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Electronic Supporting Information (ESI)

Mass transport effects in gas-phase selective hydrogenation of 1,3-butadiene over supported Pd

Oscar E. Brandt Corstius[a], M. Kikkert[a], S.T. Roberts[b], E.J. Doskocil[c], J.E.S. van der Hoeven[a], P.E. de Jongh[a]*

[a]Materials Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands
[b]Applied Sciences, bp Innovation and Engineering, BP plc, Saltend, Hull, HU12 8DS, United Kingdom
[c]Applied Sciences, bp Innovation and Engineering, BP plc, Chicago, IL, 60606, United States
*corresponding author: P.E.deJongh@uu.nl

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Heat and mass transport phenomena

Table S1. Properties of reaction gasses.

	Molar fraction	Molar mass	Diffusion volume[1]	Bulk diffusivity[a,1]	Viscosity	Thermal conductivity	Heat capacity
Reactant	[-]	$\times 10^{-3}$ kg/mol	$\times 10^{-5}$ m^3/mol	$\times 10^{-6}$ m^2/s	$\times 10^{-6}$ Pa s	$\times 10^{-3}$ W/(mK)	J/(molK)
Butadiene	0.3%	54.09	7.79	n.a.[a]	8.66—10.5[2]	15.0—24.3[3]	79.9—97.7[4]
Propylene	30%	42.08	6.14	6.50—9.63	8.96—10.7[2]	17.0—25.6[5]	63.8—78.8[6]
Hydrogen	20%	2.016	0.707	4.01—5.94	8.93—10.4[7]	179—210[8]	28.7—28.9[9]
Helium	49.7%	4.003	0.288	3.41—5.05	19.7—23.1[7]	154—180[8]	18.5—17.2[9]
Mixture	100%	15.18	n.a.	1.52—2.45[b]	14.3—16.8	118—139	34.3—37.4

[a] Defined as the diffusivity of butadiene in the other gas. [b] Determined by the Wilke-equation (Eq. S3). Temperature-dependent values are listed between the minimum and maximum temperature of the catalytic test, 25—100 °C.

Gas diffusion

For the transport properties of the reaction gas (Table S1), the value of the mixture is determined as the sum of the four components as:

$$P_{mix} = \sum (x_i \, P_i) \qquad \text{Eq. S1}$$

where P_i is the property of interest and x_i is the molar fraction of each reactant. For simplicity, the initial molar fractions are used throughout the calculations. Even at the highest observed catalytic activity (100% butadiene and 5% propylene conversion at 100 °C) the average value of the transport properties of the mixture only varied by less than 0.8% because of the large excess of H_2 and He.

Diffusion volumes (ν_i) of each reactant were estimated for C_4H_6, C_3H_6, He and H_2.[10] The diffusion of butadiene (BD) in the individual gasses ($D_{BD,i}$) was calculated from Fuller, Schettler and Giddings[1] as:

$$D_{BD,i} = \frac{3.2 \times 10^{-8} \, T^{1.75} \sqrt{\dfrac{1}{m_{BD}} + \dfrac{1}{m_i}}}{p \, ({\nu_{BD}}^{1/3} + {\nu_i}^{1/3})^2} \qquad \text{Eq. S2}$$

where T is the temperature (K), m_i is the molar mass (kg/mol) and p is the pressure (101325 Pa). The total diffusivity of butadiene in the reaction mixture is calculated with Wilke-equation[11] as:

$$D_{BD,mix} = (1 - x_{BD}) \times \Big(\sum_{i \neq BD} \frac{x_i}{D_{BD,i}}\Big)^{-1} \qquad \text{Eq. S3}$$

which results in a bulk diffusivity of 1.52—2.45×10^{-6} m^2/s for butadiene between 25—100 °C.

For diffusion inside the catalyst grains, in the presence of narrow pores, limitation due to gas-solid interactions should be taken into account in addition to gas-gas interactions. The Knudsen diffusion (D_K) is calculated as

$$D_K = \frac{2r_{pore}}{3}\sqrt{\frac{8\,R\,T}{\pi\,m_{BD}}} \qquad \text{Eq. S4}$$

where R is the ideal gas constant (8.3145 $m^3\ Pa\ K^{-1}\ mol^{-1}$) and r is the estimated pore radius:

$$r_{pore} = \frac{2\varepsilon_{cat}}{\rho_{cat}S} \qquad \text{Eq. S5}$$

where ε_{cat} is the catalyst porosity (0.82 m^3/m^3_{cat}), ρ_{cat} is the catalyst density (657 kg/m^3_{cat}) and S is the surface area of the catalyst (500×10^3 m^2/kg). This results in an estimated pore radius of 3.1×10^{-9} m (3.1 nm) and D_K between 7.1—8.0×10^{-7} m^2/s.

From the combined resistivity of Knudsen diffusion and bulk diffusivity of butadiene, the effective diffusivity of butadiene ($D_{BD,eff}$) is calculated as:

$$D_{BD,eff} = \frac{\varepsilon}{\tau}\left(\frac{1}{D_{BD,mix}} + \frac{1}{D_K}\right)^{-1} \qquad \text{Eq. S6}$$

where τ is the catalyst tortuosity, which can be estimated from $\tau = 1/\sqrt{\varepsilon}$.[12] This results in an $D_{BD,eff}$ of 3.5—3.9×10^{-7} m^2/s between 25—100 °C.

Activity

The volumetric reaction rate can be estimated for any catalytic system, for example by taking known turnover frequency (TOF) from the literature as:

$$R^{est.}_{vol.} = \frac{TOF\ D\ m_{metal}\ \rho_{cat}}{M_{metal}\ m_{cat}} \qquad \text{Eq. S7}$$

where TOF is the intrinsic surface-averaged activity ($molecules\ surface\text{-}atom^{-1}\ s^{-1}$)[13], D is the catalyst dispersion[14] and M_{metal} is the molar mass of the metal.

In absence of mass transfer limitations, the temperature-dependent rate of the reaction, r, is:

$$r = Ae^{-E_{act}/(RT)} \qquad \text{Eq. S8}$$

with A as the pre-exponential factor and E_{act} the activation energy of the reaction (J/mol). From the logarithmic relation of the ratio, the activation energy can be determined.

$$ln(r) = ln(A) - \frac{E_{act}}{R}\frac{1}{T} \qquad \text{Eq. S9}$$

Hence, $\frac{E_{act}}{R}$ can be derived from the slope of an $ln(r)\ vs. \frac{1}{T}$ plot. Similarly, E_{act} can be directly obtained from the slope of a $Rln(r)\ vs. \frac{1}{T}$ plot. This relation can also be used to derive a temperature from known E_{act}, one relative activity (r_1) value at known temperature (T_1), and one activity (r_2) at unknown temperature (T_2) as follows:

$$\frac{r_2}{r_1} = \frac{Ae^{-E_{act}/(RT_2)}}{Ae^{-E_{act}/(RT_1)}} = e^{-\frac{E_{act}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)} \qquad \text{Eq. S10}$$

$$ln\left(\frac{r_2}{r_1}\right) = \frac{-E_{act}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \text{Eq. S11}$$

$$\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{-R}{E_{act}} ln\left(\frac{r_2}{r_1}\right) \qquad \text{Eq. S12}$$

$$\frac{1}{T_2} = \frac{-R}{E_{act}} ln\left(\frac{r_2}{r_1}\right) + \frac{1}{T_1} \qquad \text{Eq. S13}$$

$$T_2 = \left(\frac{-R}{E_{act}} ln\left(\frac{r_2}{r_1}\right) + \frac{1}{T_1}\right)^{-1} \qquad \text{Eq. S14}$$

Heat transfer

The adiabatic temperature rise (ΔT_{ad}) in the reactor due to exothermic reactions can be calculated as:

$$\Delta T_{ad} = \frac{\sum_{i=BD,PP,n-but}(x_i \, X_i \mid \Delta_r H_i|)}{C_{p,gas}} \qquad \text{Eq. S15}$$

where $\Delta_r H_i$ is the hydrogenation reaction enthalpy of each reactant (see section 2.4 in the main text). $C_{p,gas}$ is the heat capacity of the gas mixture (Table S1) which we assume constant even at full butadiene conversion since the molar fraction of is very low (0.3%) and conversion of propylene was always below 5%. For full butadiene semi-hydrogenation, this results in a temperature increase of the reaction gas of 9.1 °C, which increases up to 60 °C when 5% propylene conversion and 10% butane formation are considered.

External heat transfer limitations are calculated by the temperature difference over the gas film that surround the catalyst grain.[15]

$$\Delta T_{film} = \frac{\sum_{i=BD,PP,n-but}(R^{Obs}_{vol.,i} \mid \Delta_r H_i|)}{\alpha_p \, a_V} \qquad \text{Eq. S16}$$

where in $R^{Obs}_{vol.,i} \times | \Delta_r H_i|$ the produced heat by hydrogenation of butadiene, propylene and butene. α_p is the transfer coefficient (W/(m^{2}K)), which is defined as:

$$\alpha_p = \frac{Nu \, \lambda_{gas}}{d_p} \qquad \text{Eq. S17}$$

where λ_{gas} is the thermal conductivity of the gas (Table S1) and Nu is the Nusselt number, defined as:

$$Nu = 2 + 1.1 Re^{0.6} Pr^{1/3} \qquad \text{Eq. S18}$$

Where Prandtl number, Pr, is defined as:

$$Pr = \frac{C_{p,gas} \, \mu}{\lambda_{gas}} \qquad \text{Eq. S19}$$

To exclude external heat transfer effects to alter the catalytic activity by more than 5%, ΔT_{film} should be less than $0.05\gamma_b/T$, where T is temperature and γ_b is the dimensionless activation energy:

$$\gamma_b = \frac{E_{act}}{R\,T} \qquad \text{Eq. S20}$$

with E_{act} in J/mol, which for E_{act} of 50×10^3 J/mol results in ΔT_{film}<0.74 K at 25 °C and <1.2K at 100°C.

Internal heat transport limitations are calculated as the difference between catalyst grain edge and the average grain temperature as:

$$\Delta T_{int,av} = \frac{{d_p}^2 \sum_{i=BD,PP,n-but}(R_{vol.,i}^{Obs} \mid \Delta_r H_i \mid)}{60\,\lambda_{cat}} \qquad \text{Eq. S21}$$

where λ_{cat} is the heat conductivity of the catalyst grain, which because of the high heat transfer properties of graphite[16], we assume to be limited by Pd (72.1-73.5 W/(mK) for 25-100 °C)[17].

Analogous to external heat transport, deviations less than 5% of the catalytic activity when ΔT_{int}<$0.05\gamma_b/T$.

External mass transfer limitations

To understand the effect of external diffusion limitations by the Carberry number, Ca, is calculated which describes the difference between butadiene concentration at the catalyst grain exterior surface compared to the bulk gas-phase concentration. In other words, Ca=0.75 if the surface concentration is 25% of the reactor inlet concentration.

$$Ca = \frac{R_{vol.}^{Obs}}{k_g\, a_V\, C_{13bd}^0} = \frac{C_{BD}^0 - C_{BD}^{surf}}{C_{BD}^0} < \frac{0.05}{|n|} \qquad \text{Eq. S22}$$

where, $R_{vol.}^{Obs}$ is the volumetric reaction rate of the catalyst ($mol\, {m_{cat}}^{-3}\, s^{-1}$), k_g is external mass transfer coefficient ($m^3\, m^{-2}\, s^{-1}$), a_V is the external surface area of the catalyst grain ($6/d_p$ for spherical shape, where d_p is the average catalyst grain size in meters), C_{BD}^i is the concentration of butadiene in the bulk (C_{BD}^0= 0.3 mol% = 0.123 $mol\, {m_{gas}}^{-3}$ at 25°C) and at the external surface of the grain (C_{BD}^{surf}) which can be rewritten to determine surface concentration as:

$$C_{BD}^{surf} = C_{BD}^0(1 - Ca) = \eta_{ext}\, C_{BD}^0 \qquad \text{Eq. S23}$$

where η_{ext} is the effectiveness factor of external diffusion.

The external mass transfer coefficient, k_g, is calculated as

$$k_g = D_{BD,mix}\, a_V\, Sh \qquad \text{Eq. S24}$$

where $D_{BD,mix}$ is molecular diffusivity of butadiene in the gas mixture (see Eq. S3) and Sherwood number, Sh is defined as:[18]

$$Sh = 2 + 1.1Re^{0.6}Sc^{1/3} \qquad \text{Eq. S25}$$

where the Reynolds number, Re, is defined as:

$$Re = \frac{d_p\, \rho_{gas}\, u}{\mu} \qquad \text{Eq. S26}$$

with ρ_{gas} the gas density (0.62-0.50 $kg\ m^{-3}$), u the superficial gas velocity (0.067-0.084 $m\ s^{-1}$) and μ the gas mixture viscosity (Table S1).

The Schmidt number, Sc, is defined as:

$$Sc = \frac{\mu}{\rho_{gas}\, D_{BD,mix}} \qquad \text{Eq. S27}$$

This results in a value of Carberry number between 0 and 1. For a criterion of less than 5% resistance of activity due to external diffusion limitations, Ca should be less than $0.05/|n|$, where n is the reaction order (-0.25 for butadiene).[19]

Table S2. Calculated heat and mass transport. Catalytic data taken from 180 µm 2.6_Pd/C.

T_{set}	°C	25	100		T_{set}	°C	25	100
$X_{C_4H_6}$	%	26	91		$\Delta T_{int,bulk}$	°C	0.022	0.35
$X_{C_3H_6}$	%	0.07	5		ΔT_{ad}	°C	3.4	59
$S_{C_4H_{10}}$	%	0.5	10		Ca	-	0.011	0.031
$R_{vol.}^{Obs}$	$mol/m^3 s$	14.1	253		η_{ext}	%	98.9	96.9
ΔT_{film}	°C	0.03	0.44		Φ	-	0.09	0.3
$\Delta T_{int,av}$	°C	0.012	0.23		η_{int}	%	95.0	87.0

Additional catalyst characterisation

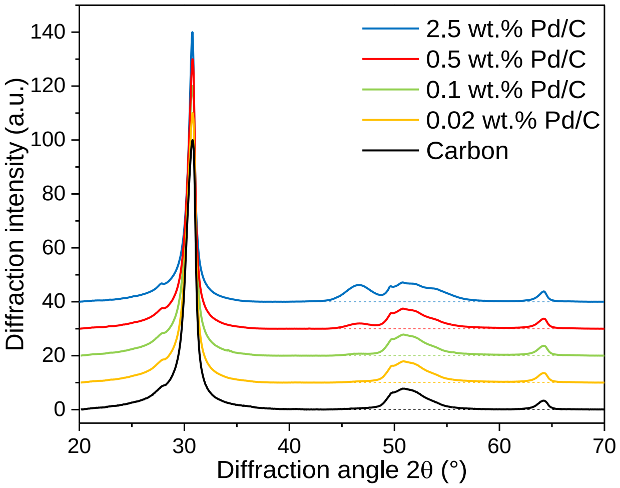

Figure S1. X-ray diffractograms of Pd/C catalysts, normalised to carbon peak at 30° 2θ.

Catalytic tests

Activity

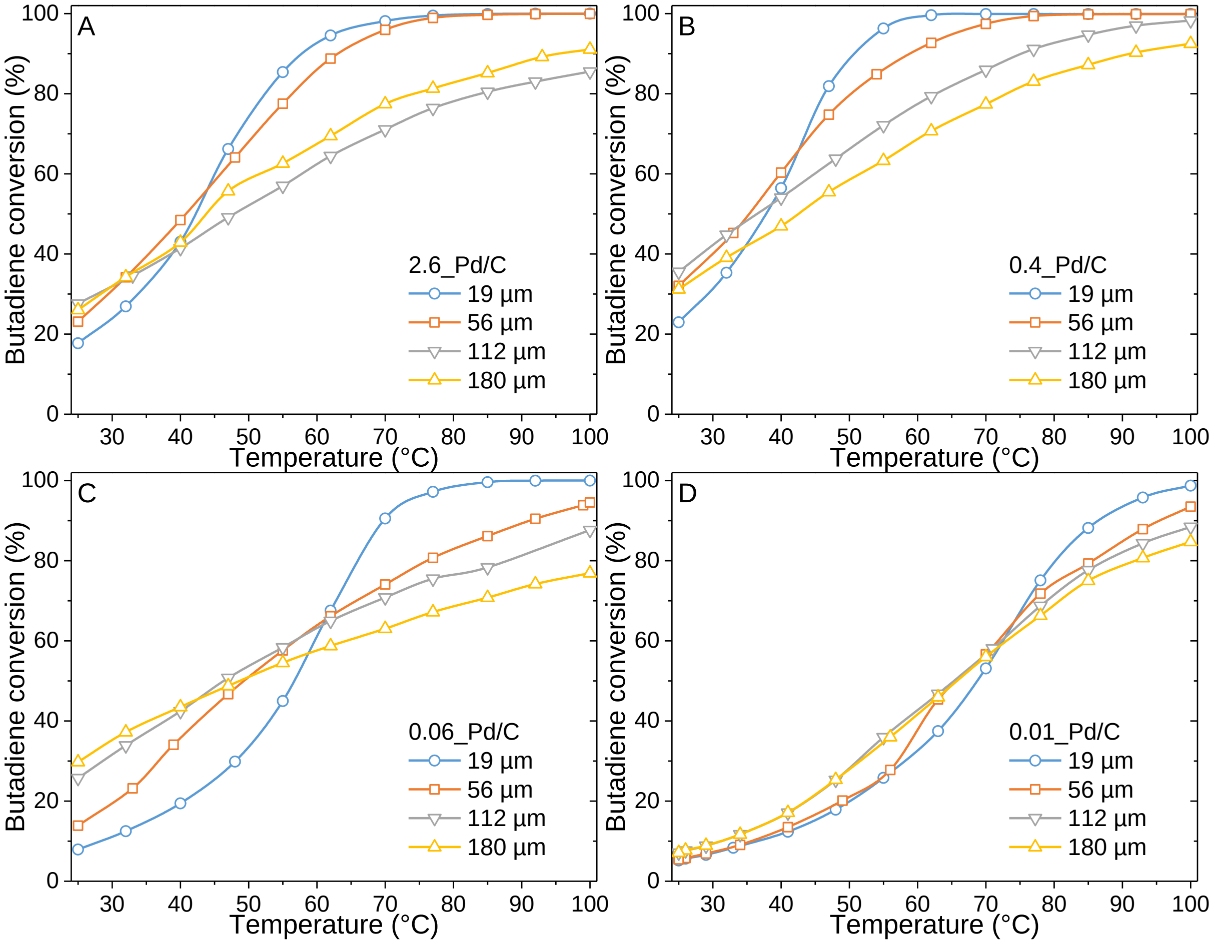

Figure S2. Butadiene conversion overview for all tested catalysts. All reactors are loaded with 2.50 mg of (diluted) Pd/C catalyst, resulting in 0.50 µg Pd per reactor.

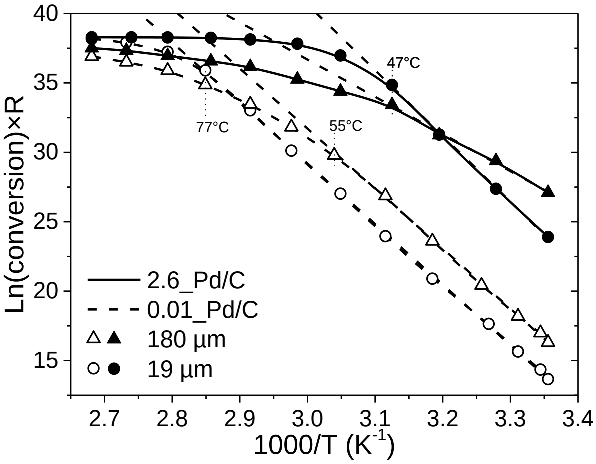

Figure S3. Arrhenius plot of catalysts depicted in Figure 2A of the main text. Dashed lines indicated the fitted data used for the determination of apparent activation energy.

Selectivity

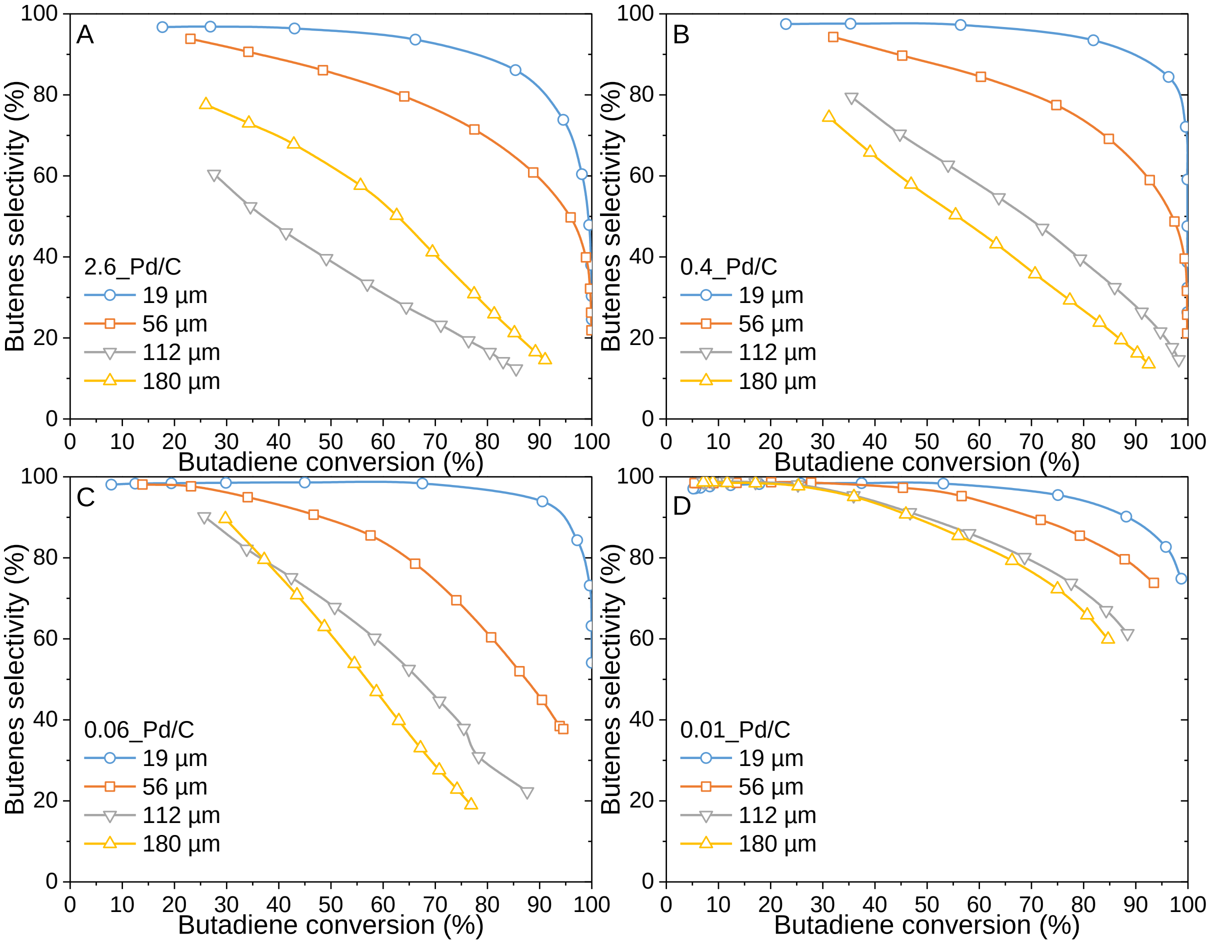

Figure S4. Butene selectivity overview for all tested catalysts. All reactors are loaded with 2.50 mg of (diluted) Pd/C catalyst, resulting in 0.50 µg Pd per reactor.

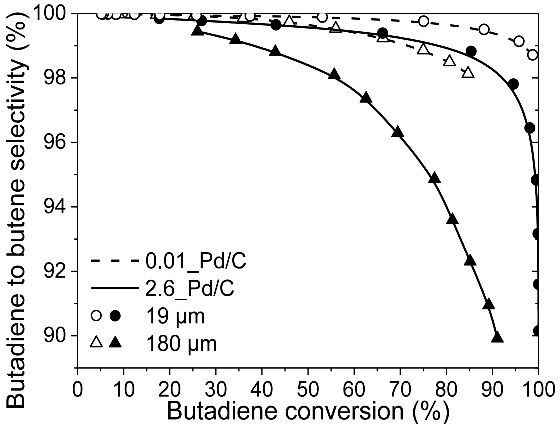

Figure S5. Selectivity to butenes, considering only the C_4H_x molecules, as a function of butadiene conversion.

Internal effectiveness factor

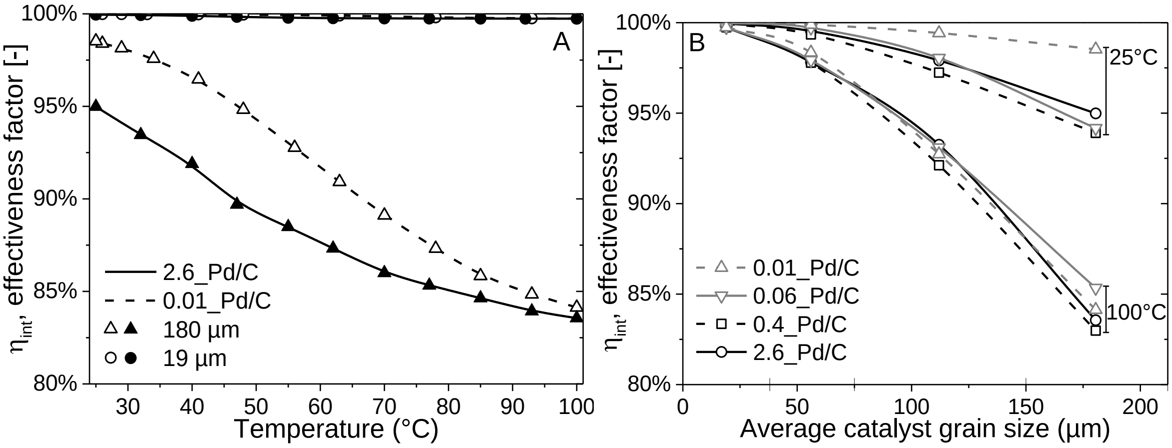

Figure S6. Internal effectiveness factor. Derived from the Weisz-modulus by Eq. 12 for the data in Figure 5 of the main text.

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