



Short communication

# Fischer–Tropsch synthesis over Co/TiO<sub>2</sub> catalyst: Effect of catalyst activation by CO compared to H<sub>2</sub>



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## ABSTRACT

Co/TiO<sub>2</sub> catalyst activation for Fischer–Tropsch (FT) reaction by CO in comparison to H<sub>2</sub> has been performed. The catalyst, prepared by incipient wetness impregnation, has been characterized using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses after separate reduction using CO and H<sub>2</sub> respectively. Temperature programmed reduction (TPR) analyses were also conducted to study the reduction behaviour of the catalyst in presence of H<sub>2</sub> and CO respectively. CO improved catalyst reduction and produced a more stable and active catalyst with higher selectivity and yield for C<sub>5+</sub> hydrocarbons at extended time-on-stream.

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## 1. Introduction

Fischer–Tropsch (FT) synthesis is a process that converts synthesis gas into liquid fuel over metal catalysts. Supported cobalt, fused iron and precipitated iron catalysts are the most used in commercial applications [1]. An activation process that consists of reducing the cobalt oxides particles in the catalyst to metallic cobalt is always required prior to the FT reaction. H<sub>2</sub> is usually used to activate cobalt catalysts at 250–400 °C [1]. This standard catalyst activation is usually limited by some interaction between the support and cobalt. Cobalt-support compound formation has been reported to form in supported cobalt catalysts during activation using H<sub>2</sub> [2–7]. Jongsomjit et al. [7] reported the formation of Co-titanate during standard reduction of a Co/TiO<sub>2</sub> catalyst using H<sub>2</sub>. The formed compound cannot be reduced below 800 °C and limits the degree of reduction for the catalyst. In some cases, the formation of these cobalt-support compounds is influenced by the presence of water produced during the reduction process [3]. Only a limited amount of literature has reported to date on cobalt catalyst activation process that does not involve water formation. Li et al. [8] used CO to activate a ruthenium-promoted Co/TiO<sub>2</sub> catalyst at 523 K and 1.68 MPa and compared its performance for FT reaction with an H<sub>2</sub>-activated catalyst. They measured lower activity and good stability on the CO-reduced catalyst. Pan and Bukur [9] reduced Co/ZnO catalyst with CO at 523 K and measured lower activity and olefin content, and more methane compared to the H<sub>2</sub>-reduced sample. These predominantly negative effects of cobalt catalyst activation by CO on the FT reaction performance could most likely be due to the low temperature and

high CO partial pressure used for catalyst activation. Cobalt carbide and CoO were the major phases in the catalyst sample reduced by CO at 523 K [9].

To the best of our knowledge, there is no other report on the effect of activating cobalt-based catalyst with CO, under conditions that avoid cobalt carbide formation, on catalyst performance for FT reaction. Hence the aim of this study is to investigate the effect of Co/TiO<sub>2</sub> catalyst activation by diluted CO (5% CO in He) at 350 °C on FT reaction performance.

## 2. Experimental procedure

## 2.1. Catalyst preparation and characterization

The details on catalyst preparation are reported in earlier studies [10, 11].

Temperature programmed reduction (TPR) was performed using 100 mg of fresh Co/TiO<sub>2</sub> catalyst sample. Bulk Co<sub>3</sub>O<sub>4</sub> samples (10 mg) were also used to facilitate reduction peak identification. The sample was first degassed at 150 °C in a flow of Ar (30 Nml/min) for 45 min and then cooled to 60 °C before replacing the Ar flow with the analysis gas (5% H<sub>2</sub> in Ar or 5% CO in He, 30 Nml/min) to start the TPR analysis. The temperature was increased at a rate of 10 °C/min.

X-ray diffraction (XRD) analysis was carried out using Rigaku Ultima IV X-ray powder diffractometer with PDXL analysis software. The following analysis parameters were used: Cu-Kα (λ = 1.54 Å) radiation source, current and voltage set at 30 mA and 40 kV and step width of 2θ = 0.01°.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos Axis Ultra DLD system. The following settings were

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used: monochromatic Al K $\alpha$  X-ray source operating at 120 W; pass energies of 160 eV for survey spectra; 40 eV for high resolution scans; hybrid operation mode using a combination of magnetic immersion and electrostatic lenses; acquisition area of approximately  $300 \times 700 \mu\text{m}^2$ ; take off angle of  $90^\circ$  and a base pressure of ca.  $1 \times 10^{-9}$  Torr.

## 2.2. Catalyst evaluation

500 mg of fresh catalyst (particles with sizes between 0.5 and 1 mm) were loaded in a fixed-bed stainless steel reactor (internal diameter: 16 mm, length: 260 mm) and dried at  $150^\circ\text{C}$  in a flow of  $\text{N}_2$  (30 Nml/min) for 60 min before exposure to the reducing gas mixture. Catalyst reduction was done at  $350^\circ\text{C}$  (heating rate:  $10^\circ\text{C}/\text{min}$ ) for 14 h using 5%  $\text{H}_2$  in Ar or 5% CO in He (30 Nml/min) at atmospheric pressure.

FT runs were performed at  $220^\circ\text{C}$ , 20 bar using a premixed gas with  $\text{H}_2$ :CO ratio of ca. 2 and a feed flowrate of ca. 10 Nml/min. The outlet gas stream was analysed by online gas chromatography using a Supel-Q Plot fused silica capillary column  $30 \text{ m} \times 0.32 \text{ mm}$  and a stainless steel general 60/80 Carboxen 1000.

## 3. Results and discussion

### 3.1. Catalyst characterization.

The data for TPR analysis using  $\text{H}_2$  or CO are summarized in Fig. 1.

The first reduction peak for bulk  $\text{Co}_3\text{O}_4$  in presence of CO (Fig. 1a) started from ca.  $237^\circ\text{C}$  and reached its maximum value at ca.  $342^\circ\text{C}$ . It can be attributed to the first reduction step of  $\text{Co}_3\text{O}_4$  to CoO. A second peak starting at ca.  $370^\circ\text{C}$  showed a rapid CO consumption rate up to a temperature of  $390^\circ\text{C}$  after which an almost steady CO consumption rate was observed up to ca.  $407^\circ\text{C}$  followed by a maximum value at ca.  $437^\circ\text{C}$ . This peak can be attributed to the reduction of CoO to  $\text{Co}^0$ . The peak starting at ca.  $480^\circ\text{C}$  is attributed to significant carbon deposition. In presence of  $\text{H}_2$ , the bulk  $\text{Co}_3\text{O}_4$  sample (Fig. 1b) showed two peaks with maximum values at ca.  $350$  and  $424^\circ\text{C}$  attributed to the two-step reduction of  $\text{Co}_3\text{O}_4$  to Co and  $\text{Co}^0$ . The data show that bulk  $\text{Co}_3\text{O}_4$  can be reduced by CO or  $\text{H}_2$  in a similar temperature range. The data for the supported catalyst in presence of CO (Fig. 1c) also showed two peaks with their maxima at ca.  $351$  and  $413^\circ\text{C}$  respectively. These peaks, also attributed to the two-step reduction of  $\text{Co}_3\text{O}_4$  to CoO and  $\text{Co}^0$ , are well in the same temperature range as that required for the reduction of bulk  $\text{Co}_3\text{O}_4$ . However, a delayed peak for carbon deposition was only observed from ca.  $560^\circ\text{C}$  compared to  $480^\circ\text{C}$  in the case of bulk  $\text{Co}_3\text{O}_4$ . The role of the  $\text{TiO}_2$  support in delaying carbon deposition is unclear and will require future investigation. A significant shift of

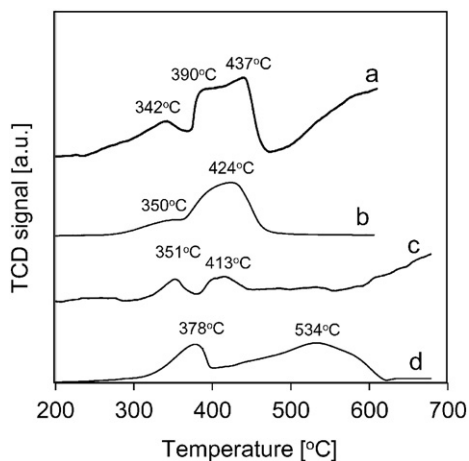


Fig. 1. TPR data for bulk  $\text{Co}_3\text{O}_4$  using a) CO; b)  $\text{H}_2$ , and for  $\text{Co}/\text{TiO}_2$  sample using c) CO and d)  $\text{H}_2$ .

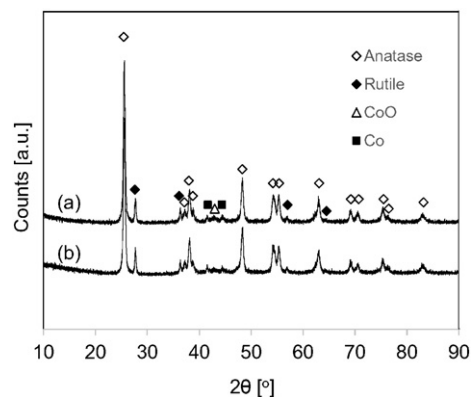


Fig. 2. XRD data for  $\text{Co}/\text{TiO}_2$  catalyst after reduction with a)  $\text{H}_2$ ; b) CO.

reduction peaks to higher temperatures was observed for the TPR analysis of the  $\text{TiO}_2$ -supported cobalt catalyst sample using  $\text{H}_2$  (Fig. 1d). The first reduction peak, attributed to the first reduction step of  $\text{Co}_3\text{O}_4$  to CoO reached its maximum at ca.  $378^\circ\text{C}$  compared to  $351^\circ\text{C}$  in the presence of CO (Fig. 1c). In addition, a broad reduction peak with maximum at ca.  $534^\circ\text{C}$  and extending up to ca.  $620^\circ\text{C}$  suggests the second reduction step of cobalt species with various levels of interaction with the  $\text{TiO}_2$  support to  $\text{Co}^0$ . These data suggest that reduction using  $\text{H}_2$  leads to strong cobalt–titania interactions in the catalyst compared to CO. It is possible that the latter prevented or limited these interactions in the catalyst during the reduction process to improve catalyst reducibility. Previous studies [5,11] have also reported improved cobalt catalyst reduction due to the presence of CO in the reducing gas.

XRD analyses were performed to confirm the cobalt phases that were present in the catalyst after reduction with CO or  $\text{H}_2$  at  $350^\circ\text{C}$  for 14 h as described in Section 2.2. The samples were cooled to room temperature under the flow of the reducing gas and passivated using

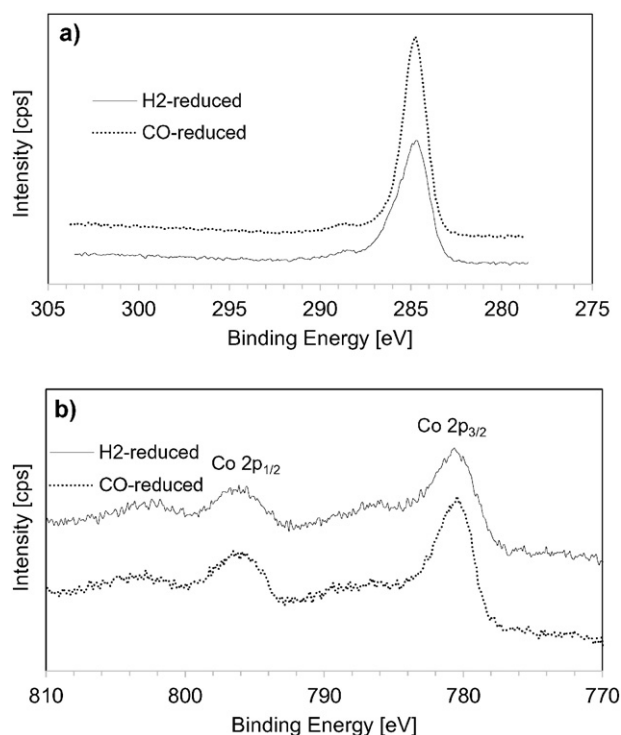


Fig. 3. XPS data for a) C 1s and b) Co 2p.

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