Electronic Supplementary Material

Novel synthesis of thick wall coatings of titania supported Bi poisoned Pd catalysts and application in selective hydrogenation of acetylene alcohols in capillary microreactors

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Effect of hexane evaporation on the hydrogenation kinetics

Fig. ESI-1 shows the partial pressures of hexane, 2-methyl-3-butyn-2-ol (MBY) and hydrogen at different reaction temperatures, which were calculated using the k_La value of $1 s^{-1}$ reported for the channels of 670 μm in hydraulic diameter,[1] Antoine equation for hexane and MBY, [2,3] and considering linear decrease of pressure inside the reactor. As a result of quick hexane evaporation, its partial pressure quickly achieved saturation leading to dilution of hydrogen.

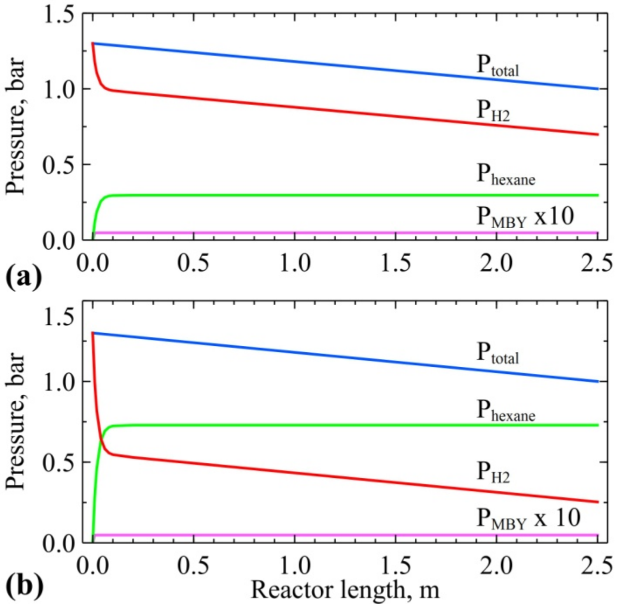

Fig. ESI-1. Partial pressure of hexane, hydrogen and MBY along the capillary reactor at (a) 310 K and (b) 335 K.

Considering that the hydrogenation rate is a first order reaction in hydrogen and zero order in MBY,[4] the effect of hexane evaporation on the reaction kinetics was estimated using equation (ESI-1), where r_T and k_T are the apparent hydrogenation reaction rate and the rate constant at the reaction temperature of T, p_{H2} is the hydrogen partial pressure in the reactor position of l, and L, total length of the reactor.

$$\frac{r_{335}}{r_{310}} = \frac{k_{335}}{k_{310}} \frac{\int_0^L p_{H2,\,335K}(l)\, dl}{\int_0^L p_{H2,\,310K}(l)\, dl} \qquad \text{(ESI-1)}$$

The first factor in equation (ESI-1), the ratio of the rate constants, shows the effect of temperature on the reaction kinetics and increases with the reaction temperature. The second factor shows the effect of hydrogen partial pressure and decreases with temperature as a result of hexane evaporation. The value of the first factor varies between 2.0 and 2.8, depending on the activation energy, which was reported in the literature to be between 25 and 36 kJ/mol.[4,5] The second factor in equation (ESI-1) was calculated to be 0.43, showing that the decrease in hydrogen partial pressure was balanced by the increase in intrinsic kinetics as a result of higher reaction temperature.

Mass- and heat- transfer effects

Toluene is a less volatile solvent, resulting in similar hydrogen pressures of 1.23 and 1.10 bar at 310 and 335 K, respectively. For the MBY solution in toluene, the effect of solvent evaporation was expected to be less pronounced, while its viscosity similar to that of hexane provided similar hydrodynamic behaviour. Hence, a significant increase of the hydrogenation rate at higher temperatures is expected in toluene.

Fig. ESI-2a shows the MBE yield as a function of liquid flow rate at three reaction temperatures obtained for the MBY hydrogenation in toluene. Similar to the hexane solution (Fig. 8 in the main manuscript), the MBE yield at the reaction temperature of 310 K achieved a maximum at a liquid flow rate of about 40 μL/min, where the product of MBY conversion and the MBE selectivity was the highest. At higher reaction temperatures, however, a significant increase in the reaction rate was observed. At 335 K, MBE was further hydrogenated consuming more than 1 mol of hydrogen per mol of MBY in the entire flow rate range studied, while at 350 K, the fully hydrogenated product was obtained leading to zero MBE yield at a flow rate up to 45 μL/min (Fig. ESI-2b). Importantly, the apparent hydrogenation reaction rates increased by 130 % with the temperature increase from 310 to 335 K, which is in good agreement with the reported kinetic studies of hydrogenation.[4,5] Considering external mass transfer limitations, the reaction rate was expected to be proportional to temperature in the power of 0.75,[6] leading to apparent reaction rate increase of less than 10 % in the studied temperature range, showing that mass transfer limitations did not apply for the studied capillary reactor. Furthermore, Warnier shown that external mass transfer limitations cannot be reached prior to reaching internal (pore) limitations in the semi-hydrogenation in capillary microreactors.[7]

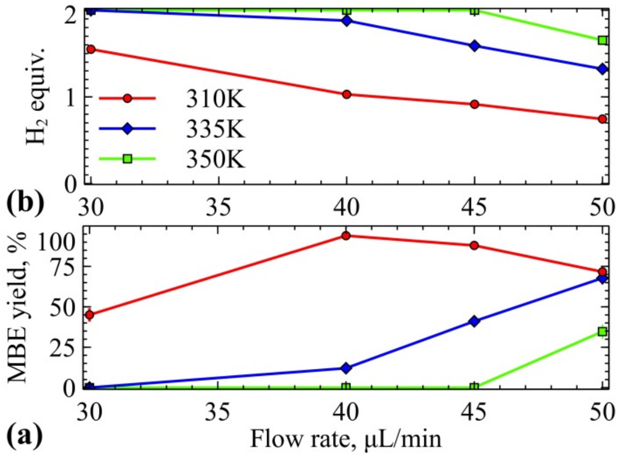

Fig. ESI-2. (a) MBE maximum yield as a function of the reaction temperature and the MBY solution flow rate. (b) Corresponding hydrogen consumption by MBY (1200 mol/m^3 MBY in toluene, 10 mL/min (STP) H_2 flow).

In order to estimate pore diffusion, the Thiele modulus was calculated (ESI-2), where d is the average coating thickness, D_{eff} - efficient diffusion coefficient of hydrogen though the catalyst pores and k_v - overall volumetric rate constant.[8]

$$\phi = d\sqrt{k_v / D_{eff}} \tag{ESI-2}$$

The efficient diffusion coefficient of hydrogen in the catalyst pores was estimated to be 10^{-9} m^2 s^{-1} as described by Vannice.[9,10] The overall volumetric rate constant was calculated using equation (ESI-3),

$$k_v = \frac{-\Delta F_{MBY}}{A\,L}\frac{H}{p_{H2}} \tag{ESI-3}$$

where ΔF_{MBY} is the change in the MBY molar concentration in the reactor of the length L and cross-section A; H is Henry constant (in Pa m^3 mol^{-1}) of hydrogen solubility in hexane[11,12] and p_{H2} hydrogen partial pressure estimated earlier for hexane solution. A high-boundary estimation of the overall volumetric rate constant in the hexane solution at 335 K provided a value of 0.6 s^{-1}, resulting in the value of Thiele modulus of 0.089 and the effectiveness factor ($\eta = \tanh(\phi)/\phi$) of 0.997. The value of the effectiveness factor very close to 1 shows that there is no internal mass transfer limitations.[8] Because the concentration of the reactant in liquid phase is 2 orders of magnitude higher than that of hydrogen, internal diffusion of organic species is not a limiting step either. Furthermore, very high alkene selectivity observed in the work could not be reached in case of pore diffusion limitations of the liquid reactant.[13] It confirms the conclusion that mass transfer limitations did not apply, and the reactions were controlled by intrinsic kinetics of the hydrogenation reaction.

Similarly, Anderson criterion calculated as described by Mears[14,15] (ESI-4) showed that the heat generated had very little effect on the reaction kinetics.

$$N_{W-P} = \frac{\Re\, R_p^2}{C\, D_{eff}} \qquad \text{(ESI-4)}$$

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