



# On the superior activity and selectivity of PtCo/Nb<sub>2</sub>O<sub>5</sub> Fischer Tropsch catalysts



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## ABSTRACT

In this study Co/Nb<sub>2</sub>O<sub>5</sub> catalysts and the effect of Pt-promotion thereon are investigated in comparison with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>- and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-supported catalysts for the Fischer Tropsch (FT) synthesis. Upon Pt-promotion of Co/Nb<sub>2</sub>O<sub>5</sub> the cobalt-weight normalized FT activity was found to increase by a factor of 2.4, while the high C<sub>5+</sub> selectivity of 85 wt% was maintained. Based on environmental TEM results no indications were found that Pt affected the cobalt particle size in Co/Nb<sub>2</sub>O<sub>5</sub> catalysts. A kinetic study indicates an increased number of active sites upon Pt-promotion whereas Steady-State Isotopic Transient Kinetic Analysis experiments show that a combination of an increased number of active sites and an increased turnover frequency is at the origin of the enhanced activity in Co/Nb<sub>2</sub>O<sub>5</sub> catalysts upon Pt-promotion. Pt was tentatively proposed to bring about more efficient promotion of Co by NbO<sub>x</sub> being present as smaller clusters.

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## 1. Introduction

The price of crude oil and the call for cleaner transportation fuels have stimulated the development of methods to synthesize liquid hydrocarbons from alternative carbon feedstocks such as natural gas, coal and biomass which can be converted into syngas, a mixture of CO and H<sub>2</sub>. Via the Fischer Tropsch reaction, typically catalyzed by iron or cobalt catalysts, hydrocarbons can be produced from syngas and can be used as high-quality transportation fuels or chemicals. Iron catalysts at high temperatures are typically used for the synthesis of lower olefins [1], whereas silica-, alumina- or titania-supported cobalt catalysts at low temperatures give rise to heavy hydrocarbons [2–5].

The selectivity of cobalt catalysts toward liquid hydrocarbons (C<sub>5+</sub>) is affected by process conditions such as temperature [6,7], pressure [8] and CO conversion [9] and catalyst properties such as support acidity [10,11] and pore diameter [5,10] and can be promoted by partially reducible transition metal oxides such as MnO and ZrO<sub>2</sub> [12–17]. These promoters can be present as small particles in the close proximity to cobalt or as support material in the case of Co/TiO<sub>2</sub> [16,18,19] or Co/Nb<sub>2</sub>O<sub>5</sub> [6,20–24] catalysts. For Nb<sub>2</sub>O<sub>5</sub>-supported cobalt catalysts, high selectivities toward heavy

hydrocarbons were reported at 1 bar by Schmal and coworkers [20–24] and more recently at 20 bar by den Otter et al. [6]. The promoting effect of niobia as support material at low pressure was extensively studied by XPS, TPR, TPO, CO TPD and IR spectroscopy and was attributed to partial reduction of the support and consequent strong metal support interaction (SMSI) [25–29]. The presence of Co<sup>0</sup>-NbO<sub>x</sub> species was confirmed by Mendes et al. in Co/Nb<sub>2</sub>O<sub>5</sub> catalysts [27] and model catalysts [28].

Noble-metal addition is a well-known method to enhance the activity of Fischer Tropsch catalysts by facilitating cobalt oxide reduction and consequently increasing the number of active sites [30–33]. During Fischer–Tropsch catalysis, Pt is not expected to be active as catalyst due to the low CO dissociation activity; however, it might assist by facilitating H<sub>2</sub> dissociation or act as adsorption site for CO [34]. Upon noble metal promotion of Co/TiO<sub>2</sub> and Co/Nb<sub>2</sub>O<sub>5</sub> catalysts [2,35–37] and recently also niobia-promoted Co/SiO<sub>2</sub> catalysts [8], an increase in the cobalt-weight normalized activity was observed which could not be explained only by an increased number of active sites.

In this study the extent and origin of Pt-promotion on the activity and selectivity of Co/Nb<sub>2</sub>O<sub>5</sub> Fischer Tropsch catalysts are investigated in comparison with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>- and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-supported catalysts using among other environmental Transmission Electron Microscopy (TEM) [38], a kinetic study and Steady-State Isotopic Transient Kinetic Analysis (SSTIKA) [39].

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## 2. Materials and methods

### 2.1. Preparation

Niobium oxide hydrate (HY-340, AD/4465, 72.6 wt% Nb<sub>2</sub>O<sub>5</sub>, LOI 26.7 wt%, purity data see Supporting Information) was obtained from Companhia Brasileira de Metalurgia e Mineração – CBMM and calcined at 600 °C (5 °C min<sup>-1</sup>, 2 h) in stagnant air to obtain crystalline Nb<sub>2</sub>O<sub>5</sub> (T-phase, S<sub>ABET</sub>: 16 m<sup>2</sup> g<sup>-1</sup>, PV: 0.06 mL g<sup>-1</sup>). γ-Al<sub>2</sub>O<sub>3</sub> (Sasol, Puralox SSCa-5/200, S<sub>ABET</sub>: 185 m<sup>2</sup> g<sup>-1</sup>, PV: 0.5 mL g<sup>-1</sup>) and α-Al<sub>2</sub>O<sub>3</sub> (BASF, S<sub>ABET</sub>: 7 m<sup>2</sup> g<sup>-1</sup>, PV: 0.015 mL g<sup>-1</sup>) were used as received. For physisorption isotherms and pore size distributions, see SI Fig. S1.

Supports were sieved to 75–150 μm and dried at ~80 °C for 1 h in dynamic vacuum. Cobalt was deposited by impregnation [40] in static vacuum (10<sup>-2</sup> bar) under mechanical mixing at room temperature with an aqueous 4.0 M Co(NO<sub>3</sub>)<sub>2</sub> solution or by co-impregnation with an aqueous 4.0 M Co(NO<sub>3</sub>)<sub>2</sub>, 0.03 M Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Co/Pt = 140) solution, aiming for a cobalt loading of 2–8 mg<sub>Co</sub> m<sup>-2</sup>. 2.0 g Nb<sub>2</sub>O<sub>5</sub> was impregnated with 0.54 mL, and 2.0 g α-Al<sub>2</sub>O<sub>3</sub> was impregnated with 0.55 mL of the precursor solution. 3.0 g γ-Al<sub>2</sub>O<sub>3</sub> was, in two subsequent cycles impregnated with 4.6 mL of the precursor solution, and each impregnation was followed by drying and calcination (vide infra). Impregnated volumes were up to a factor of 5 (Nb<sub>2</sub>O<sub>5</sub>) and 18 (α-Al<sub>2</sub>O<sub>3</sub>) higher than the pore volume determined using N<sub>2</sub> physisorption (SI, Fig. S1); however, all catalysts remained dry during impregnation, indicating porosity was mainly present in macropores (>50 nm). After drying overnight at 60 °C in stagnant air, the cobalt nitrate precursor was calcined at 350 °C (3 °C min<sup>-1</sup>, 2 h) in a 1 L min<sup>-1</sup> g<sub>sample</sub><sup>-1</sup> N<sub>2</sub> flow. Cobalt loading is expressed as the mass of metallic cobalt per gram of reduced catalyst. An overview of the prepared catalysts can be found in Table 1.

### 2.2. Characterization

Samples were analyzed after cobalt nitrate decomposition as described above (calcined) and after reduction at 350 °C, 3 °C min<sup>-1</sup>, 2 h in 25 vol% H<sub>2</sub>/N<sub>2</sub> (GHSV 60 \* 10<sup>3</sup> h<sup>-1</sup>) and subsequent exposure to air at room temperature (passivated).

Environmental Powder X-ray diffraction (XRD) patterns were measured using a Bruker-AXS D8 Advance X-ray diffractometer using Co Kα radiation (λ = 1.789 Å). Calcined and passivated samples were analyzed in air at room temperature and heated to 350 °C (5 °C min<sup>-1</sup>, 2 h) in 25 vol% H<sub>2</sub>/He (Co/γ-Al<sub>2</sub>O<sub>3</sub>: 500 °C) in the X-ray diffractometer.

TEM samples were prepared by dry dispersion of the passivated catalyst onto a Mo grid with a holey carbon supporting film. TEM analysis was performed using an FEI Titan ETEM G2 microscope described before [38]. Samples were observed in vacuum at room temperature and in 100 Pa H<sub>2</sub> at 350 °C, microscope was operated at 300 kV, and elemental analysis was performed using Scanning

Transmission Electron Microscopy-Electron Energy Loss Spectroscopy (STEM-EELS).

Temperature programmed reduction (TPR) experiments were performed using a Micromeritics Autochem 2920 instrument. 25–100 mg calcined catalyst (6–7 mg Co) was dried at 120 °C for 1 h in an Ar flow and reduced up to 1000 °C (10 °C min<sup>-1</sup>) in a 5 vol% H<sub>2</sub>/Ar flow.

H<sub>2</sub> chemisorption measurements were performed using a Micromeritics ASAP 2020 instrument. 50–200 mg calcined catalyst was dried for 1 h in dynamic vacuum at 100 °C and reduced in an H<sub>2</sub> flow at 350 °C, 1 °C min<sup>-1</sup> for 2 h, (Co/γ-Al<sub>2</sub>O<sub>3</sub>: 500 °C). H<sub>2</sub> adsorption isotherms were measured at 150 °C, as recommended by Reuel for supported cobalt particles [41]. For all catalysts, metallic cobalt-specific surface area and average particle size were calculated assuming full reduction to Co<sup>0</sup>, a surface stoichiometry H/Co = 1 and an atomic cross-sectional area of 0.0662 nm<sup>2</sup>.

CO chemisorption measurements were performed in a setup described before [42]. 30–100 mg calcined catalyst (75–150 μm) diluted with an equal mass of SiC was reduced at 350 °C, 5 °C min<sup>-1</sup>, for 2 h (Co/γ-Al<sub>2</sub>O<sub>3</sub>: 500 °C) in 10 mL min<sup>-1</sup> H<sub>2</sub>. The amount of reversibly adsorbed CO was determined from a <sup>12</sup>CO/Ar to <sup>13</sup>CO/Kr switch (1.5/33.5 mL min<sup>-1</sup>) at 100 °C, 1.85 bar. Effluent gas was analyzed using a Balzers QMG 422 Quadrupole mass spectrometer. Surface residence time (τ<sub>CO</sub>) was determined by integration of the normalized transient curve: τ<sub>i</sub> = ∫<sub>0</sub><sup>∞</sup> F<sub>i</sub>(t) dt and was corrected for gas phase hold-up using the Ar signal. Amount of reversibly adsorbed CO (N<sub>CO,total</sub>) was calculated using the CO inlet flow (Q<sub>CO,in</sub>): N<sub>CO,total</sub> = τ<sub>CO</sub> \* Q<sub>CO,in</sub>.

### 2.3. Fischer Tropsch synthesis

Catalyst testing at 1 bar was performed using a U-shaped, continuous down-flow, fixed bed reactor system. 10–50 mg calcined catalyst (75–150 μm) was diluted with 200 mg SiC (200–400 μm) and loaded in a glass reactor, ID = 3 mm, to achieve a bed height of 2 cm. 500 mg SiC was loaded on top of the catalyst bed to ensure gas preheating. A thermocouple was placed in the catalyst bed to control temperature, and deviation from target temperature was <1 °C. The catalysts were reduced at atmospheric pressure in a 33 vol% H<sub>2</sub>/Ar flow, GHSV 1.7 \* 10<sup>5</sup> – 3.7 \* 10<sup>5</sup> h<sup>-1</sup>, at 350 °C, 5 °C min<sup>-1</sup>, for 2 h (Co/γ-Al<sub>2</sub>O<sub>3</sub>: 500 °C). After cooling to 220 °C the gas stream was switched to synthesis gas, H<sub>2</sub>/CO = 2.0 v/v, GHSV 25 \* 10<sup>3</sup> – 100 \* 10<sup>3</sup> h<sup>-1</sup>, CO conversion 1–5%. Products up to C<sub>18</sub> were analyzed using an online Varian 430-GC equipped with FID. Activity and selectivity were calculated based on the hydrocarbons formed. The reported catalyst performance was determined after at least 15 h on stream. A kinetic study was performed in this setup, H<sub>2</sub> flow (4–8 mL min<sup>-1</sup>, p<sub>H2</sub> = 0.27–0.53 bar) and CO flow (2–4 mL min<sup>-1</sup>, p<sub>CO</sub> = 0.13–0.27 bar) were varied independently, and total gas flow was kept constant at 15 mL min<sup>-1</sup> by addition of Ar (4–8 mL min<sup>-1</sup>). H<sub>2</sub> and CO reaction orders (Y and Z, respectively) and pre-exponential factor k' were determined from the

**Table 1**

Cobalt loading based on intake, number of reversible CO adsorption sites determined using CO chemisorption at 100 °C (N<sub>CO,total</sub>), adsorbed amount of H<sub>2</sub> (N<sub>H2</sub>) and apparent Co particle size (d<sub>Co</sub>, H<sub>2</sub>) determined using H<sub>2</sub> chemisorption and estimated Co particle size from environmental TEM (d<sub>Co</sub>, TEM).

	Co loading		N <sub>CO,total</sub> (mmol <sub>CO</sub> g <sub>Co</sub> <sup>-1</sup> )	N <sub>H2</sub> (mmol <sub>H2</sub> g <sub>Co</sub> <sup>-1</sup> )	d <sub>Co</sub> , H <sub>2</sub> (nm)	d <sub>Co</sub> , TEM (nm)
	(wt%)	(mg <sub>Co</sub> m <sup>-2</sup> )				
Co/Nb <sub>2</sub> O <sub>5</sub>	5.9	3.9	0.28	0.36	24	9.2
PtCo/Nb <sub>2</sub> O <sub>5</sub>	5.9	3.9	0.48	0.45	19	8.7
Co/γ-Al <sub>2</sub> O <sub>3</sub>	28	2.1	0.20	0.45	19	
PtCo/γ-Al <sub>2</sub> O <sub>3</sub>	28	2.1	0.43	0.65	13	
Co/α-Al <sub>2</sub> O <sub>3</sub>	6.3	8.4	0.38	0.53	16	
PtCo/α-Al <sub>2</sub> O <sub>3</sub>	6.0	8.0	0.55	0.62	14	

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