Hierarchical mesoporous Pd/ZSM-5 for the selective catalytic hydrodeoxygenation of m-cresol to methylcyclohexane

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Catalyst synthesis

Synthesis of hierarchical ZSM-5

The hierarchical ZSM-5 zeolites were synthesised using the "protozeolitic units silanization" method reported previously (*Catal. Today*, 2011, **168**, 86-95). A solution of tetraethylorthosilicate (TEOS), tetrapropylammonium hydroxide (TPAOH, 40 % aqueous solution), aluminum isopropoxide (AIP) and distilled water was prepared to obtain Si/Al atomic ratios of 30 and 100 by variance of the AIP concentration. Precrystallization was conducted under reflux with stirring at 90 ºC for 20 h. 8 mol % (with regards to the silica content) of the seed silanization agent (phenylaminopropyltrimethoxysilane, PHAPTMS, Scharlab) was then added to the mother liquor and stirred at 90 ºC for a further 6 h. The final solution was crystallized in a stainless steel autoclave fitted with a Teflon liner at 170 ºC for 7 days.

Solid products were separated via centrifugation and washed several times before drying overnight at 110 ºC under air. Resulting materials were finally calcined in static air at 550 ºC for 5 h. The samples are denoted as h-ZSM-5 (X), where X is the theoretical Si/Al atomic ratio in the precursor gel. Additionally, a nanocrystalline ZSM-5 (Südchemie) was purchased and denoted as c-ZSM-5.

Incipient Wetness Impregnation of Supports with Palladium

Support materials were impregnated with Palladium via the incipient wetness technique, using an acidified $PdCl_2$ solution with a calculated concentration to deposit 1 wt.% of metal. The volume of the solution added to 2g of support was equal to twice to total pore volume from Ar physisorption measurements. Prior to impregnation, supports were outgassed in a rotary evaporator under vacuum. Following this, the $PdCl_2$ solution was added and the resulting slurry sonicated for 30 minutes, followed by rotation under vacuum for 5 h to homogenize and dry the materials.

The obtained catalysts were dried overnight in air at 110 ºC and calcined under static air at 550 ºC for 5 h. Subsequently, the catalysts were reduced in a quartz reactor with a ramp rate of 2 ºC min^{-1} to 450 ºC using an H_2 flow rate of 30 ml min^{-1}. The obtained catalysts are denoted as Pd/h-ZSM-5 (X) and Pd/c-ZSM-5.

Materials characterisation

Elemental analysis for determination of support Si/Al ratio and absolute Pd loading (wt.%) was conducted through inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Varian VISTA-AXCCD spectrophotometer. Sample digestion was undertaken using an aqueous mixture of 5:1 HF/H_2SO_4.

Textural properties of supported catalysts were obtained using argon adsorption isotherms at 87 K, which were obtained using a Quantachrome AUTOSORB instrument. Samples were outgassed at 300 °C for 3 h under vacuum (P < 10−5 mm Hg) prior to argon physisorption. The pore size distributions of the all materials were determined by the non-local density functional theory (NLDFT)

model, assuming cylindrical pore geometry. X-ray diffraction patterns of bare zeolite supports were recorded using a Philips X'PERT MPD diffractometer using Cu Kα radiation (λ = 0.154 nm). Diffractograms were recorded between 5-50° with a step size of 0.1° and a scan rate of 10 s. Characterisation of support acidity was undertaken through NH_3 adsorption and temperature programmed desorption using a Micromeritics Autochem 2910 sorption analyser. Samples were outgassed in flowing He (50 mL min^{-1}) and heated to 550°C (15°C min^{-1} ramp rate) before cooling to 180°C for saturation under flowing NH_3 for 30 minutes (35 mL min^{-1}). Physisorbed NH_3 was removed under flowing He (50 mL min^{-1}) for 90 minutes before increasing the temperature to 550°C (15°C min^{-1} ramp rate). Continuous recording of the signal from a thermal conductivity detector was used to determine the NH_3 desorption temperatures. Palladium dispersion and crystallite size were determined through CO chemisorption using a Quantachrome ChemBET. Samples were degassed under flowing He (10 mL min^{-1}) at 120°C for 1h prior to reduction under flowing H_2 (10 mL min^{-1}) at 150°C then cooled under flowing He to 30°C for analysis. Sequential injections of neat CO (50μL) were introduced into the flowing He stream until saturation was detected through the thermal conductivity detector. Dispersions were reported using a stoichiometry of Pd/CO = 2 and particle size calculations used the shape factor of 6 across all samples, often implemented for small, spherical crystallites.

Catalytic Hydrodeoxygenation Reactions
Hydrodeoxygenation reactions were undertaken in a 100 mL stainless steel autoclave (Parr 5500 series) fitted with a glass liner insert. In a typical experiment, the reactor was charged with 0.05g of catalyst and 50 mL of stock solution giving a total m-cresol concentration of 6 mmol in n-dodecane, along with 1.39 mmol (0.5 mL) n-tetradecane as a calibration standard. The reactor was sealed and purged three times with N_2 before heating to 200°C under inert atmosphere without stirring. Once the desired temperature was reached, the t_0 sample was removed from the reactor and the vessel pressurised to 20 bar of H_2 and stirring started (800rpm). Periodic samples (1 mL) were removed through the dip-tube sampling system and diluted 1:1 v/v with ethyl acetate before injection into the calibrated gas chromatograph (Bruker Scion 456GC fitted with ZB-50 column, 30m x 0.32mm x 0.25μm). Conversions across the reaction duration were calculated from **Equation S1**, where n_t is the number of mmol m-cresol at time, t, and n_0 is the initial m-cresol concentration prior to addition of hydrogen. Selectivity (% S) is defined from **Equation S2** and is based solely on the three major liquid phase products, where $n_{x=i}$ is the number of moles of product, i, and Σn_x denotes the total amount of products detected:

$$\% \, Conversion \; = \; \frac{(n_0 - n_t)}{n_0} \; x \; 100$$

<div align="center">

Equation S1

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$$\% \, Selectivity \; = \; \frac{n_{x=i}}{\Sigma n_x} \; x \; 100$$

<div align="right">

Equation S2

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where i = 3-methylcyclohexanone, 3-methylcyclohexanol or methylcyclohexane.

Table S1 Textural properties of Pd/ZSM-5 catalysts

Sample	S_{BET}^a (m²/g)	V_T^b (cm³/g)	V_{MIC}^b (cm³/g)	V_{PS}^b (cm³/g)	S_{PS}^c (m²/g)	Pd surface area (m².g⁻¹)
c-ZSM-5(30)	404	0.471	0.181	0.290	90	
Pd/c-ZSM-5(30)	377	0.434	0.171	0.263	80	17
h-ZSM-5(30)	479	0.503	0.149	0.354	220	
Pd/h-ZSM-5(30)	477	0.497	0.130	0.366	251	56
h-ZSM-5(100)	511	0.522	0.194	0.328	174	
Pd/h-ZSM-5(100)	486	0.557	0.165	0.363	149	20

Vt: total pore volume; VMic: micropore volume; Vps: secondary porosity volume; Sps: secondary porosity surface
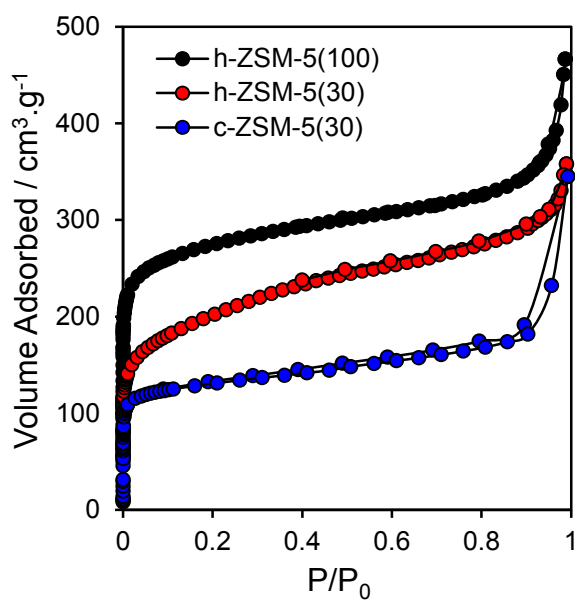
Fig. S1 Argon adsorption-desorption isotherms of conventional and hierarchical ZSM-5 supports. Isotherms offset for clarity.
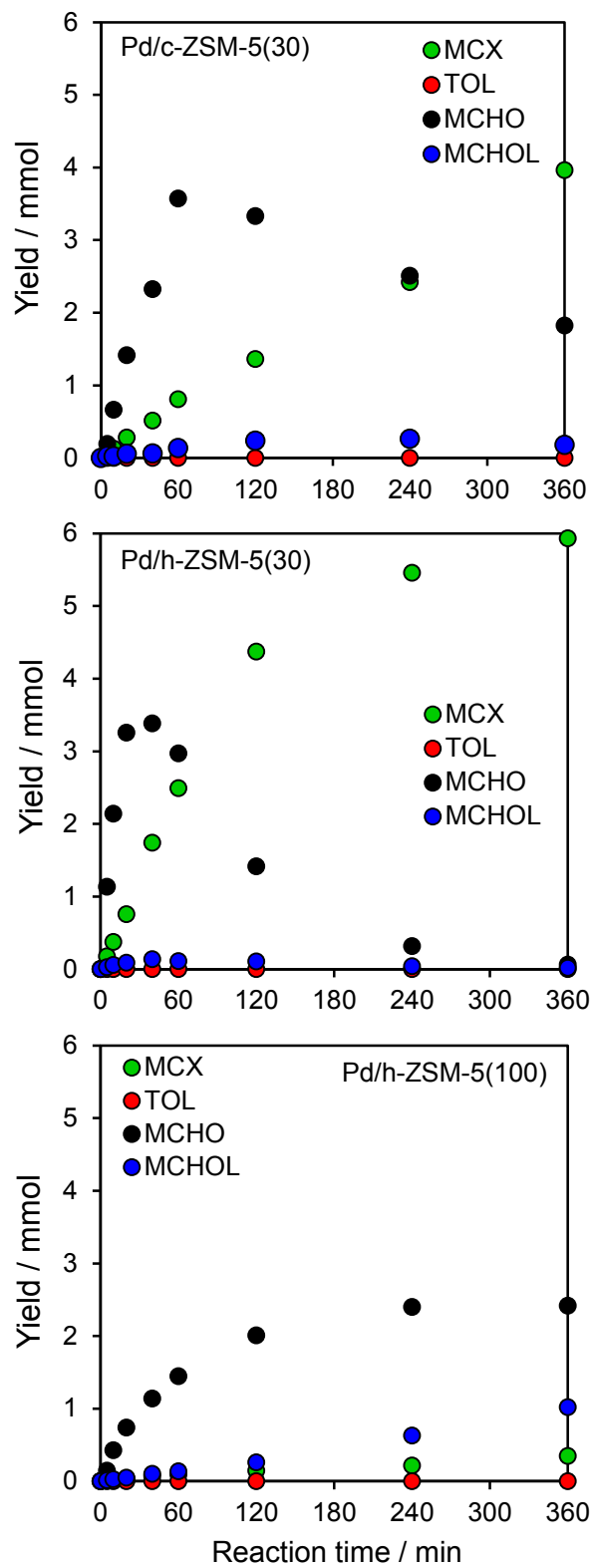
Fig. S2 Time-dependent product yields of conventional and hierarchical Pd/ZSM-5 catalysts.