Modelling atomic layer deposition overcoating formation on a porous heterogeneous catalyst

Supporting information

Niko Heikkinen[a]*, Juha Lehtonen[a], Laura Keskiväli[a], Jihong Yim[b], Shwetha Shetty[c], Yanling Ge[a], Matti Reinikainen[a], Matti Putkonen[c]

[a] VTT Technical Research Centre of Finland, P.O.Box 1000, FIN-02044 VTT, Espoo, Finland.

[b] Department of Chemical and Metallurgical Engineering, Aalto University School of Chemical Engineering, Kemistintie 1, Espoo, Finland.

[c] University of Helsinki, Department of Chemistry, P.O.Box 55, FIN-00014, Helsinki, Finland.

niko.heikkinen@vtt.fi; juha.lehtonen@vtt.fi; laura.keskivali@vtt.fi; jihong.yim@aalto.fi; shwetha.ariyadka@helsinki.fi; yanling.ge@vtt.fi; matti.reinikainen@vtt.fi; matti.putkonen@helsinki.fi

* Corresponding author.
E-mail address: niko.heikkinen@vtt.fi (Niko Heikkinen).

1   Introduction

This work presents a coupled diffusion-reaction differential equation model to estimate ALD overcoating penetration into a Co-Pt/TiO$_2$ porous catalyst, similar to commercial catalysts listed by Rytter & Holmen [1]. The model is used to estimate deposition thicknesses with a given set of catalyst structural parameters and precursor parameters. The presented model is compared against microscopy (TEM and SEM) measurement data. In addition to the prepared diffusion-reaction model, the overcoated samples were studied in the Fischer-Tropsch reaction, where 20 and 30 cycle ALD overcoated samples present a decreased rate of deactivation. Although the deactivation rate could be decreased, this benefit comes with a price of promoted methanation activity and decreasing chain propagation α-value. The chain propagation α-value was decreasing linearly with respect to overcoating thickness from 0.917 (non-overcoated catalyst) to 0.908 (30 deposition cycles).

The Fischer-Tropsch (FT) reaction and a cobalt-based catalyst was selected due to its attractiveness in many renewable resource utilisation schemes [2]. Recently, the effect of water has gained interest related to the Fischer-Tropsch catalyst development [3–7]. This is partly due to development of carbon capture and utilisation (CCU) concepts, where a significant amount of water might enter the FT step from the upstream reverse water-gas shift (rWGS) unit. For this reason, protective ALD overcoating's present an interesting approach to maintain catalyst activity in high conversion-level and added water conditions.

2   Materials and methods

2.1   Catalyst testing

The continuous FT experiments were performed in a tubular fixed-bed reactor system (Hastelloy C, 9.1 mm i.d.) at a temperature of 210 °C, pressure of 15 bar and a H$_2$/CO ratio of 2.0. The reaction pressure was set to 15 bar to avoid water condensation in the reaction temperature (210 °C). A detailed equipment description can be found elsewhere [8]. Prior to FT reaction, the tubular reactor was packed with a catalyst bed of 1 gram and reduced at 400 °C with H$_2$ (100 cm$^3_{STP}$ min^{-1} g$_{cat}^{-1}$) for 16 h. During the initial start-up phase, reaction conditions were slowly increased to T = 210 °C, P = 15 bar, H$_2$/CO inlet molar ratio of 2.0. Four different reaction conditions were applied in the FT run (steps A to D). Table S1 presents these steps, where first steps (reaction step A and B) are referred to as dry conditions, having only indigenous water present in the catalyst bed. After reaching stationary conditions (time-on-stream 48-72 h), the added water or wet conditions were initiated by replacing He flow with water vapour. As all ALD overcoated catalyst samples had decreased initial activity, the inlet flows of the reactants were adjusted to achieve similar conversion level with all catalysts in step B. Table S1 summarises the reaction conditions, where co-fed water addition resulted in simulated a CO

conversion level of ~70%. Simulated conversion was determined as a fraction of the added H_2O partial pressure to the partial pressure of H_2, resulting in a similar total amount of H_2O in the catalyst bed as would be produced at 70% CO conversion. Wet conditions were produced with an HPLC pump (Gilson 307, Gilson Inc. USA) and ultra-pure, degassed distilled water by feeding the water into a coiled evaporator (at 400 °C) and mixing the water vapour into the $H_2/CO/N_2$ stream before reactor inlet.

Table S1, Reaction condition summary for each experimental step. Temperature and pressure fixed to 210 °C and 15 bar$_g$ in all steps.

Reaction step	$y_{H_2}^0$ [mol-fraction]	y_{CO}^0 [mol-fraction]	$y_{N_2}^0$ [mol-fraction]	y_{He}^0 [mol-fraction]	$y_{H_2O}^0$ [mol-fraction]	$\dfrac{P_{added\ H_2O}^0}{P_{H_2}^0}$	Simulated conversion level (%)
A & B, DRY	0.36	0.18	0.04	0.42	0	0	-
C, WET	0.36	0.18	0.04	0	0.42	1.17	70
D, DRY	0.36	0.18	0.04	0.42	0	0	-

After wet conditions (at step C), with a high simulated CO conversion level, the water addition was stopped after 132 h TOS, reverting to step B conditions. This was done to evaluate reversible or irreversible effects on the catalyst activity. Both step C and D lasted for 60 - 70 h enabling reaction stabilisation during and after co-fed water. Gas compounds (H_2, N_2, CO, CO_2, C_1-C_{14} hydrocarbons) were analysed on-line with gas chromatograph TCD/FID (Shimadzu GC-2030) having precolumn (Porapak-Q, 1 mm i.d. x 1.8 m), an analytical column (Carboxen-1000, 1 mm i.d. x 2.5 m) and DB-1 capillary column (i.d. 0.25 mm x 60 m x 1 µm). The detailed product collection procedure and analytical methods are reported elsewhere [9].

3   Results and discussion

3.1   Overcoating effect on catalyst performance at Fischer-Tropsch reaction

The catalyst performance was evaluated in the Fischer-Tropsch reaction. The continuous FT experiment consisted of four reaction conditions, of which the most important was Step C, simulated high conversion level (~70%) reaction conditions. Figure S1 presents the overall catalyst activity as CO conversion as a function of time-on-stream (TOS, h).
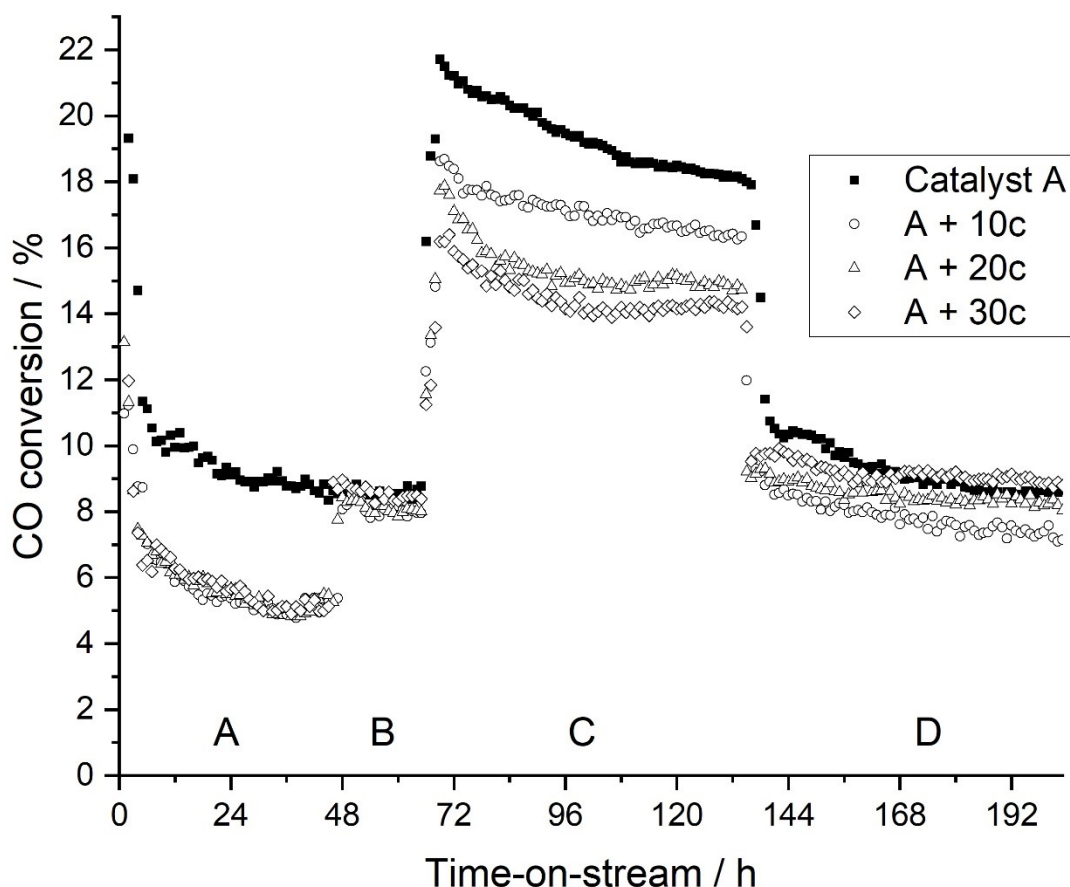
Figure S1, Fischer-Tropsch reaction overall activity as carbon monoxide conversion versus time-on-stream. Catalyst A non-overcoated sample and three samples with 10, 20, and 30 cycle ALD overcoating. Reaction steps A (initial activity), B (conversion adjusted to ~9%), C (added water conditions, simulated conversion level ~70%) and D (back to step B conditions, no added water to reactor inlet).

The experiments were started with an initial activity phase (Step A), where non-overcoated Catalyst A stabilised to 8.8 % CO conversion. With ALD overcoated catalysts, the initial activity was identical throughout steps A and B. During step B with the overcoated catalyst sample, the feed rate flow was adjusted to achieve ~8 % CO conversion level. Although ALD overcoated catalysts had no overall activity difference during step A and B, the selectivities in Table S2 show that methane selectivity increased along the thickening overcoating. This behaviour continued during step C, i.e., in added water conditions, where methane selectivity increases from 6.8 % to 10.1 % with 10c and 30c ALD overcoatings, respectively. Interestingly, the selectivity trend remains similar between dry and wet conditions, however, the overall activity alters significantly during wet conditions (step C). According to Figure S1 (Step C), the overall activity decreases upon the thickening overcoat layer. At the end of step C, the corresponding CO conversions were 18.2, 16.3, 14.7 and 14.1 for Catalyst A, 10c, 20c and 30c, respectively. Regarding the overcoating deactivation prevention, the Figure S1 CO conversion stabilisation after 96 h might support this assumption. In addition, step D dry conditions resulted in increased activity for the thickest overcoated sample (A + 30c).

Added water conditions regarding Co/TiO$_2$ catalysts has been reported both to increase [5,10] and decrease the catalyst activity [11]. Our results in Figure S1 would support the literature regarding increased activity. It has been hypnotized, that TiO$_2$ as a support contain a separate intraparticle water phase, assisting CO and H$_2$ transport [12]. This water layer would assist reagent gas transport to otherwise diffusion or transport limited reaction surfaces, thus increasing the overall activity of the catalyst. It is also postulated that the positive effect of water for Co/TiO$_2$ catalysts might be due to a reversal of the encapsulation of the cobalt crystal with titania [13].

An additional factor in the reactor experiment might originate from the changing gaseous compound during dry and wet conditions. The dry conditions have a He flow that is replaced with water during the added water conditions. Although reactor equipment was adjusted to vaporize and transport water in gaseous form, it was possible that slightly lower volumetric flow was achieved with the added water feed. This lower volumetric flow would lead into slightly higher conversion level in added water conditions (Step C).

Table S2, Compound selectivity for CH$_4$, C$_2$-C$_4$, C$_{5+}$, CO$_2$ and olefin to paraffin ratio. DRY condition is without co-fed water, after initial activity phase (at time-on-stream 48h), at the same conversion level (~5%$_{CO}$). WET condition selectivity from co-fed water addition phase (at time-on-stream 48h) and CO conversion level 15-18%.

Sample	CH$_4$ (m-%) DRY	CH$_4$ (m-%) WET	C$_{5+}$ (m-%) DRY	C$_{5+}$ (m-%) WET	C$_2$-C$_4$ (m-%) DRY	C$_2$-C$_4$ (m-%) WET	CO$_2$ (mol-ppm) DRY	CO$_2$ (mol-ppm) WET	*O/P ratio DRY	*O/P ratio WET
Catalyst A	8.9	6.6	86.5	88.6	4.6	4.9	nd	1462	1.37	0.97
A + 10c	5.8	6.8	88.8	88.2	5.4	5.3	nd	3024	1.23	2.63
A + 20c	7.7	7.5	86.4	87.5	5.9	5.0	nd	2804	0.98	2.60
A + 30c	8.1	10.1	84.9	83.6	7	6.3	nd	661	0.82	1.88

DRY = experimental condition without co-fed water
WET = experimental condition with co-fed water addition
nd = not detected
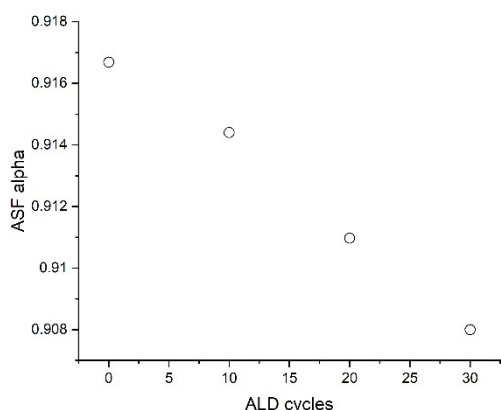**Average O/P ratio from C$_4$-C$_6$ hydrocarbons*

Figure S2, Anderson–Schulz–Flory chain propagation (alpha) value as a function of ALD cycles. Chain propagation α-value measured from produced FT wax fraction, C$_{40}$-C$_{60}$.

Figure S2 presents the measured Anderson–Schulz–Flory chain propagation (α) values from collected wax samples after FT reaction. The plot presents decreasing linear behaviour as a function of thickening overcoating. The discrepancy between Table S2 dry condition selectivity values and Figure S2 ASF-α values were due to sample collection. Table S2 selectivities were determined separately for dry and wet conditions from online measurement data, and wax samples were collected after the reaction was terminated. Therefore, the wax sample presented an averaging mixture throughout the whole experiment. CO_2 was only detected during wet conditions. Interestingly, the CO_2 concentration had a maximum (3024 mol-ppm) related to 10c catalyst samples; whereas other samples showed 1462 mol-ppm for non-overcoated catalyst and 2804 and 661 mol-ppm for 20c and 30c samples, respectively. CO_2 formation results from the water-gas shift reaction. Table S2 indicates a higher WGS activity for 10c and 20c catalysts compared to the non-overcoated sample. A lower WGS activity could be possible with a 30c sample; however, a detailed comparison was difficult due to the varying conversion level. The olefin to paraffin ratio related to C_4-C_6 hydrocarbons decreased in dry conditions along the thickening overcoating. This behaviour was changed during wet conditions, where the O/P ratio of ALD overcoated samples was 2-3 times higher than that of the non-overcoated catalyst. This was assumed to result from suppressed hydrogenation activity related to overcoated catalysts. This assumption was supported by the Figure S2 ASF-α value, where supressed hydrogenation would result in decreasing chain propagation probability.

The ALD overcoating effect on selectivity is a sum of several factors. One factor is the altered physi-chemical environment due to added overcoating, where reactant gases and reaction products must diffuse, adsorb-desorb and diffuse away from the catalyst active sites. According to Lögdberg et al. [14], the Co-based FT catalyst has separate active sites for methane formation and chain propagation. Overcoating might decorate selectively active sites, shown by Lu et al. [15] with Pd nanoparticles, where initial Al_2O_3 ALD cycles preferably attached to low coordination sites. In our study, despite the extensive catalyst TEM analysis, no Co particles were found to have ALD overcoating. This was due to sample preparation, where catalyst particles were crushed and analysed with TEM. As the overcoating penetrated ~10-17 μm surface layer of a 400 μm diameter catalyst particle, the volume-fraction of overcoated Co particles was very low. Despite the lack of direct particle visualisation, Table 3 and Figure 6 (at the main manuscript) TEM measurement results could indirectly support the assumption of the site favoured overcoating formation. This variation might result from the low coordination site preference during initial ALD cycles, influencing the coverage of separate methanation and chain propagation sites.

References

[1]   E. Rytter, A. Holmen, Catalysis Today 275 (2016) 11–19.

[2]   F.V.F.V. Vázquez, J. Koponen, V. Ruuskanen, C. Bajamundi, A. Kosonen, P. Simell, J. Ahola, C. Frilund, J. Elfving, M. Reinikainen, N. Heikkinen, J. Kauppinen, P. Piermartini, Journal of CO2 Utilization 28 (2018) 235–246.

[3]   E. Rytter, Ø. Borg, N.E. Tsakoumis, A. Holmen, Journal of Catalysis 365 (2018) 334–343.

[4]   S. Lögdberg, M. Boutonnet, J.C. Walmsley, S. Järås, A. Holmen, E.A. Blekkan, Applied Catalysis A: General 393 (2011) 109–121.

[5]   C.J. Bertole, C.A. Mims, G. Kiss, Journal of Catalysis 210 (2002) 84–96.

[6]   L. Fratalocchi, C.G. Visconti, L. Lietti, G. Groppi, E. Tronconi, E. Roccaro, R. Zennaro, Catalysis Science and Technology 6 (2016) 6431–6440.

[7]   E. Rytter, A. Holmen, ACS Catalysis 7 (2017) 5321–5328.

[8]   M. Marchese, N. Heikkinen, E. Giglio, A. Lanzini, J. Lehtonen, M. Reinikainen, Catalysts 9 (2019) 717.

[9]   N. Heikkinen, L. Keskiväli, P. Eskelinen, M. Reinikainen, M. Putkonen, Catalysts 11 (2021) 672.

[10]   S. Storsæter, Borg, E.A. Blekkan, B. Tøtdal, A. Holmen, Catalysis Today 100 (2005) 343–347.

[11]   J. Li, G. Jacobs, T. Das, B.H. Davis, Applied Catalysis A: General 233 (2002) 255–262.

[12]   S. Krishnamoorthy, M. Tu, M.P. Ojeda, D. Pinna, E. Iglesia, Journal of Catalysis 211 (2002) 422–433.

[13]   A.K. Dalai, B.H. Davis, Applied Catalysis A: General 348 (2008) 1–15.

[14]   S. Lögdberg, J. Yang, M. Lualdi, J.C. Walmsley, S. Järås, M. Boutonnet, E.A. Blekkan, E. Rytter, A. Holmen, Journal of Catalysis 352 (2017) 515–531.

[15]   J. Lu, J.W. Elam, P.C. Stair, Accounts of Chemical Research 46 (2013) 1806–1815.