

## Electronic Supplementary information

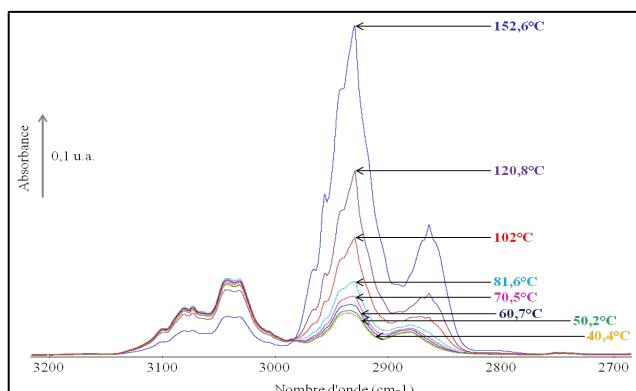
### Materials.

The Pt loading on the Pt/SiO<sub>2</sub> was 0.5 wt.% and its dispersion was 20%, determined from H<sub>2</sub> chemisorption. The Pt loading on the Pt@Silicalite-1 was 1 wt.% and its dispersion was 10%, calculated from the particle size distribution determined by the TEM analysis.

### 10 Hydrogenation catalytic tests.

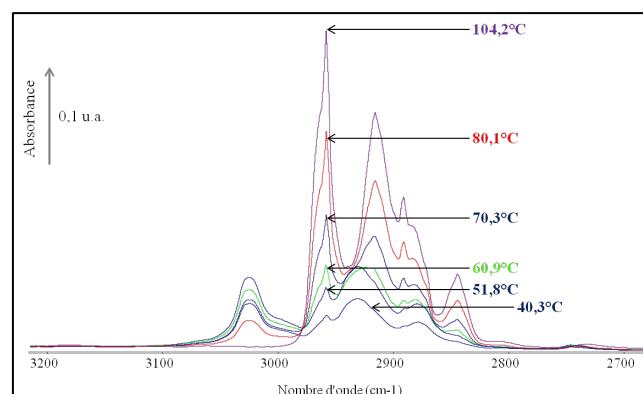
The toluene and mesitylene hydrogenation were carried out using a tubular quartz plug flow reactor placed in a tubular furnace. 20 ± 0.1 mg of catalysts were used, held between quartz wool plugs. Each arene was fed separately using a saturator kept at 0°C. 20 mL/min of pure hydrogen was used as carrier gas and fed through one saturator at a time. The reactor effluent was then diluted with 380 mL/min of Ar before reaching a 2 m path-length gas cell fitted in a Thermo FT-IR spectrophotometer. The proportion of the reactant and the corresponding saturated product were determined through integration of two zones in to the C-H stretching spectral region. In the case of toluene, methylcyclohexane was the only product observed (Fig. S1), while trimethylcyclohexane was the only product obtained in the case of using mesitylene (Fig. S2).

25 The turn-over frequencies (TOFs, expressed as molecules of toluene converted per second per surface Pt atoms) are given in Fig. S3 as an Arrhenius plot. The TOFs reported corresponded to conversion lower than 15%.



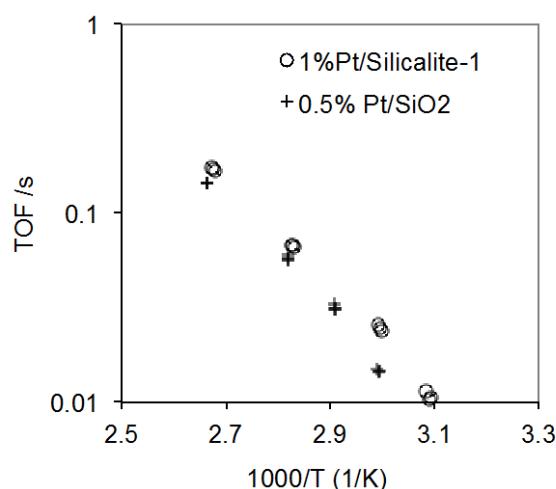
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**Figure S1 :** FT-IR spectrum obtained at various temperature of the reactor during the hydrogenation of toluene over the 0.5% Pt/SiO<sub>2</sub>. The spectrum observed at 40.4°C is essentially only that of toluene, while the spectrum of methylcyclohexane is superimposed at higher temperatures.



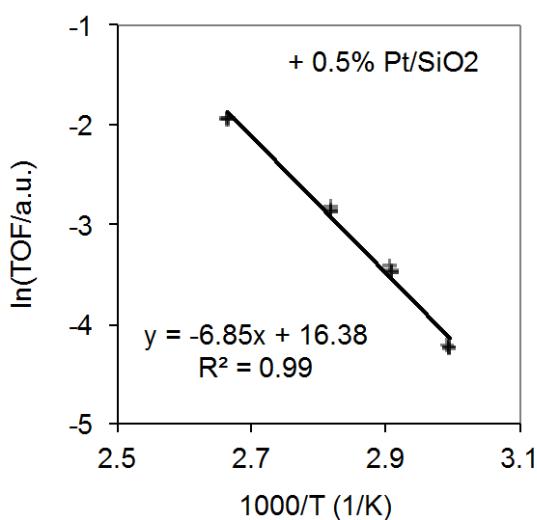
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**Figure S2 :** FT-IR spectrum obtained at various temperature of the reactor during the hydrogenation of mesitylene over the 0.5% Pt/SiO<sub>2</sub>. The spectrum observed at 40.3°C is essentially only that of mesitylene, while the spectrum of trimethylcyclohexane is superimposed at higher temperatures.

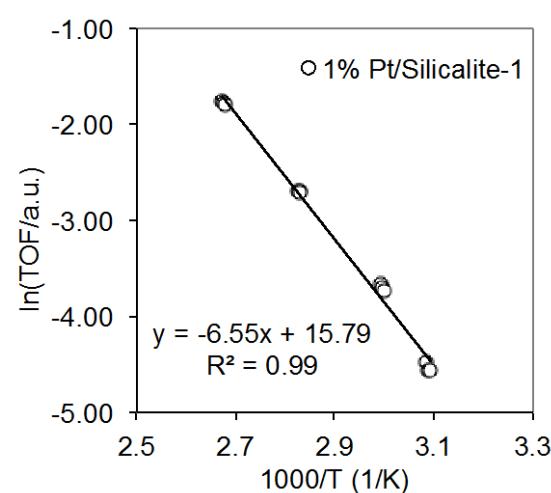


**Figure S3 :** Turn-over frequencies (TOF) for the hydrogenation of toluene measured at various temperatures.

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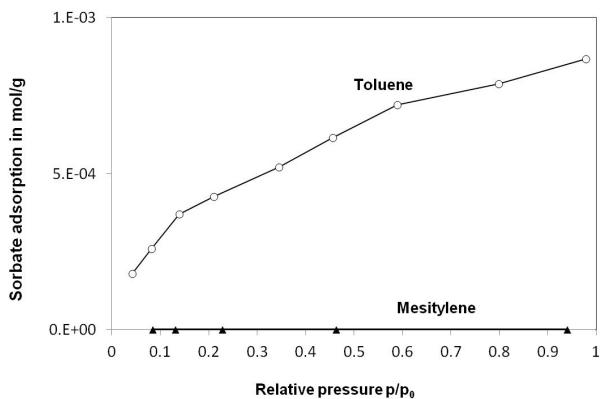
5 **Figure S4 :** Arrhenius-type plot relating the logarithm of turnover frequency (TOF) versus the reciprocal temperature for the hydrogenation of toluene over the 0.5% Pt/SiO<sub>2</sub>. The corresponding apparent activation energy is 57 kJ mol<sup>-1</sup>.



15 **Figure S5 :** Arrhenius-type plot relating the logarithm of turnover frequency (TOF) versus the reciprocal temperature for the hydrogenation of toluene over the 1% Pt/Silicalite-1. The corresponding apparent activation energy is 54 kJ mol<sup>-1</sup>.

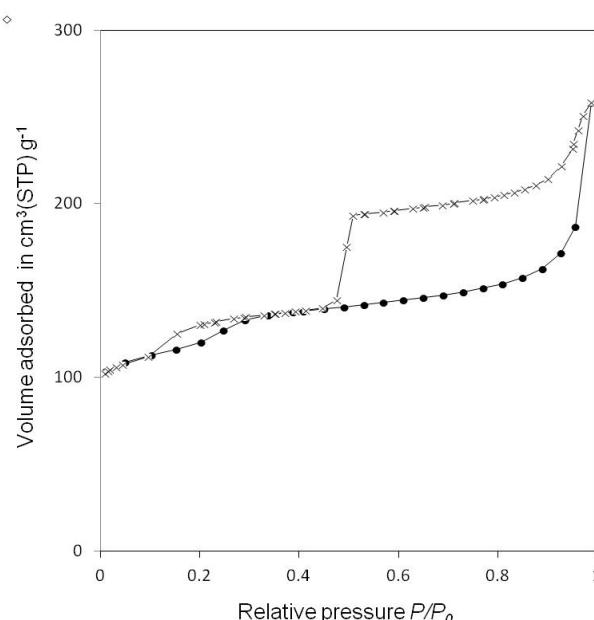
### Adsorption properties of the Silicalite-1 material.

The adsorption of toluene and mesitylene over the silicate-1 hollow boxes (free of Pt) was measured over a BelSorp Max apparatus (BelJapan) at 20°C (Fig. S6). As expected, the 25 adsorption was negligible in the case of mesitylene, while toluene could enter and adsorb in the pores of the MFI-structure silicalite-1.



30 **Figure S6 :** Adsorption isotherm of toluene and mesitylene over the silicalite-1 hollow box sample at 20°C.

The adsorption/desorption isotherm of N<sub>2</sub> at -193°C over the 35 Pt@silicate-1 hollow boxes was also measured (Fig. S7). The corresponding BET surface area was 409 m<sup>2</sup>g<sup>-1</sup>.



40 **Figure S7 :** Adsorption and desorption isotherm of over the Pt@silicalite-1 hollow box sample at -196°C.