Supporting Information

Influence of support acidity on the performance of size-confined Pt nanoparticles in the chemoselective hydrogenation of the model aromatic ketone acetophenone

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Small angle XRD patterns
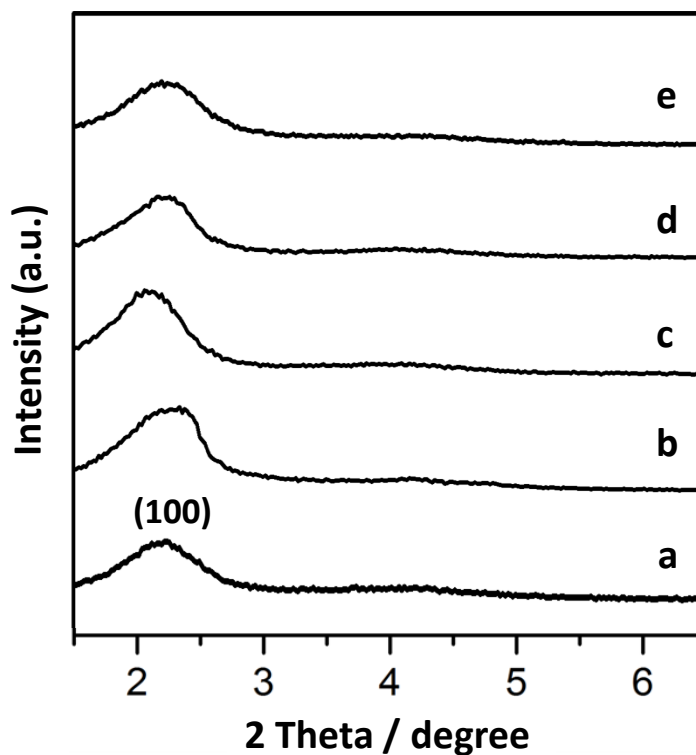
Figure S1. Small-angle XRD patterns of (a) Pt/[Al]MCM-41/50, (b) Pt/[Al]MCM-41/40, (c) Pt/[Al]MCM-41/30, (d) Pt/[Al]MCM-41/20, and (e) Pt/[Al]MCM-41/10.

XRD patterns recorded in the small-angle region ($2\theta = 1.5° - 7°$) of the Pt/MCM-41 materials with different Si/Al ratios are shown in Fig. S1. The broadening of the d(100) reflection at 2.3° for decreasing Si/Al ratios of the Pt/[Al]MCM-41 materials, indicates a distortion of the long-range order of the hexagonal structure of the support materials, and is a consequence of the aluminum incorporation into the silica framework.[1,2] However, the incorporation of aluminum did not distort the essentially mesoporous structure of the supports.[3,4]
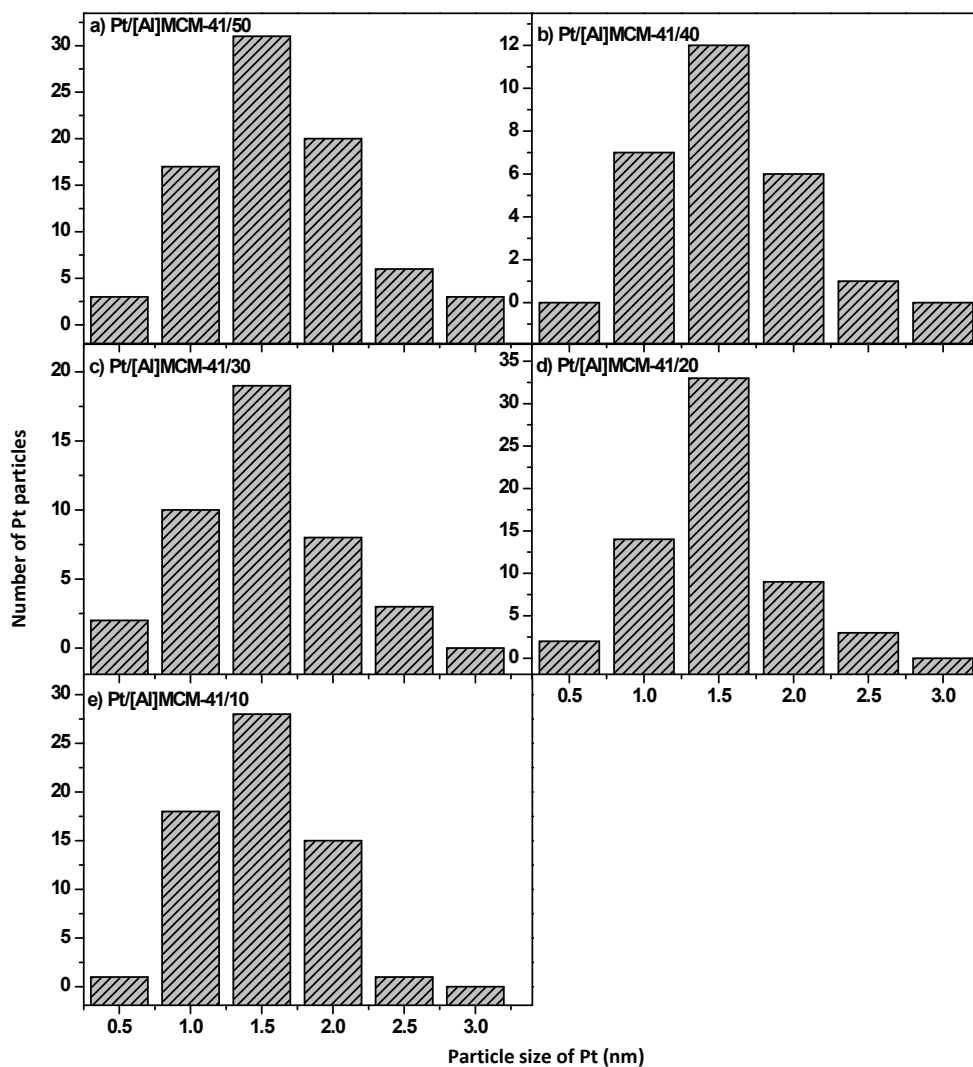
Figure S2. Pt particle size distribution (histograms) of (a) Pt/[Al]MCM-41/50, (b) Pt/[Al]MCM-41/40, (c) Pt/[Al]MCM-41/30, (d) Pt/[Al]MCM-41/20, and (e) Pt/[Al]MCM-41/10.

In the image: Map data-au 458 / MAG: 1000000 x HV: 200.0 kV / 20 nm
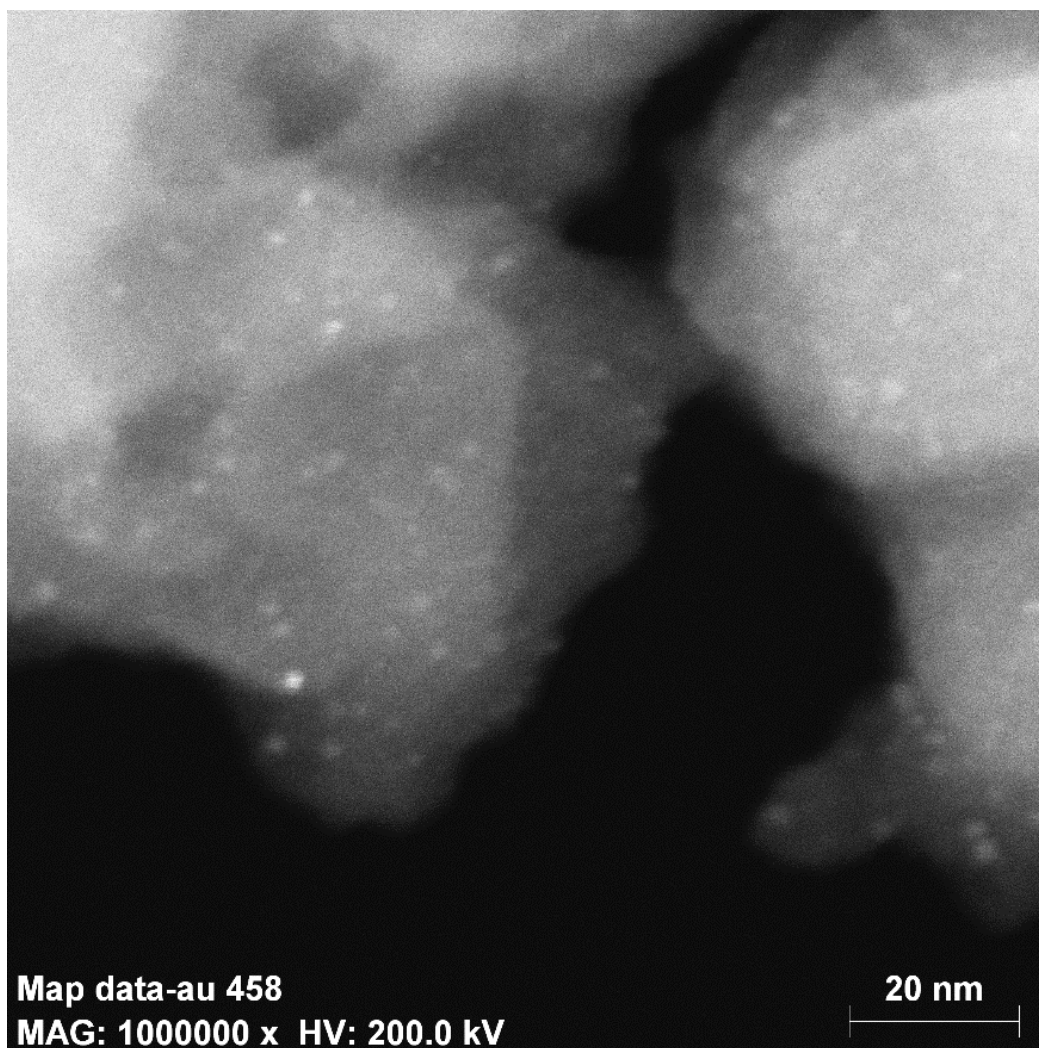
Figure S3. STEM image of Pt/[Al]MCM-41/10.
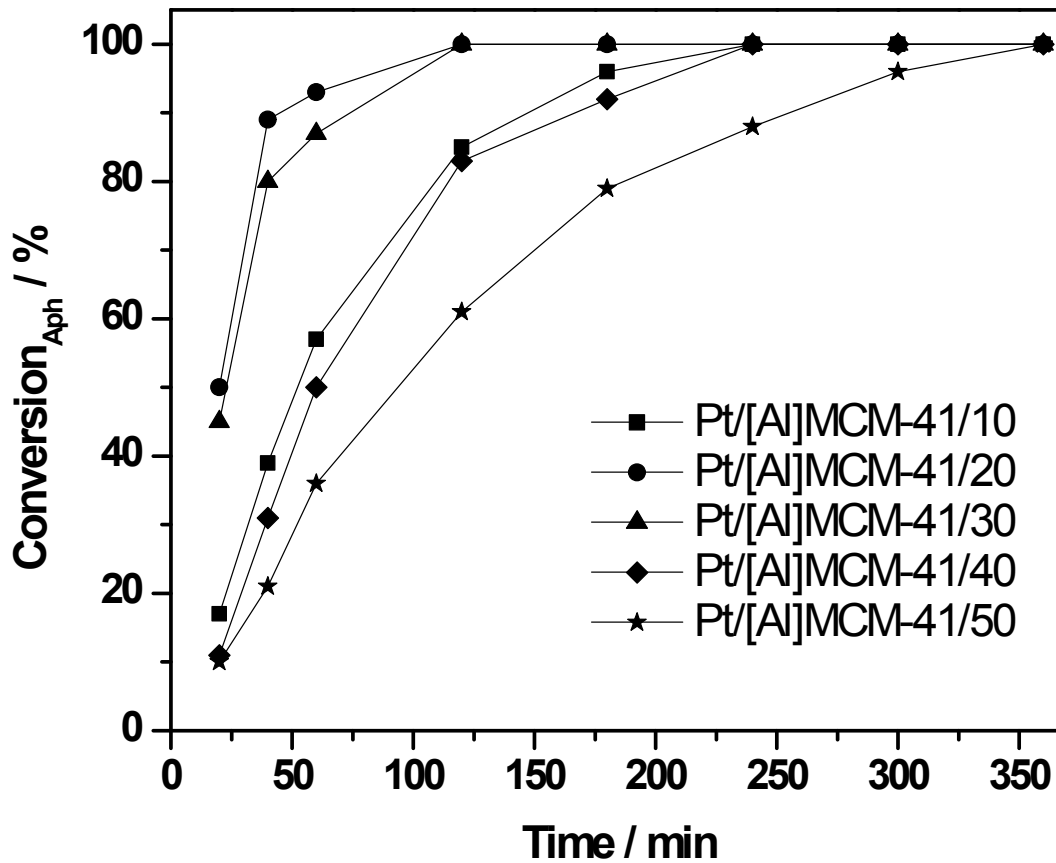
Figure S4. Catalytic conversion of Aph over Pt/[Al]MCM-41 with Si/Al ratio of 50 (★), 40 (◆),

30 (▲), 20 (●), and 10 (■). Conditions: Aph (60 mg) in hexane (6 ml) solution, 20 mg

Pt/[Al]MCM-41 catalyst added, 1 bar H_2 , room temperature, 360 min reaction time.
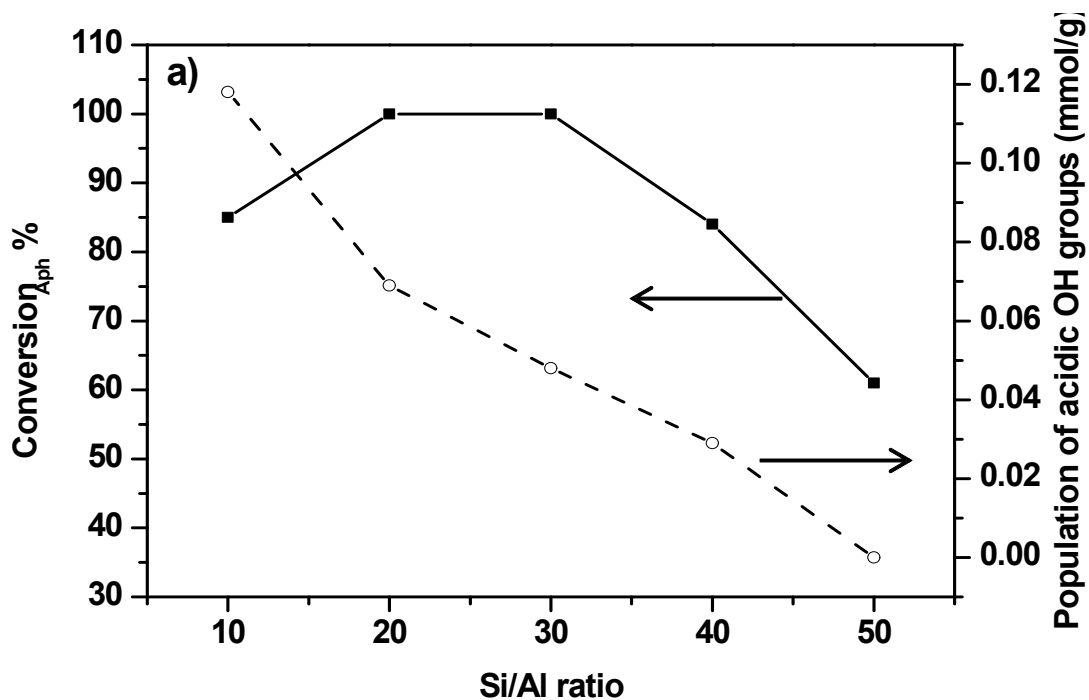
Figure S5. Aph conversion determined after a reaction time of 2 h (■) and population density of surface acid sites (○) as a function of Si/Al ratios of Pt/[Al]MCM-41catalysts under study.

The Aph conversion determined after a reaction time of 2 h increased from 61 to 100 % when the population of acidic OH groups increased from 0 to 39.9×10^{-3} BAS/nm^2. Further increase of the population of acidic OH groups to 70.4×10^{-3} BAS/nm^2 to a decrease of Aph conversion to 85 %. The observed behaviour is similar to that observed after 20 min Aph conversion shown in Fig. 6a. A possible reason for this behaviour is discussed in Section 3.4 in the manuscript.

Estimation of the Weisz–Prater criterion and its verification on the mass transfer behavior over Pt/[Al]MCM-41 catalysts

In order to check whether the catalytic results were influenced by intraparticular mass transfer, we applied the Weisz-Prater (W–P) criterion.[5]

$$\varphi_{W-P} = \frac{r_a \times R_p^2}{C_s \times D_{eff}} \qquad \text{Eq. 1}$$

where r_a is the initial global reaction rate, R_p is the catalyst particle radius, C_s is the substrate concentration on the catalyst surface, and D_{eff} is the effective diffusivity of the reactants in the pores.

Based on the method by Wilke and Chang,[6] the diffusivity of a dilute H_2 gas solute in a hexane or acetophenone (Aph) solvent is calculated according to:

$$D_{1,2} = 1.1728 \times 10^{-16} \frac{T\sqrt{\chi M_2}}{\eta_2 V_1^{0.6}} \qquad \text{Eq. 2}$$

where T is the reaction temperature (293 K), χ is the solvent association parameter that has been taken as 1 due to the non- or weak polarity of hexane and Aph, M_2 is the molecular weight of solvent, η_2 is the viscosity of the solvent at the reaction temperature (ca. 3.07×10^{-4} Pa·s for hexane and 9.3×10^{-4} Pa·s for Aph), and V_1 is the molar volume of the gas solute at the normal boiling point (0.0286 m³/kmol). The diffusivities of H_2 in hexane and Aph are estimated to be 0.77×10^{-5} cm²/s and 0.3×10^{-5} cm²/s, respectively.

The diffusivity of H_2 in the mixture is estimated using Eq. 3:

$$D_{H_2, mixt} = \frac{(D_{H_2, hexane}\eta_{hexane}^{0.5})^{x_{hexane}}(D_{H_2, Aph}\eta_{Aph}^{0.5})^{x_{Aph}}}{\eta_{mixt}^{0.5}} \qquad \text{Eq. 3}$$

where $D_{H_2, hexane}$ or $D_{H_2, Aph}$ represent the diffusivity of hydrogen in hexane and Aph, respectively, x_{hexane} and x_{Aph} are the mole fraction of hexane and Aph in the mixture, and $\eta_{mixt} = \eta_{hexane}^{x_{hexane}} \times \eta_{Aph}^{x_{Aph}}$.

The diffusivity of H_2 in the mixture is estimated to $D_{H_2, mixt} = 0.78 \times 10^{-5}$ cm^2/s.

Due to the low mole fraction of Aph in hexane, the diffusivity of Aph in the mixture could be estimated as reported previously [7], by

$$D_{Aph, mixt} = 4.4 \times 10^{-15} \frac{T}{\eta_{hexane}} \left(\frac{V_{hexane}}{V_{Aph}}\right)^{1/6} \left(\frac{L_{hexane}^{vap}}{L_{Aph}^{vap}}\right)^{1/2} \qquad \text{Eq. 4}$$

where V_{hexane} (0.128 m^3/kmol) and V_{Aph} (0.121 m^3/kmol) are the molar volumes of hexane and acetophenone at the normal boiling point, and L_{hexane}^{vap} (2.89×10^7 J/kmol) and L_{Aph}^{vap} (4.4×10^7 J/kmol) are the enthalpies of vaporization at the normal boiling point. The estimated $D_{Aph, mixt} = 3.4 \times 10^{-5}$ cm^2/s.

The effective diffusivity of the reactants in the pores of Pt/[Al]MCM-41 (D$_{eff}$) can be calculated applying Eq. 5

$$D_{eff} = D_b \frac{(1-\lambda)^2}{1+P\lambda} \qquad \text{Eq. 5}$$

where λ is the ratio of the diffusing molecule radius to the average pore radius of the catalyst, and P is a fitting parameter and estimated as 16.3 here. When $D_{H_2, mixt}$ and $D_{Aph, mixt}$ are introduced, the effective diffusivity of the H_2 and Aph can be determined as $D_{eff/H_2} = 0.33 \times 10^{-5}$ cm^2/s and $D_{eff/Aph} = 5.1 \times 10^{-9}$ cm^2/s.

The initial global reaction rate r_a was determined based on kinetic data taken at 10 % Aph conversion using Eq. 6:

$$r_a = \left(\frac{m_{Aph} \times 10\%}{M_{Aph} \times t}\right) \times \left(\frac{m_{cat}}{\rho_{cat}}\right)^{-1} \qquad \text{Eq. 6}$$

where m_{Aph} and M_{Aph} is the mass of Aph and its molecular weight, t is the reaction time at 10 % Aph conversion, m_{cat} and ρ_{cat} are the mass of the catalyst and its bulk density, respectively. Based on this, the reaction rates r_a are 4.6 μmol/s·cm^3 for Pt/[Al]MCM-41/50, 5.1 μmol/s·cm^3 for Pt/[Al]MCM-41/40, 18.3 μmol/s·cm^3 for Pt/[Al]MCM-41/30, 22.9 μmol/s·cm^3 for Pt/[Al]MCM-41/20, and 7.6 μmol/s·cm^3 for Pt/[Al]MCM-41/10.

Finally, the Weisz–Prater criterion could be estimated based on the above calculations. Additionally, C_s for Aph could be estimated according to its mole fraction after 10 % conversion (i.e. 7.5×10^{-5} mol/cm^3) and the surface concentration of H_2 is estimated as 1.3×10^{-4} mol/cm^3 [8]. The resulting W-P criterion ($\varphi_{W-P/Aph}$ = 0.004 << 0.3, and φ_{W-P/H_2} = 4.3 $\times10^{-6}$ << 0.3) indicates that the reaction rates were not significantly affected by internal diffusion phenomena.

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