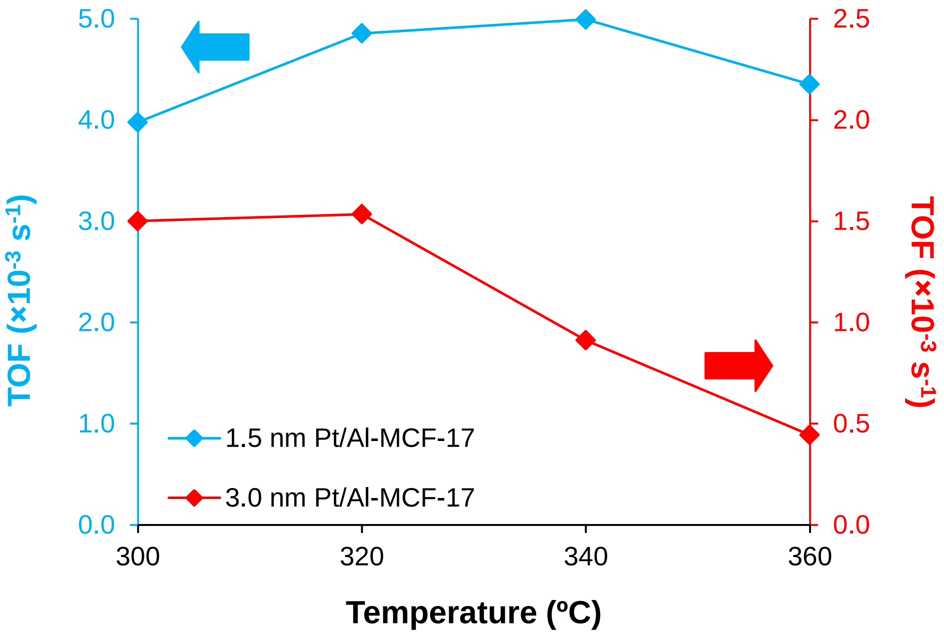

Figure S6. Catalytic activity of 1.5 nm (blue) and 3.0 nm (red) platinum nanoparticles supported on Al-MCF-17 as a function of temperature increased in sequential order from 300 ºC to 360 ºC. Note that the values on y-axes are positioned not to equivalent scale to make the deactivation rate for 3.0 nm Pt/Al-MCF-17 more apparent. 1.5 nm Pt/Al-MCF-17 is both more active and more stable than 3.0 nm Pt/Al-MCF-17. The deactivation is more likely due to coke formation. After the reaction, no significant sintering of the platinum nanoparticles was observed. The TOFs are calculated by normalizing the total conversion rate to Brønsted acid sites.

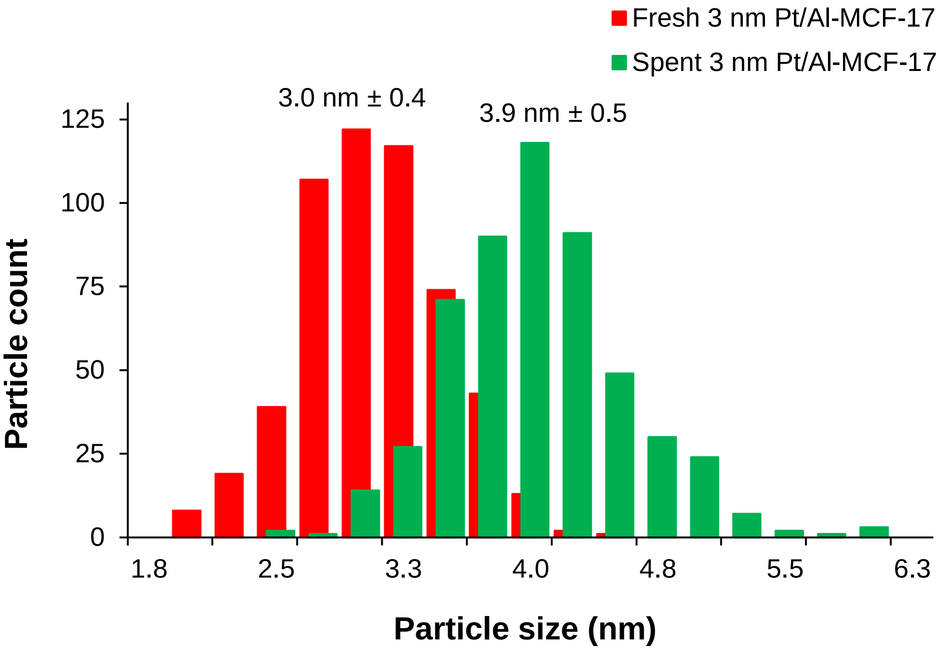

Figure S7. The difference in platinum particle size and size distribution before (red) and after (green) the reaction for 3.0 nm Pt/Al-MCF-17 as characterized by TEM.

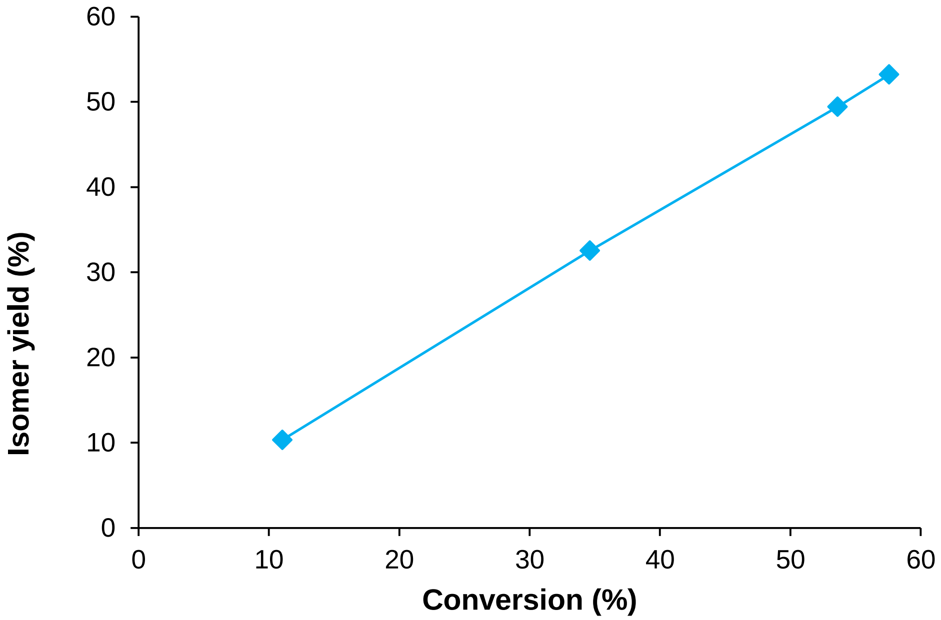

Figure S8. Isomer yield as a function of reaction conversion. The conversion was controlled by increasing catalyst bed, i.e., residence time while keeping reaction temperature constant at 300 °C and 1 bar.

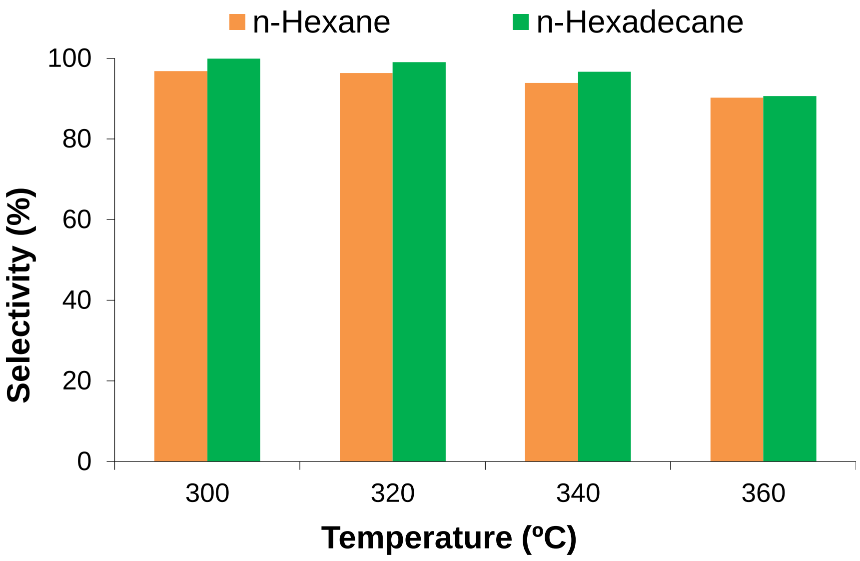

Figure S9. Total isomer selectivity for gas-phase n-hexane and n-hexadecane conversions on Pt/Al-MCF-17 at 1 bar and 300 – 360 ºC. Both reactants were converted to their corresponding isomers with nearly 100% selectivity despite large difference in molecular weight.

References

1. P. Schmidt-Winkel, W. W. Lukens, P. Yang, D. I. Margolese, J. S. Lettow, J. Y. Ying and G. D. Stucky, *Chemistry of Materials*, **2000**, 12, 686-696.

2. V. V. Pushkarev, K. An, S. Alayoglu, S. K. Beaumont and G. A. Somorjai, *Journal of Catalysis*, **2012**, 292, 64-72.

3. X. Zhang, D. Liu, D. Xu, S. Asahina, K. A. Cychosz, K. V. Agrawal, Y. Al Wahedi, A. Bhan, S. Al Hashimi and O. Terasaki, *Science*, **2012**, 336, 1684-1687.

4. N. Musselwhite, K. Na, K. Sabyrov, S. Alayoglu and G. A. Somorjai, *Journal of American Chemical Society*, **2015**, 137, 10231-10237.

5. K. Na, M. Choi and R. Ryoo, *Journal of Materials Chemistry*,**2009**, 19, 6713-6719.