



## K-doping of Co/Al<sub>2</sub>O<sub>3</sub> low temperature Fischer–Tropsch catalysts

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### ABSTRACT

The effect of potassium doping on Co/Al<sub>2</sub>O<sub>3</sub> Fischer–Tropsch catalyst has been investigated using in situ IR spectroscopic measurements and catalytic activity tests in flow reactor. The data confirm the inhibiting effect of K doping on reducibility and catalytic activity, together with a stabilization of the catalytic activity, a reduction of methane selectivity and a slight increase of CO<sub>2</sub> selectivity.

CO adsorbs over the Co/Al<sub>2</sub>O<sub>3</sub> catalyst forming on-top surface carbonyls, responsible for a Infrared CO stretching band at a position more typical of fcc 100 face than of hcp 0001 face. In the presence of hydrogen CO adsorption shifts in part from terminal to bridging sites. Potassium doping significantly increases the electron donating ability of cobalt metal particles, as evidenced by the shift down of 15 cm<sup>-1</sup> of the CO stretching frequency of adsorbed carbon monoxide. CO adsorbed on surface defects is also evident. After CO adsorption at 250 °C even lower frequency carbonyls are observed only on the K-doped catalyst (2000 and 1825 cm<sup>-1</sup>) providing evidence of a stronger interaction of CO with the surface. At 250 °C in the presence low pressure of CO + H<sub>2</sub>, methane, ethylene and other lower olefins form in the IR cell. The ethylene/methane molar ratio produced over the K-doped catalyst is definitely higher than over the K-free sample, suggesting that potassium favours the first chain growth step in the Fischer–Tropsch process thus allowing decreased selectivity to methane. Reasons for the increased catalyst stability are briefly discussed.

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### 1. Introduction

Discovered by Fischer and Tropsch in 1923 [1,2], the Fischer–Tropsch (FT) process has been developed at the industrial level to produce synthetic fuels and chemicals starting from coal, in Germany up to the end of World War II and in South Africa mainly during the period of the embargo [3]. The low-temperature Fischer–Tropsch process, performed at 200–250 °C, 20–30 bar over Co-based catalysts (Co-LTFT), represents today a promising option to convert syngas produced from natural gas into of middle distillate and hydrocarbon waxes both applicable to produce high cetane number and sulphur-free Diesel fuels [4]. Among the different metals active as FT catalysts, Cobalt represents the best choice for this application [5] for its moderate price (definitely lower than that of noble metals but much higher than that of iron), high activity with stoichiometric syngases arising from methane steam reforming, good selectivity to high molec-

ular weight paraffins and low selectivity to methane, olefins and oxygenates. Among possible supports, alumina is a good choice because of its availability with texture suitable to Slurry Bubble Column Reactors (SBCR-LTFT). The group of Forzatti and coworkers gave relevant contributions in understanding the role of different variables on Co-LTFT kinetics, proposing a complete mechanistic kinetic model based on H-assisted CO activation [6], as well as on the development of monolithic reactors for this process [7].

The cobalt FT catalysts are usually supported on high surface area alumina and typically contain between 15 and 30 wt%/wt% of cobalt. To stabilize them and decrease selectivity to methane, these catalysts also contain small amounts of noble metal promoters [8] (typically 0.05–0.1% weight of Ru, Rh, Pt or Pd) and/or an oxide promoter as well (zirconia, lanthana, cerium oxide, 1–10%). The noble metal doping has been supposed to improve the reducibility of cobalt, while the support and the oxide promoters may have a role in controlling the size of the cobalt metal to an optimal value. However, cobalt/alumina catalysts still have difficult reducibility due to the high metal dispersion, are prone to deactivation phenomena [9] including poor stability and mechanical resistance in the hydrothermal conditions of the SBCR-FT reaction.

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Alternatives to the Co-LTFT process are the High Temperature Fischer–Tropsch process (HTFT), on iron-based catalysts at 300 °C and the low temperature process performed with iron catalysts (Fe-LTFT) which, due to the high activity of the catalyst in the water gas shift reaction, are more indicated for coal-based FT syntheses. They produce more oxygenates and a slightly different molecular weight distribution for hydrocarbons [10].

Several companies are involved in recent years in extensive R&D programs to develop such kind of GtL (gas to liquids) technologies. Eni has developed a proprietary slurry reactor LTFT technology jointly with IFP-Axens and built a 20 bpd FT plant in the Sannazzaro Refinery (Pavia, Italy) [11], working since 2000.

Iron-based FT catalysts are commonly activated by potassium doping [12]. On the contrary, K-doping of Co catalysts, although increasing selectivity to high molecular weight products [13], is reported to decrease significantly the reaction rate [14]. In spite of the potential practical interest [15], few data are reported in the literature concerning the effects of K-doping on Co-based FT catalysts. This point may be of interest to understand better the behaviour of such a catalytic systems and to improve the catalyst formulation.

## 2. Experimental

The catalysts were prepared according to the procedure described in Ref. [16]. The support was Siralox 5/170 from Sasol. The virtual composition of this support is 95% Al<sub>2</sub>O<sub>3</sub>, 5% SiO<sub>2</sub>, pore volume 0.49 cm<sup>3</sup>/g, average pore diameter 83 Å, surface area 170 m<sup>2</sup>/g. The undoped catalyst, hereinafter denoted as CoA, has a total cobalt content of 20.4 wt%. The potassium doped sample, hereinafter denoted as CoKA, has virtually the same cobalt content, and an additional potassium content of 0.50 wt%.

The catalyst has been reduced in a fixed bed PFR in H<sub>2</sub> flow at GHSV = 2 NI h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, 673 K, atmospheric pressure for 16 h. The total metallic cobalt content in the reduced catalysts has been determined by iodometric titration.

Catalytic tests have been carried out in 500 cm<sup>3</sup> autoclaves equipped with stirrer (operated at 800 rpm) and thermocouple. Inlet gases (N<sub>2</sub>, CO, H<sub>2</sub>, and He) are fed via mass flow controller and distributed through a dip tube to the bottom of the CSTR. Outlet products are collected from the top side of the autoclave equipped with a metallic sintered filter. Reaction products are condensed in two water cooled vessels. The first is kept at the operating pressure (20 bar), the second at atmospheric pressure. Uncondensable gases are fed to a micro-GC for on line analysis.

The catalyst (30 g) is dispersed in Durasyn® 170, a commercially available hydrogenated synthetic hydrocarbon and loaded into the autoclave. Catalytic tests discussed here have been performed at 503 K, P<sub>tot</sub> = 20 barg, H<sub>2</sub>/CO = 1.75, inerts (N<sub>2</sub> + He) 30%. GHSV was decreased step by step from 5.5 to 4 to 3.5 NI h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. Each step was kept for 50 h.

CO conversion, CO<sub>2</sub> and CH<sub>4</sub> selectivity, H<sub>2</sub>/CO usage ratio, defined as H<sub>2</sub> consumption/CO consumption [mol/mol], were calculated using He (5% in the inlet gas) as internal standard. Partial pressures of CO and H<sub>2</sub> in the outlet gas were calculated assuming all hydrocarbons –CH<sub>n</sub>–, but CH<sub>4</sub>, condensed while N<sub>2</sub>, He, CH<sub>4</sub> and CO<sub>2</sub> and H<sub>2</sub>O in the gas phase.

Assuming ideal CSTR reaction rate can be expressed as

$$r = \frac{F_{\text{CO}}^{\circ} X_{\text{CO}}}{W_{\text{cat}}} \quad (1)$$

where  $r$  is the reaction rate, [mol CO<sub>reacted</sub> s<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>],  $F_{\text{CO}}^{\circ}$  is the inlet CO flow rate [mol/s],  $X_{\text{CO}}$  is the CO conversion, and  $W_{\text{cat}}$  is the catalyst weight [g].

Reaction rate can be also expressed according to a Sarup and Wojciechowski [17] derived rate equation

$$r = k \frac{p_{\text{H}_2}^{0.5} \cdot p_{\text{CO}}^{0.5}}{(1 + bp_{\text{CO}}^{0.5})^2} = k \cdot \Phi(p_i) \quad (2)$$

where  $k$  is the kinetic constant [mol s<sup>-1</sup> bar<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>],  $p_i$  is the partial pressure of H<sub>2</sub> and CO [bar],  $b$  is the CO adsorption constant = 0.835589 bar<sup>-0.5</sup>.

Combining Eqs. (1) and (2), the kinetic constant can be derived according to Eq. (3)

$$k = \frac{F_{\text{CO}}^{\circ} X_{\text{CO}}}{W_{\text{cat}}} \cdot \frac{1}{\Phi(p_i)} \quad (3)$$

The kinetic constant does not depend on operating conditions but on the temperature only according to the Arrhenius equation. Under the further assumption that Cobalt based catalyst have the same activation energy, catalysts are conveniently compared using a kinetic constant ratio, AV defined as

$$AV = \frac{k_{\text{cat}}(T)}{k_{\text{ref}}(T)} \quad (4)$$

The kinetic constant of the catalyst CoA after 120 h on stream has been assumed as reference catalyst activity  $k_{\text{ref}}$ .

IR skeletal studies have been performed using KBr pressed disks. Diffuse reflectance UV–Vis spectra have been recorded with the pure powders on a Jasco V-570 instrument. For IR adsorption studies, pressed disks of the pure catalysts powders were activated “in situ” by using an infrared cell connected to a conventional gas manipulation/outgassing ramp. All catalysts were first submitted to a treatment in oxygen 200 Torr at 350 °C, for 1 h, followed by evacuation at the same temperature before the adsorption experiments. In order to obtain the reduced catalysts, after the mentioned evacuation, catalyst disks were put in contact with a H<sub>2</sub> pressure ~400 Torr at 350 °C, two cycles for 30 min, and successively outgassed at the same temperature. CO adsorption was performed at –140 °C by the introduction of a known dose of the gas (10 Torr) inside the low temperature infrared cell containing the previously activated wafers. IR spectra were collected upon warming under evacuation in the temperature range –140 °C/room temperature, with a Nicolet Nexus FT instrument.

## 3. Results and discussion

### 3.1. Bulk characterization of oxidized undoped and K-doped catalyst precursors

In Fig. 1 the skeletal IR spectra of the support Siralox and of the two catalysts are compared. The strong and complex absorption in the region 950–450 cm<sup>-1</sup> is typical of a spinel transitional alumina (delta phase) partially evolved towards a theta phase [18]. A weak tail towards higher frequencies is associated to the Si–O modes of the small amounts of silica in the support.

The spectrum of the undoped catalyst shows the same absorption with superimposed two quite sharp bands at 660 and 560 cm<sup>-1</sup>. These absorptions are typical of cobalt spinels such as Co<sub>3</sub>O<sub>4</sub> and CoAl<sub>2</sub>O<sub>4</sub> whose spectra are also reported in the figure. The position of the lower frequency peak is actually intermediate between those of the two spinels [19], suggesting, in agreement with the literature, that the spinel phase in our case can have intermediate composition, i.e. near to Co<sub>2</sub>AlO<sub>4</sub> (i.e. a solid solution of cobalt aluminate and cobaltite Co<sub>1+x</sub>Al<sub>2-x</sub>O<sub>4</sub> with  $x = 1$ ) [20]. More likely, we can have the coexistence of Co<sub>3</sub>O<sub>4</sub> and CoAl<sub>2</sub>O<sub>4</sub> and/or some gradient of concentration of Al and cobalt, the former increasing towards the bulk. The spectrum of the K-doped catalyst is essentially identical with that of the undoped catalyst. In particular

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