Electronic Supplementary Information (ESI) for

“In-situ XRD investigation of the evolution of alumina-supported cobalt catalysts under *realistic conditions of Fischer-Tropsch synthesis”*

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Contents

1. *In situ* time-resolved XRD experiments

The *in-situ* XRD patterns were measured using the two-circle diffractometer equipped by six detectors having Si(111) analyzer crystals and Na-I scintillation counters. The X-ray beam wavelength (λ) was set to 0.5 Å by Si(111) channel-cut monochromator. The known amount of catalyst (7-10 mg) was loaded in the quartz capillary (OD=1 mm, wall thickness=0.020 mm) and pressed from both sides with quartz wool. The capillary reactor used for *in-situ* XRD measurements is displayed in Fig. S1. The capillary was attached to the stainless steel holder using high temperature epoxy glue. A Cyberstar gas blower was used to control the capillary reactor temperature. The total pressure in the reactor (up to 20 bar) was regulated by

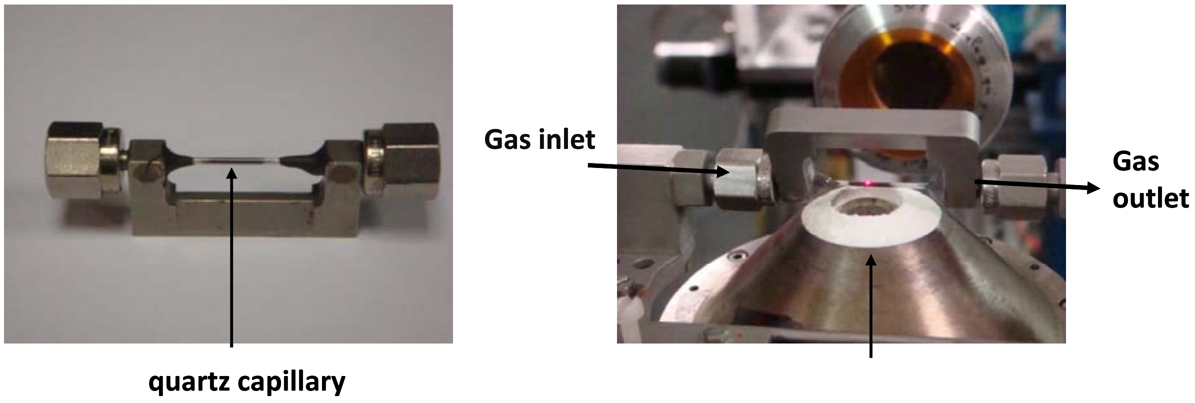

Fig. S1. Capillary reactor used for *in-situ* XRD measurements.

a back pressure controller. The gas lines before and after the reactor were heated up to 200°C using Horst heating tape to prevent condensation of liquid products. The liquid and solid products (water and heavy hydrocarbons) were collected downstream of the reactor in the stainless steel container at room temperature. Before the FT tests the catalyst were reduced in hydrogen flow at 623 K at atmospheric pressure (temperature ramp of 3 K/min) and cooled down to 323 K in H_2 flow. Fig. S2 shows the *in-situ* XRD patterns of the reduced CoPt/Al_2O_3-573 and CoPt/Al_2O_3-773.

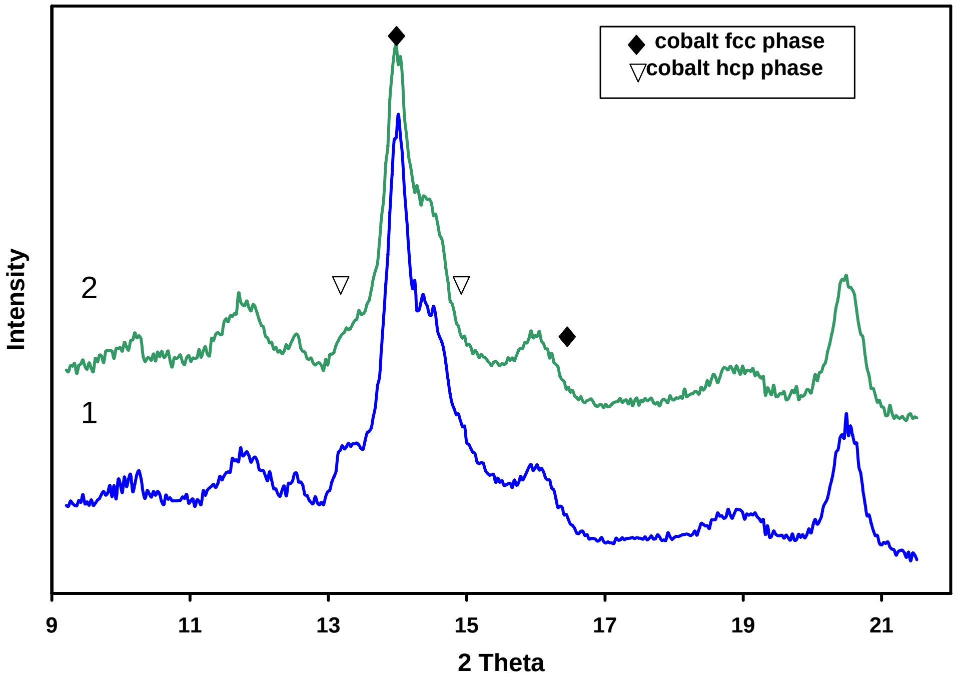

Fig. S2. *In-situ* synchrotron XRD diffraction patterns of CoPt/Al_2O_3-573 (1) and CoPt/Al_2O_3-773 (2) catalysts after reduction at 623 K in hydrogen. The XRD patterns were measured in hydrogen flow at 623 K (λ=0.5 Å).

After the reduction, the catalyst exposed to the syngas (H_2/CO=2) at atmospheric pressure. Then the system was pressurized up to 20 bar and temperature of the catalyst was risen up to 493 K under syngas flow. The time-resolved XRD patterns were recorded *in-situ* under gas flows at desired temperatures and pressures. The measuring time per an XRD pattern in the 2θ range between 9.2 and 21.5° was close to 10 min. The evolution of the *in-situ* XRD patterns of CoPt/Al_2O_3-773 catalyst (λ=0.5 Å) during FT reaction is shown in Figure S3. The quality of whole patterns matching was evaluated using conventional weighted profile agreement factor (R_{wp}):

$$R_{wp} = 100\left[\frac{\sum_{i=1,n} w_i |y_i - y_{c,i}|^2}{\sum_{i=1,n} w_i y_i^2}\right]^{1/2}$$

where **n** is the total number of points used in the refinement, $\mathbf{y_i}$ the observed intensity at point **i**, $\mathbf{y_{ci}}$ is the calculated intensity at point **i** and $\mathbf{w_i}$ the number of the observation at point **i** calculated at each cycle supposing a Poissonian distribution:

$$w_i = 1/\sigma^2_{calc,i}$$

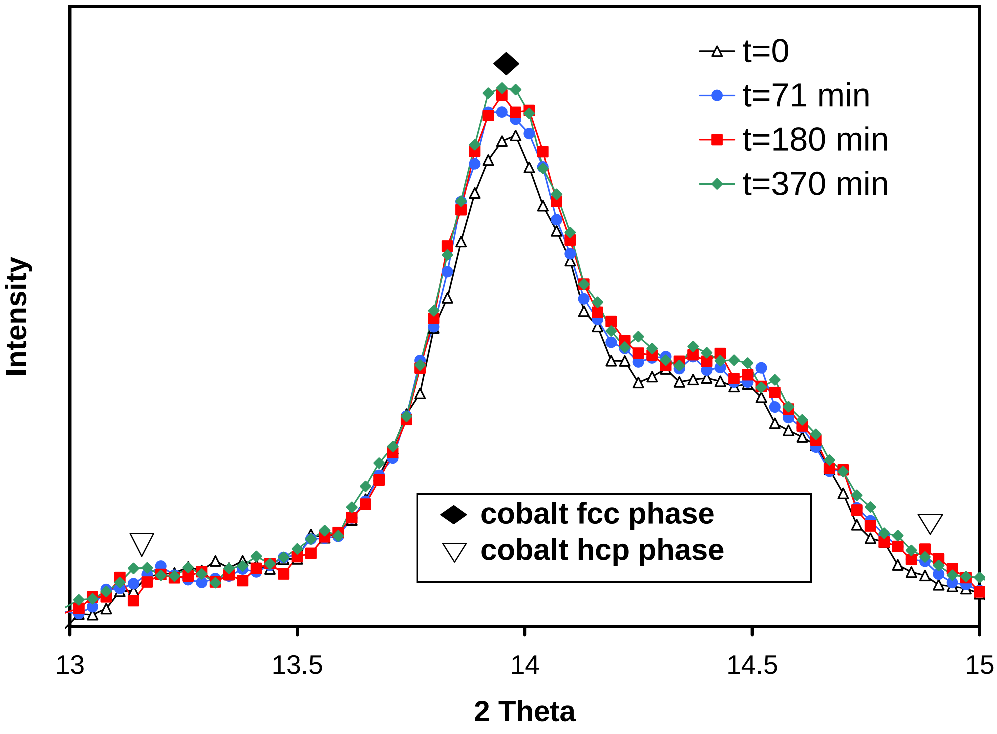

Fig. S3. *In-situ* time-resolved XRD patterns of CoPt/Al_2O_3-573 catalyst (λ=0.5 Å) measured at the realistic conditions of FT synthesis (T=493 K, P=20 bars, H_2/CO=2). The positions of metallic Co fcc and hcp peaks are indicated.

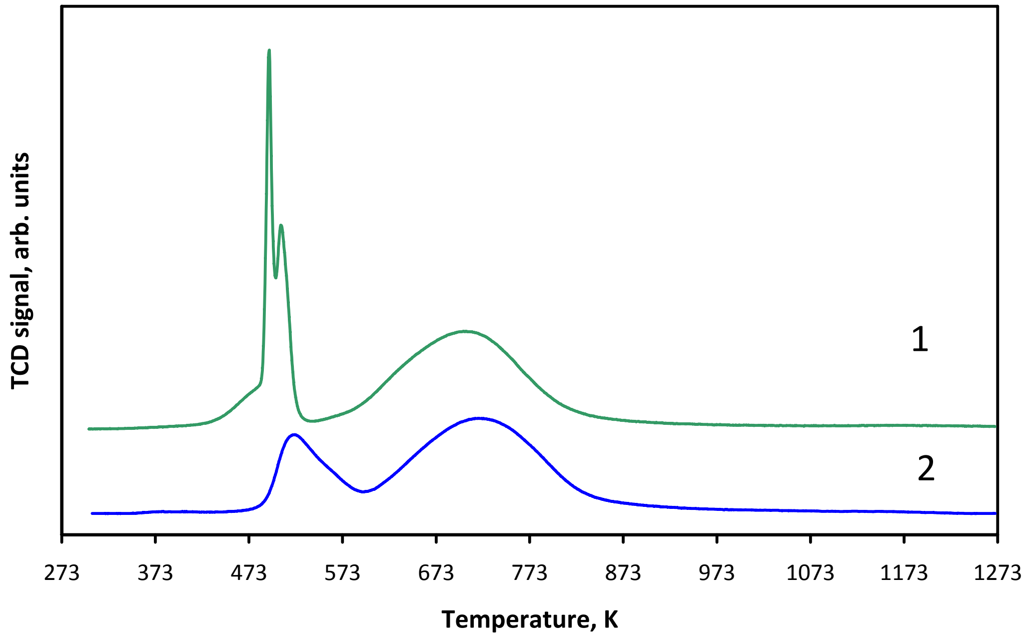

Fig. S4. TPR profiles of cobalt alumina supported Fischer-Tropsch catalysts: (1) CoPt/Al_2O_3-573 and (2) CoPt/Al_2O_3-773 (5%H_2/Ar, ramp 5 K/min). For clarity the original TPR profiles are offset on the vertical scale.

2. TPR analysis

The TPR profiles of the catalysts (Fig. S4) exhibit several hydrogen consumption peaks attributed to two-step reduction of Co_3O_4 to metallic cobalt which proceeds via intermediate phase of CoO[1,2]:

$Co_3O_4 + H_2 = 3CoO + H_2O$

$CoO + H_2 = Co + H_2O$.

The TPR peaks at 473-523 K corresponds to the reduction of Co_3O_4 to CoO, while high temperature peaks at 673-773 K are related to the reduction of CoO to metallic cobalt. In addition, the TPR profile of CoPt/Al_2O_3-573 also exhibits a sharp peak at 494 K which is attributed to the decomposition of residual nitrate species in the presence of hydrogen. Higher calcination temperature results in a slight shift of TPR profiles to higher temperatures, which can be attributed to partial substitution of Co^{3+} in Co_3O_4 spinel framework by Al^{3+} ions from the support.[3,4] The TPR technique did not reveal any noticeable concentration of cobalt aluminates, which are reducible at temperatures higher than 973 K.

This peak assignment is consistent with the TPR quantitative analysis. Indeed, the amounts of hydrogen consumed during TPR experiments were respectively 1.22 and 1.05 mol H_2/mol Co for CoPt/Al_2O_3-573 and CoPt/Al_2O_3-773 samples. This indicates high extent of cobalt reduction in the TPR experiments. At cobalt reduction of 100%, the expected amount of consumed hydrogen would be 1.33 mol H_2/mol Co.

TPR profiles were deconvoluted into lower (430-543 K for CoPt/Al_2O_3-573 and 479-600 K for CoPt/Al_2O_3-773) and higher temperature peaks. The ratios of lower to higher temperature TPR peaks were 0.326 for CoPt/Al_2O_3-773 and 0.408 for CoPt/Al_2O_3-573. The expected stoichiometric ratio of hydrogen peaks attributed to the reduction of Co_3O_4 to CoO and to the reduction of CoO to metallic cobalt is 0.33 provided all cobalt is reduced to the metal phase.

Table S1. Fischer-Tropsch (FT) catalytic performance of alumina-supported cobalt catalysts in the steady state conditions (P=20 bar, H_2/CO=2, T=493 K).

Catalyst	Reactor	FT reaction rate (mol_{CO} s^{-1} mol $cobalt^{-1}$)	GHSV (cm^3/g h)	X_{CO} (%)	S_{CH4} (%)	C5+ productivity (g_{HC}/h g_{cat})
CoPt/Al_2O_3-573	Fixed bed	4.59 10^{-3}	14000	39	8.0	0.70
CoPt/Al_2O_3-573	Capillary	4.21 10^{-3}	25000	20	5.0	-
CoPt/Al_2O_3-773	Fixed bed	3.62 10^{-3}	10500	41	10.0	0.57

3. Catalytic measurements

The catalytic performance of alumina-supported cobalt catalysts was evaluated both in a fixed-bed stainless steel reactor and in the capillary cell (which was used for *in-situ* XRD measurements). The catalyst loadings were 1 g for the fixed-bed and 7-10 mg for the capillary reactors, respectively. Carbon monoxide containing 5% of N_2 was used as an internal standard. Analysis of H_2, CO, CO_2, and CH_4 was performed using CTR-1 or molecular sieves columns, while gaseous and liquid hydrocarbons were separated on Poraplot Q and SimDist columns. Table S1 summarizes the catalytic performance data. The FT reaction rate is expressed as cobalt-time yield[5], which is calculated using carbon monoxide conversion, carbon monoxide partial pressure at the inlet of the reactor, gas–space velocity, and amount of cobalt in the reactor (mole CO converted/mole total cobalt-s). The hydrocarbon selectivities are calculated on carbon basis. Fig. S5 shows hydrocarbon wax detected in the stainless steel container downstream of the capillary reactor (loaded with CoPt/Al_2O_3-573 catalyst) after 8 h on stream under conditions of FT synthesis.

Fig. S5. Hydrocarbon wax (6 mg) uncovered downstream of the *in-situ* capillary cell after 8 hours at the conditions of FT synthesis.

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