Electronic Supplementary Information (ESI) for

"Fischer-Tropsch Reaction in the Aqueous Phase over Rhodium Catalysts: A Promising Route to Selective Synthesis and Separation of Oxygenates and Hydrocarbons"

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Experimental

Catalyst synthesis

Preparation of the Rh/SiO₂ catalysts

The Rh(10%)/SiO$_2$ and Rh(20%)/SiO$_2$ catalysts were prepared by incipient wetness impregnation of commercial silica with a water solution of rhodium trichloride hydrate (Acros Organics), using a weight loading of 10% and 20%. The impregnated sample was dried in an oven at 80°C 12 h followed by calcination at 400°C for 4 h.

Preparation of Rh non-supported nanoparticles

The Rh nanoparticles were prepared using the w/o microemulsion method. Initially, 2.5 g of CTAB (cetyltrimethylammonium bromide) was dispersed in 3.0 g of hexanol with stirring. Afterward, 4.5 g of water containing 0.5 M RhCl$_3$*H$_2$O was added. An optically transparent microemulsion system (M1) was obtained. A separate microemulsion (M2) was prepared by mixing 0.113 g NaBH$_4$ in 4.5 g of water, 2.5 g of CTAB, and 3.0 g of hexanol. Microemulsion M2 was then added drop by drop to microemulsion M1. The resulting microemulsion was then stirred for 1 h. The prepared catalyst with Rh nanoparticles is denoted as Rh-Nps. The prepared sample was separated by centrifugation and subsequently washed with water. After, the prepared Rh nanopartciles were dried at 80 °C for 12 h.

Synthesis of rhodium complex

[LRhCl(PPh₃)]. Ligand N,N'-propanebis(3-phormyl-5-tert-butyl-salicylaldimine) (L) (0.11 g, 1.0 mmol) dissolved in hot dry methanol (10 mL) was added to a methanolic solution (10 mL) of Rh(PPh$_3$)$_3$Cl (0.23 g, 1.0 mmol), (Ph = phenyl) dropwise with constant stirring. The solution obtained was stirred for 10 min. A solution of TEA (0.10 g, 1.0 mmol) in 10 mL of methanol was added to the reaction mixture dropwise. A brown reaction mixture formed and was stirred under reflux for 10 h.

The solvent was distilled off under vacuum, the orange residue crystallized and washed with ethyl ether (3 × 5 mL). Yield 0.34 g, 38% based on L, m.p.: 190-200 ºC. The complex structure was confirmed by FT-IR, ^{1}H- NMR and elemental analysis

FT-IR, (ν, cm^{-1}) (KBr Disc): 3056br, 2955s, 1669s, 1623s, 1560m, 1361s, 1233w (br, broad; s, sharp; m, medium; w, weak).

^{1}H NMR (600 MHz, CDCl$_3$) : δ = 10.55 (CHO, 2H) ; 8.45-8.35 (CH, 2H) ; 7.95-7.05 (ArH, 4H) ; 4.18 (CH$_2$, 4H) ; 3.49-3.40 (CH$_2$, 2H) ; 1.53-1.05 (CH$_3$, 18H) and 7.82-7.40 (P(C$_6$H$_5$)$_3$).

Elemental Analysis Data. Calculated. (%) for C$_{45}$H$_{34}$ClN$_2$O$_4$PRh: C, 63,42; H, 5.91; N, 3.29. Found: C, 63,56; H, 5.80; N, 3.20.

Preparation of Rh-complex/SiO$_2$ catalyst

The cx-Rh(10%)/SiO$_2$ catalyst was prepared by impregnation method of commercial silica with a rhodium complex (*[LRhCl(CH$_3$OH)]*), in ethanol, using a weight loading of 10%. After impregnation the sample was dried in an oven at 80°C 12 h and calcined at 400ºC for 4 h. The TGA data suggest (**Fig. S3**) that catalyst calcination at 400°C for 4 h results in decomposition of the Rh Schiff complex.

Catalyst characterization

The catalyst reducibility was studied using temperature-programmed reduction (TPR) system with an Autochem II (Micrometrics) apparatus. The samples were reduced under a flow of 5 % H$_2$ in argon (50 mL/min) and heated up to 800 °C at a rate of 5°C/min.

The transmission electron microscopy (TEM) analysis were carried out on a Tecnai instrument equipped with a LaB6 crystal operated at 200 kV. Before the analysis, the samples were dispersed by ultrasound in ethanol for 5 min, and two drops of the suspension was deposited onto a carbon membrane on a 300 mesh copper grid.

The X-ray diffraction (XRD) spectra were made with a D8 Advance diffractometer equipped with an energy dispersive type detector and a monochromatic CuK_α radiation source (40 kV and 30 mA). The scan range was set to $2\Theta = 5\text{-}80^\circ$ with a step size of 0.02° and a step time of 0.5 s.

Catalytic testing

The catalytic experiments were carried out in a 25 ml stirred stainless steel autoclave operating in a batch mode. For FTS, about 0,1-0,3 g of freshly prepared catalyst was dispersed into 5 ml of deionized water. The catalyst was reduced at 170°C with 2.0 MPa of hydrogen for 2 h. After cooling to room temperature, hydrogen was released and 3.0 MPa syngas was added. H_2/CO mole ratio equal to 2:1. The autoclave was then heated to 180-200°C with 500 rpm stirring for 12-24 h.

The products of aqueous Fischer-Tropsch synthesis were analysed using well-defined methods. Permanent gases including H_2, CO, CO_2, CH_4 and N_2 (as the internal standard) were separated and quantified using Bruker 465-GC. Gaseous $C_1\text{-}C_7$ hydrocarbons were analysed with Micropacked GC column and flame ionization detector (FID). Liquid hydrocarbons and oxygenates were analysed with BR-Q PLOT capillary column and FID using dioxane as the intern standard.

Conversions of CO (mol %) and product selectivity (mol %) in the experiments were defined as follows:

Conversion (mol %) = (moles of CO reacted)/(moles of initial CO) ·100;

Selectivity (mol %) = (moles of C atoms of product produced)/(moles of CO reacted)·100.

The surface-specific activity (turnover frequency, TOF) for Rh catalysts in aqueous phase FT synthesis was calculated from the rate of moles of CO conversion divided by the number of surface Rh atoms:

$$TOF = \frac{N_{CO(0)} * X_{CO}}{t * D_{Rh} * N_R}$$

where $N_{CO(0)}$ is initial number of moles of CO in the reactor, X_{CO} is the CO conversion, **t** is the reaction time, N_{Rh} is the amount of Rh in the reactor, D_{Rh} is the Rh dispersion. The rhodium dispersion (D_{Rh}) was calculated assuming spherical shapes by using the following formula [1]:

$$D_{Rh} = 6\frac{Va}{Sa} * d_{vs}{}^{-1}$$

where V_a is the effective volume per metal atom (which can be derived from the molar volume of the solids), V_s the effective average surface area occupied by a metal atom in the surface, and d_{vs} the mean particle size (Sauter mean diameter, $d_{3,2}$).

The external diffusion limitation in a batch reactor were excluded by conducting the experiments with different stirring rates. No effect on the conversion was observed. The internal diffusion limitations were excluded using the Weisz-Prater criterion.[2,3]
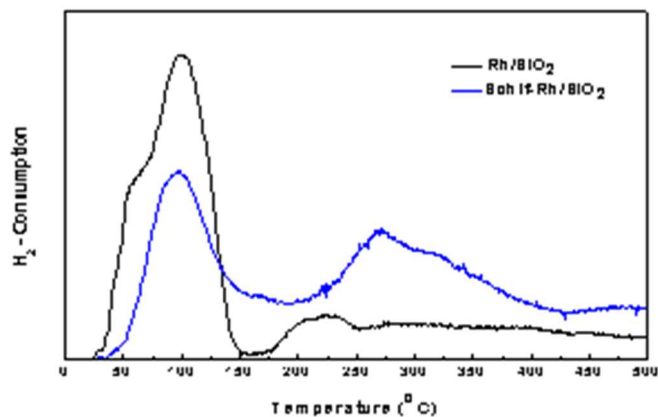
$$N_{W-P} = \frac{Rr_p{}^2}{D_{eff}C_s} \leq 0.3$$

where R = observed reaction rate (mol g^{-1} s^{-1}), r_p= catalyst particle radius (cm), D_{eff} = effective diffusivity (cm^2 s^{-1}), C_s = gas concentration at the external surface of the catalyst (mol cm^{-3}). We considered the CO conversion of 83% and reaction time of 24 h. The CO pressure was 10 bar. The catalyst particle size was of 0.010 - 0.015 cm. C_s and D_{eff} were $4.45*10^{-4}$ mol/cm^3 and $1.4*10^{-4}$ cm^2 s^{-1} [4], respectively. The N_{W-P} value is calculated to be 4.7×10^{-4}, which is much lower than 0.3.

Table S1. Detailed composition of hydrocarbons and oxygenates produced over silica supported catalysts (T = 200°C, p (CO) = 10 bar, p (H$_2$) = 20 bar, t = 24 h, stirring rate = 500 rpm)

|	T, °C	CO conversion, %	CO$_2$ selectivity, %	Carbon selectivity, % (CO$_2$ free)								
				CH$_4$	C$_2$-C$_4$ total	C$_2$-C$_4$ olefin	C$_2$-C$_4$ paraffin	C$_5$-C$_7$ total	C$_5$-C$_7$ olefin	C$_5$-C$_7$ paraffin	Olefin/ paraffin	C$_1$-C$_4$ oxyg.
Schiff – Rh - SiO$_2$	200	86	36	14.4	41.6	10.5	30.1	7.6	3.3	4.7	0.40	31.5
Schiff – Rh - SiO$_2$	195	72	30	9.4	50.3	10.0	40.3	9.6	4.0	5.6	0.31	25.9
Rh - SiO$_2$	200	72	62	33.6	35.8	6.5	29.3	8.9	3.7	5.2	0.30	13.9
Rh - SiO$_2$	180	46	34	28.2	31.1	5.4	25.7	19.2	2.7	16.5	0.19	9.0
20%Rh-SiO$_2$	200	60	38	29.3	38.8	3.7	35.1	10.9	1.9	9.0	0.13	12.1
Schiff - Rh	200	0	-	-	-	-	-	-	-	-	-	-
Rh - NPs	200	71	36	17.0	58.4	11.1	47.3	12.7	4.0	8.7	0.27	2.2

TPR

Fig. S1. TPR profile of Rh/SiO$_2$ and Schiff-Rh/SiO$_2$ catalysts, the metal loading is 10%. Rh is reduced between 50 and 150°C. Broad high temperature peaks in the profile of Schiff-Rh/SiO$_2$ are related to removal of carbon species, which remain after decomposition of the Schiff complex.
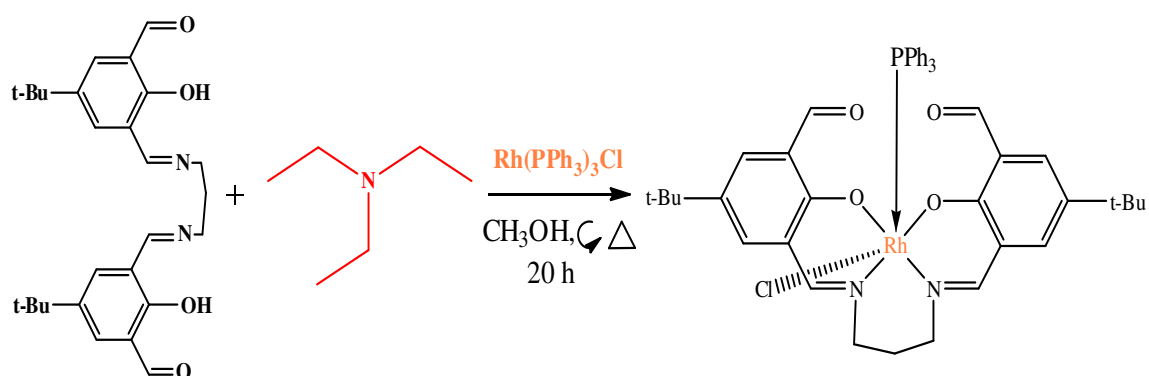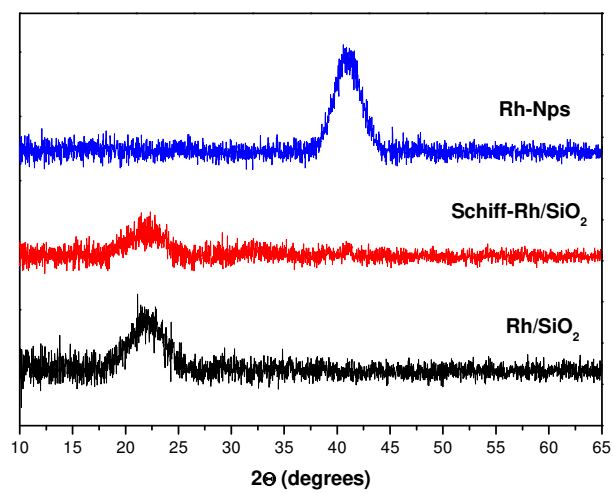

Fig. S2. The synthesis of the rhodium complex.
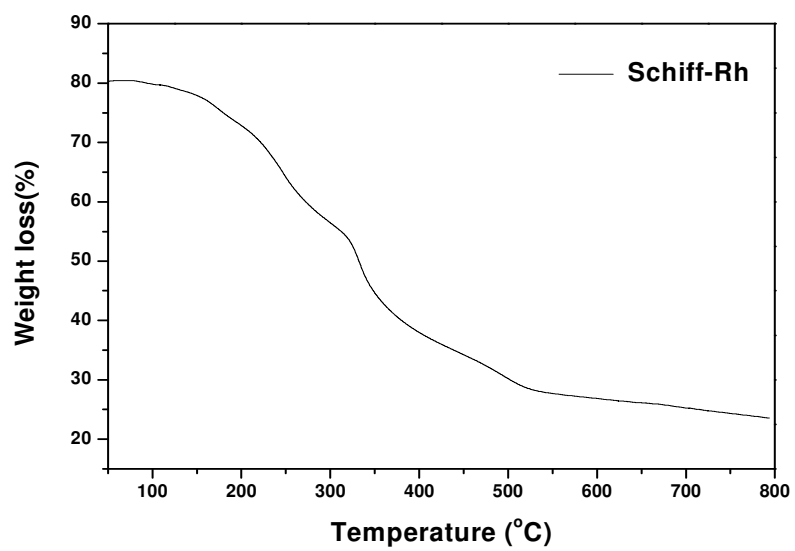
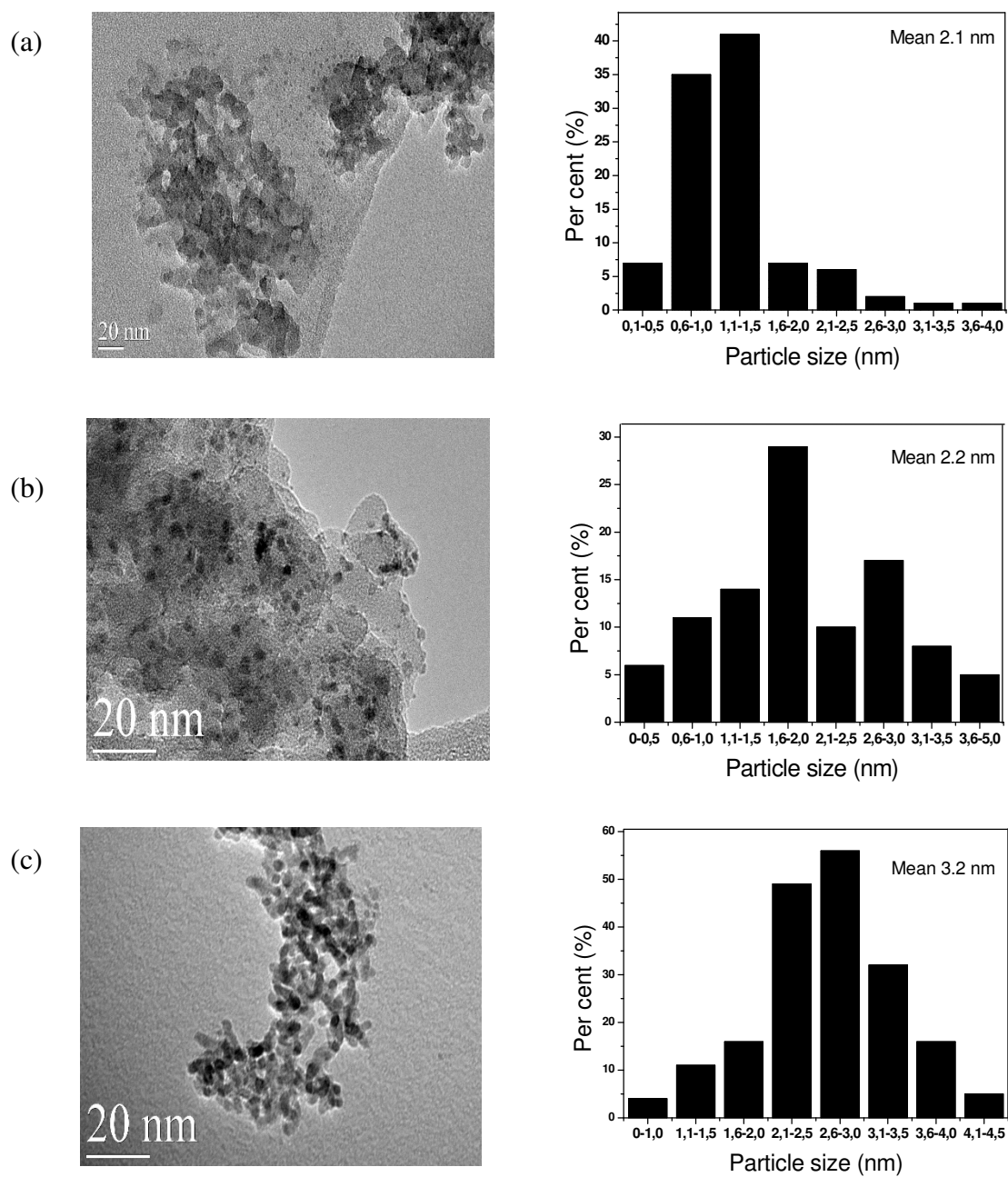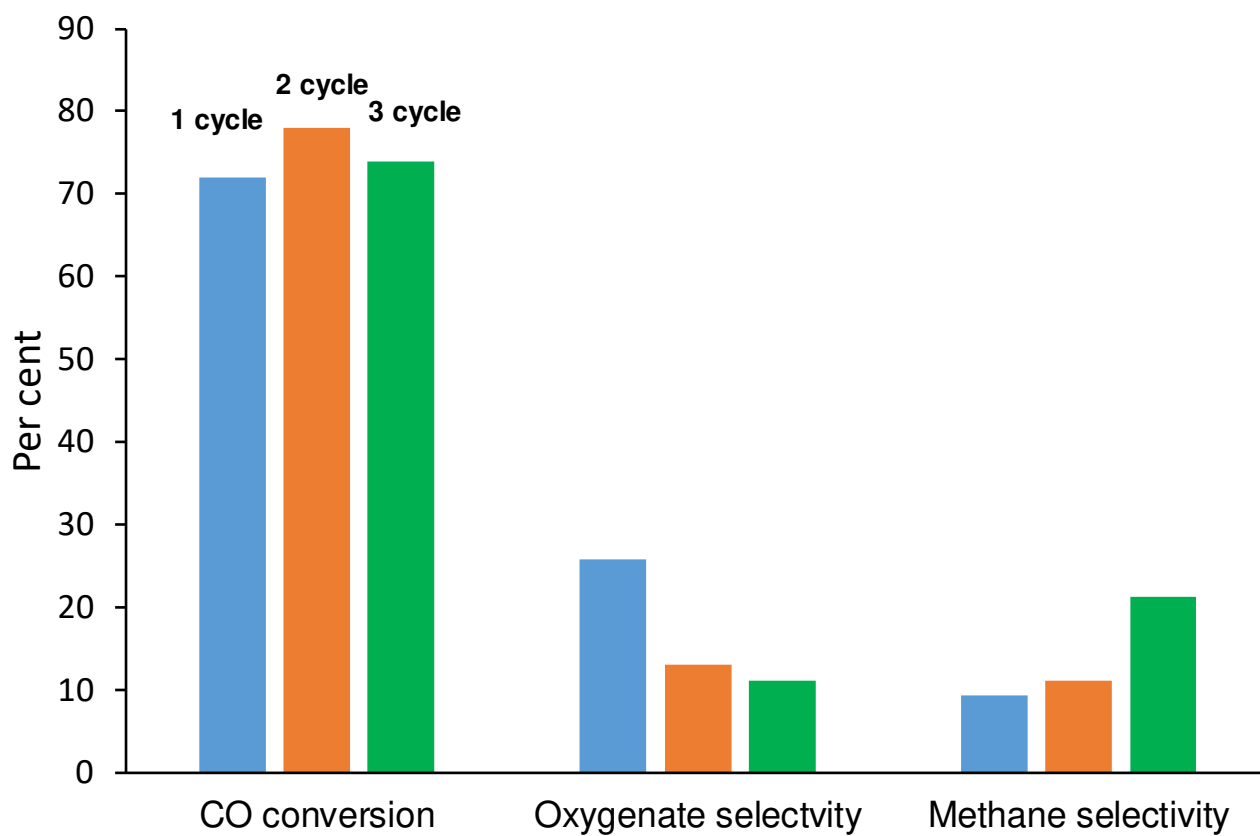**Fig. S3**. TGA curve of the Rh Schiff base complex.

XRD

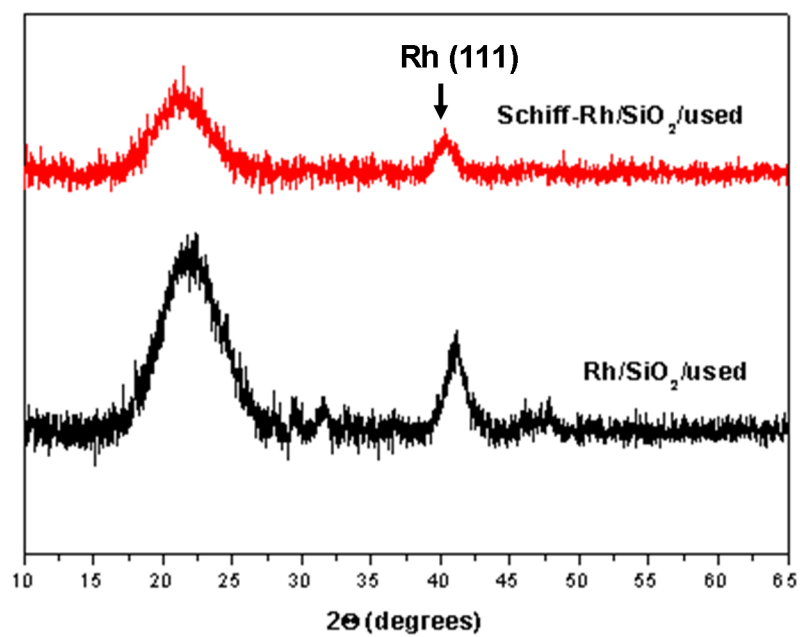**Fig. S4**. XRD patterns of the Schiff-Rh/SiO$_2$, Rh/SiO$_2$, Rh-Nps catalysts.

TEM

Fig. S5. TEM micrographs and Rh particle size distribution: (a) Schiff-Rh/SiO$_2$, (b) Rh/SiO$_2$ and (c) Rh-NPs.

Fig. S6. Catalytic performance of Schiff – Rh - SiO$_2$ in 3 consecutive reaction cycles. Conditions: T=195° C, p (CO) = 10 bar, p (H$_2$) = 20 bar, t = 24 h, stirring rate = 500 rpm.

Fig. S7. XRD patterns of the Schiff-Rh/SiO$_2$ and Rh/SiO$_2$ catalysts after reaction.

Reference

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[2]   D.E. Mears, Tests for Transport Limitations in Experimental Catalytic Reactors, Ind. Eng. Chem. Process Des. Dev. 10 (1971) 541–547. doi:10.1021/i260040a020.

[3]   P.B. Weisz, C.D. Prater, Interpretation of Measurements in Experimental Catalysis, in: 1954: pp. 143–196. doi:10.1016/S0360-0564(08)60390-9.

[4]   D. Vervloet, F. Kapteijn, J. Nijenhuis, J.R. van Ommen, Fischer–Tropsch reaction–diffusion in a cobalt catalyst particle: aspects of activity and selectivity for a variable chain growth probability, Catal. Sci. Technol. 2 (2012) 1221. doi:10.1039/c2cy20060k.