Improving Mass-Transfer in Controlled Pore Glasses as Supports for the Platinum-Catalyzed Aromatics Hydrogenation

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Electronic Supporting Information (ESI)

Figure 1: Relative volume (V_{rel}) and volume intruded (V_{int}) as a function of pore width (d_{pore}) for the Hg-intrusion profile and pore width distribution histogram of Pt/CPG(10).



Figure 2: Relative volume (V_{rel}) and volume intruded (V_{int}) as a function of pore width (d_{pore}) for the Hg-intrusion profile and pore width distribution histogram of Pt/CPG(4).



Figure 3: Powder XRD patterns of the catalysts Pt/CPG(4), Pt/CPG(10) and Pt/CPG(80).



Figure 4: SEM image of a thinned specimen prepared for TEM analysis (sample Pt/CPG(10) imbedded into epoxy resin). The dotted arrows point towards surface-near regions or regions near the middle of the spheres which are well suited for TEM investigation. The bold arrows indicate regions, where the material is thin enough to directly inspect the surface. The black regions indicate areas of very low sample thickness. Note that all discs shown here represent cross-sections through the spheres, but only the thin regions highlighted by arrows are suitable for TEM investigation.



Figure 5: Hydrogen chemisorption isotherms for the catalyst Pt/CPG(10). The dispersion is calculated by extrapolation on the strong (chemisorption) isotherm, which is derived by subtraction of the weak (physisorption) isotherm from the combined isotherm (after: M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density, Kluwer Academic Publishers, Dordrecht, 2004).



Figure 6: Hydrogen chemisorption isotherms for the catalyst Pt/CPG(80). The dispersion is calculated by extrapolation on the strong (chemisorption) isotherm, which is derived by subtraction of the weak (physisorption) isotherm from the combined isotherm (after: M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density, Kluwer Academic Publishers, Dordrecht, 2004)



Figure 7: Toluene conversion $(X_{Toluene})$ after 240 min of reaction time as a function of stirring speed for the hydrogenation of toluene over the catalysts Pt/CPG(4), Pt/CPG(10) and Pt/CPG(80), respectively $(T = 373 \text{ K}, p_{H_2} = 50 \text{ bar}, c_{aromatic} = 1.60 \text{ mol } l^{-1}$, solvent: n-hexane $(V = 75 \text{ cm}^3)$, $m_{cat} = 150 \text{ mg}$, stirring rate = 1300 min⁻¹).

Calculation of the initial reaction rates

The effectiveness factor η is defined as ratio of the observed reaction rate (r₀) and the intrinsic (i.e. not mass-transfer limited) reaction rate (r_{int}) and can be expressed as a function of the Thiele modulus (θ) as

$$\eta = \frac{r_0}{r_{int}} = \frac{3}{\theta} \left(\frac{1}{\tanh \theta} - \frac{1}{\theta} \right)$$
(1)

In case of internal mass-transfer limitation ($\theta > 5$, see Figure 7 of the original paper), the equation can be simplified to

$$\eta = \frac{r_0}{r_{int}} = \frac{3}{\theta}$$
(2)

The Thiele modulus can be defined as a function of grain size (d_{grain}) , reaction rate constant (k), surface concentration with respect to reaction order n (c_{surf}^{n-1}) and effective diffusivity (D_{eff}) :

$$\theta = d_{grain} \sqrt{\frac{k \cdot c_{surf}^{n-1}}{D_{eff}}}.$$
(3)

Substituting equation (3) in equation (2) and gives

$$\eta = \frac{r_0}{r_{int}} = \frac{3}{d_{grain} \sqrt{\frac{k \cdot c_{surf}^{n-1}}{D_{eff}}}}.$$
(4)

When considering two catalytic runs (subscript 1 and 2) with identical conditions, the intrinsic reaction rate (r_{int}), grain size (d_{grain}), reaction rate constant (k), surface concentration (c_{surf}^{n-1}) can be considered constant, resulting in

$$\frac{r_{0,1}}{r_{0,2}} = \frac{3\sqrt{D_{eff,1}}}{3\sqrt{D_{eff,2}}}$$
(5)

The Knudsen equation defines the effective diffusivity as a function of pore width (d_{pore}) , universal gas constant (R), temperature (T) and molar mass of the diffusing reactant (M)

$$D_{eff} = \frac{2}{3} d_{pore} \sqrt{\frac{8R \cdot T}{\pi M}}.$$
(6)

The effective diffusion coefficients were calculated based on this equation. The values obtained are $3.9 \ 10^{-7} \ m^2 \ s^{-1}$, $9.8 \ 10^{-7} \ m^2 \ s^{-1}$ and $7.8 \ 10^{-6} \ m^2 \ s^{-1}$ for Pt/CPG(4), Pt/CPG(10) and Pt/CPG(80), respectively. Although the effective diffusion coefficients increase with increasing pore width as expected, the absolute values are about three orders of magnitude lower than those determined via PFG-NMR and catalytic experiments.

For two catalytic runs under identical conditions the universal gas constant (R), temperature (T) and molar mass of the diffusing reactant (M) can be considered as constant (k_{diff}), resulting in

$$D_{eff} = 1.06 \, d_{pore} \, k_{diff} \,. \tag{7}$$

Equation (7) can now be substituted in equation (5) and the catalytic runs with the catalysts Pt/CPG(10) (d_{pore} = 10 nm, subscript 1) and Pt/CPG(4) (d_{pore} = 4 nm, r₀ = 0.032 mmol g⁻¹ s⁻¹, subscript 2) can be considered. Thus, we obtain

$$r_{0,1} = \frac{3\sqrt{1.06 \cdot d_{pore,1}}}{3\sqrt{1.06 \cdot d_{pore,2}}} r_{0,2} = 1.58 r_{0,2} = 0.051 \text{ mmol } g^{-1} \text{ s}^{-1}$$
(8)