

## ARTICLE

**Effect of Thermal Treatment on Structure and Catalytic Activity of Supported Fischer-Tropsch Nano-Cobalt Catalysts for Clean Fuels<sup>†</sup>**Wei Chu<sup>a\*</sup>, J. P. Hong<sup>a</sup>, E. Payen<sup>b</sup>, X. Y. Dai<sup>a</sup>*a. Department of Chemical Engineering, Sichuan University, Chengdu 610065, China;**b. Laboratoire de Catalyse de Lille, Université des Sciences et Technologies de Lille, Cite Scientifique, 59655 Villeneuve d'Ascq, Lille, France*

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A series of 15%Co/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by incipient wetness impregnation under various calcination conditions (90-500 °C), and were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy experiments (XPS), temperature programmed reduction, and catalytic measurements of hydrogenation of carbon monoxide to long-chained hydrocarbons leading to clean fuels (Fischer-Tropsch synthesis). The results of XPS show the presence of incompletely decomposed cobalt nitrate for catalysts calcined at 90-200 °C, and the presence of Co<sub>3</sub>O<sub>4</sub> for catalysts calcined at 200-500 °C. For the four alumina-supported nano-cobalt catalysts with different thermal treatment (200-500 °C), XRD and XPS results illustrated that there were mainly nano Co<sub>3</sub>O<sub>4</sub> crystalite phases of 9-10 nm and the size of cobalt nano-particles did almost not change with the different temperature of thermal treatment. This was different from that of silica-supported cobalt catalysts. The supported cobalt catalyst (CoAp340 sample) calcinated at 340 °C presented a better activity for Fischer Tropsch synthesis to clean fuels, at mild conditions like atmospheric pressure (100 kPa), 1800 mL/g/h and 190 °C; rather than high pressure (2 MPa or more).

**Key words:** Cobalt catalyst, Nano-cobalt particle, Fischer Tropsch synthesis, Reducibility, XPS, XRD, Cobalt species

**I. INTRODUCTION**

There is an increasing importance for natural gas as raw material for the modern chemical industry and clean fuels in the 21st century [1-3]. Among the approaches of natural gas conversion to liquid fuels mainly diesel, the Fischer Tropsch (FT) synthesis is one of the main routes [2,3]. Production of synthesis gas from methane or coal and the conversion of syngas to a range of fuels and chemicals could become of great interests [3-10], while the reserves of crude oil are depleted and the price of crude rises.

Many efforts have been devoted to the understanding and improvement of the cobalt-based catalysts and iron-based catalysts [2,3,6-12]. The active component, support, promoter, preparation method, thermal treatment and the interactions have important effects on the catalyst structure and performances. Cobalt catalysts have been widely investigated for the FT synthesis since they give high yields of long chain paraffins and have long active life times [5,6]. The activity of cobalt catalyst for the FT synthesis depends primarily on the overall amount of exposed metallic cobalt atoms. Thus, a highly active cobalt catalyst requires a high reducibility and a high dispersion of nano-scaled cobalt. The

hydrocarbon yields from the FT synthesis could be improved significantly by higher reducibility of cobalt oxide species in silica supported catalysts [9]. The formation of cobalt oxide species (Co<sub>3</sub>O<sub>4</sub>, amorphous cobalt oxides and cobalt silicates) depends on the surface nature of the support and the treatment conditions like calcination temperature, pH of the precursor solution, etc.

There were often important effects of the thermal treatment on the structure and performances of catalysts [9,13-15]. Cobalt precursor decomposition is an important stage in catalyst preparation. The heat released during decomposition of cobalt precursors could affect cobalt dispersion and reducibility as well as the structure of cobalt species in the final catalysts [9]. The effect of calcination temperature on the nickel state and their reduction behavior [13] and the effect of reduction temperature on the adsorptive and catalytic properties were reported.

In this work, the influences of thermal treatment on the structure and reducibility as well as the catalytic activity of alumina supported nano-cobalt catalysts were investigated, and the techniques of X-ray diffraction (XRD), X-ray photoelectron spectroscopy experiments (XPS), TPR were utilized to illustrate the phenomena and effects.

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TABLE I The supported nano-cobalt catalysts and preparation conditions with calcination in air flow and ramping rate of 60 °C/h, 15%Co, the support of Puralex SCCA 170 alumina, and cobalt precursor of nitrate

Sample	Catalyst <sup>a</sup>	T/°C
101	CoAp90	90
111	CoAp200	200
112	CoAp340	340
113	CoAp400	400
114	CoAp500	500

<sup>a</sup> The catalyst were labeled as Co-support-Temp.

## II. EXPERIMENTS

### A. Catalyst preparation

The alumina supported nano-cobalt catalysts were prepared by incipient wetness impregnation (IWI) method using aqueous solution of cobalt nitrate [9,16,17]. After the impregnation in a rota-vapor apparatus with 25 g alumina support, the catalyst samples were dried at 90 °C in an oven and then calcinated in a flow of air at a designed temperature from 200 °C to 500 °C for 10 h. The catalysts were listed in Table I, labeled 'Co-support-Temp', where Temp indicated the temperature of the oxidative thermal treatment. The catalysts were then reduced in a flow of hydrogen at 400 °C for 5 h, the temperature ramping rate during the oxidative treatment and reduction treatment was 1 and 3 °C/min, respectively.

### B. Catalyst characterizations

The XRD measurements were recorded at room temperature by a Siemens D5000 diffract-meter using Cu K $\alpha$  radiation, the scan was ranged from 55° to 70° with 0.02° steps [2,9]. The average size of Co<sub>3</sub>O<sub>4</sub> particle was calculated according to the Sherrer equation.

The XPS were performed with a VG ESCALAB 220XL spectrometer [9]. The Al-K $\alpha$  monochromatized line (1486.6 eV) was used for excitation with 300-W of applied power. The analyzer was operated in a constant pass energy mode ( $E_{\text{pass}}=40$  eV). The reproducibility was  $\pm 0.2$  eV for Co2p binding energy. The vacuum level during the experiment was better than  $10^{-7}$  Pa. The powdered catalyst was pressed as a thin pellet onto a steel block. The experimental Co2p XPS spectra of the catalysts were normalized by the intensity of Al2p line (74.6 eV) of the Al<sub>2</sub>O<sub>3</sub> support.

The temperature-programmed reduction profiles (TPR) were measured by passing 5%H<sub>2</sub>/Ar gas mixture through the catalyst while increasing the temperature at a ramping rate of 3 °C/min [18,19]. The experiments were carried out in the micro quartz reactor.

The amount of samples for all experiments was about 50 mg. The gas flow velocity was 50 mL/min. The reduction gas mixture was purified with the use of water trap and oxygen trap.

### C. Catalytic test for Fischer Tropsch synthesis over nano-cobalt catalyst

The FT synthesis was carried out in a fixed-bed stainless steel reactor with the diameter of 9 mm operating at 100 kPa and 170-210 °C. The thermocouple was in direct contact with the catalyst. The design permitted the measurement of temperature along the catalyst bed, no heat spot was detected in the catalyst bed during the FT synthesis. A gas hourly space velocity of 1800 mL/g/h at STP and a H<sub>2</sub>/CO molar ratio of 2 were used. The gas flow rates for reactant gases (CO, H<sub>2</sub>) and internal standard (N<sub>2</sub>) were controlled by mass flow controllers (Brooks) [8,9,16]. The on-line test for the FT synthesis was carried out for 24 h with the stabilization of the catalyst and the activity at steady state reached within 5 h. Reactant gases and hydrocarbon products were analyzed by gas chromatography (Hewlett-Packard 5890) with a TCD detector and a FID detector, respectively. To avoid possible condensation of the reaction products, the gas transfer lines were constantly heated. Gaseous reaction products were analyzed on-line by gas chromatography. Analysis of H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> was performed with a 13X molecular sieve column and a thermal conductivity detector. Hydrocarbons (C1-C18) were separated in 10% CP-Sil5 on a Chromosorb WHP packed column and analyzed with a flame-ionization detector. In the raw materials, the carbon monoxide contained 5%N<sub>2</sub>, which was used as an internal standard for calculating carbon monoxide conversion. The hydrocarbon selectivities were calculated on a carbon basis.

## III. RESULTS AND DISCUSSION

### A. Effects of thermal treatment on the structure of supported cobalt catalysts

#### 1. XPS results of supported nano-cobalt catalysts

The XPS experiments of five catalyst samples were performed at the oxidized state. From the results of Co2p XPS diagram for CoAp90 sample, the Co2p<sub>3/2</sub> binding energy value was 781.5 eV, the spin-orbital splitting was 16.0 eV, and there were satellite peaks at 786.5 and 803.3 eV, these results indicated that the cobalt species was Co<sup>2+</sup>, i.e., highly dispersed Co(NO<sub>3</sub>)<sub>2</sub> precursor on the surface. The XPS results of the five cobalt samples were listed in Table II.

The Co<sup>3+</sup> was the dominant cobalt species (Co<sub>3</sub>O<sub>4</sub> phase) in the four oxidized catalysts (CoAp200-CoAp500). Indeed the Co2p<sub>3/2</sub> binding energy was

TABLE II Effect of thermal treatment on XPS results of supported cobalt catalysts ( $\text{Al}2\text{p}_{3/2}=74.60$  eV for calibration, XPS source is Al K $\alpha$ )

Catalyst	Binding energy/eV			Surf. Co/mol%	$n_{\text{Co}}/n_{\text{Al}}$	$n_{\text{N}}/n_{\text{Co}}$	Cobalt species
	Co2p	O1s	C1s				
CoAp90	781.6	532.3	284.6	9.30	0.736	0.736	$\text{Co}^{2+}$
CoAp200	781.0	532.0	285.1	3.88	0.143	0.435	$\text{Co}^{3+}+\text{Co}^{2+}$
CoAp340	781.3	531.6	285.3	5.11	0.178	—	$\text{Co}_3\text{O}_4$
CoAp400	781.2	531.3	285.2	—	—	—	$\text{Co}_3\text{O}_4$
CoAp500	781.3	531.4	284.9	6.48	0.261	—	$\text{Co}_3\text{O}_4$

equal to 781.0 eV and no satellite peak was observed. The atomic ratio  $n_{\text{Co}}/n_{\text{Al}}$  determined from XPS analysis were analyzed. The value of atomic ratio  $n_{\text{Co}}/n_{\text{Al}}$  was 0.178 for the cobalt sample CoAp340 which was calcinated at 340 °C. For the cobalt sample CoAp200 calcinated at 200 °C, the value was 0.143, which was 22.2% lower than that of CoAp340 sample. The explanation was that there were still a few nitrogen atoms on the catalyst surface of CoAp200, for which there was only partly decomposition of nitrate of cobalt at the relatively low temperature of 200 °C, and these nitrogen atoms covered partly the surface cobalt. With the further increase of thermal treatment temperature to 500 °C, the surface atomic ratio  $n_{\text{Co}}/n_{\text{Al}}$  was slightly augmented to 0.261, due to the sintering of support particles and a lowered specific surface area.

## 2. Reducibility of supported nano-cobalt catalysts

Temperature Programmed Reduction experiments (TPR) were performed to investigate the reducibility of cobalt species in the four supported cobalt catalysts (CoAp200, CoAp340, CoAp400, CoAp500), from 20 °C to 780 °C with a ramping rate of 3 °C/min, the reductant flow rate of 5% $\text{H}_2$  in Argon was 50 mL/min (Table III). There were three reduction peaks for each of the samples. The TPR profile of CoAp200 was illustrated in Fig.1. For the CoAp200 sample, the peak temperatures were 203, 283, and 540 °C respectively. The low-temperature TPR peaks (203 and 283 °C) were due either to the reductive decomposition of the residual cobalt precursor or to the partial reduction of  $\text{Co}_3\text{O}_4$  to CoO respectively. These were not associated with the release of any cobalt metallic phase. This indicated that no cobalt metal phase was produced below 300 °C on the CoAp200 catalyst sample. The third reduction peak covered a wide range from 310 °C to 750 °C, with a peak temperature at 540 °C, this peak area was relatively mild. This reduction peak corresponded to the generation of metallic cobalt, which was reported like the most active species.

The TPR second peak temperature varies regularly, when the calcination temperature was augmented, this reduction peak temperature increased gradually; this reduction peak corresponded to the partial reduction of

TABLE III TPR results of four supported nano-cobalt catalysts

Catalyst	Temperature/°C		
	$T_1$	$T_2$	$T_3$
CoAp200	203	283	540
CoAp340	183	287	431
CoAp400	239	328	510
CoAp500	—	342	550 (450-660)

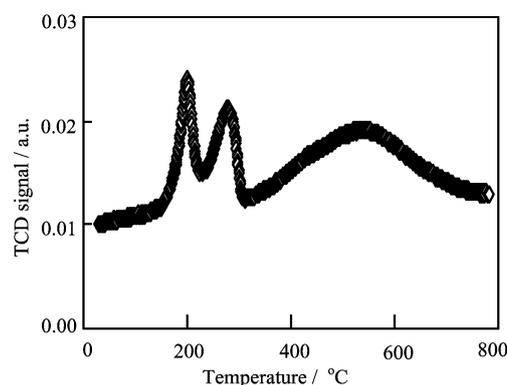


FIG. 1 TPR profile of CoAp200 sample.

$\text{Co}_3\text{O}_4$  to CoO. The temperatures of this-type reduction peak for the four supported catalysts, CoAp200, CoAp340, CoAp400, and CoAp500 samples were 283, 287, 328, and 342 °C, respectively. The enhancement of interaction between the cobalt and the support could explain these phenomena. From the comparative analysis, the reduction of CoAp340 catalyst was more easy and its generation of metallic cobalt was also. The reduction peak temperatures of CoAp340 were 183, 287, and 431 °C respectively.

## 3. Characterization of nano-cobalt oxide phases for supported catalysts

The XRD patterns of two typical alumina-supported cobalt catalysts, which were calcined at temperatures of 200 and 400 °C respectively, were demonstrated in Fig.2. The patterns were almost identical for the above

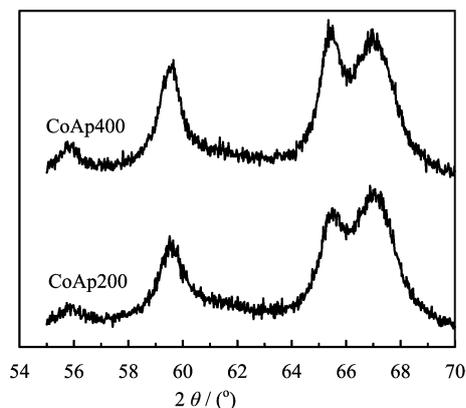


FIG. 2 XRD patterns of two samples.

two cobalt catalysts, they exhibited the peaks characteristics of  $\text{Co}_3\text{O}_4$  and  $\gamma$ -alumina.  $\text{Co}_3\text{O}_4$  was the only cobalt phase, which could be detected in the calcined catalysts by XRD. Both 422 ( $2\theta=56.0^\circ$ ) and 511 ( $2\theta=59.5^\circ$ )  $\text{Co}_3\text{O}_4$  diffraction lines could be used for calculation the particle size using the Scherrer equation, and it yields crystallites sizes about 9-10 nm in these four nano-cobalt catalysts by different thermal treatment (Table IV). The effects were very different from those of silica supported cobalt samples. Thus, thermal treatment temperature for alumina-supported cobalt catalysts seems to produce only very small impact on the nano-particle sizes of supported  $\text{Co}_3\text{O}_4$  crystallites.

#### 4. Catalytic performances for FT synthesis to clean fuels

The evaluation of catalytic performance was carried out in a continuous catalytic reactor at 170-210 °C for FT synthesis to long-chained hydrocarbons, the carbon monoxide conversion was tested and calculated with an internal standard method. The catalytic activity decreased slowly during the first hours before attaining steady state after 5 h of reaction. The hydrocarbon selectivities were evaluated for the CoAp200 catalyst after 24 h on stream at 190 °C. The  $\text{C}_{5+}\text{HC}$  is the main products, with a selectivity of 73.73%, while the selectivities of methane, of ethane, of C3-C4 hydrocarbons were 8.32%, 4.25%, and 13.7%, respectively. The conversion of carbon monoxide at 190 °C and 100 kPa was 3.28% after 24 h on stream. The conversion of carbon monoxide increased with the rising of reaction temperature from 170 °C to 210 °C. The  $\text{C}_{5+}\text{HC}$  selectivity was favored at relatively lower temperature.

Table V presented the catalytic performances of these four supported nano-cobalt catalysts CoAp200, CoAp340, CoAp400, and CoAp500, for FT synthesis at GHSV of 1800 mL/g/h after 24 h time on stream. At 190 °C, there was a value of 3.28% for carbon monoxide conversion for the CoAp200 sample, and its  $\text{C}_{5+}\text{HC}$

TABLE IV XRD results of four supported nano-cobalt catalysts

Catalyst	$2\theta/^\circ$	FWHM/ $\text{\AA}$	D-FWHM/ $\text{\AA}$
CoAp200	59.50	0.9611	95.20
CoAp340	59.46	1.0086	90.70
CoAp400	59.48	0.9271	98.68
CoAp500	59.48	0.9487	96.43

selectivity was 75.72%. When the thermal treatment temperature was risen, the  $\text{C}_{5+}\text{HC}$  selectivity increased slightly till 79.76% for CoAp500 catalyst. However, the conversion of carbon monoxide for FT synthesis was very different for these four samples. It is the CoAp340 catalyst that gave the better activity, with a value of 5.91% for CO conversion. When the reaction temperature was risen further to 210 °C, the CO conversion increased more, while the  $\text{C}_{5+}\text{HC}$  selectivity decreased significantly. The  $\text{C}_{5+}\text{HC}$  yield increased with the reaction temperature in the range of 170 °C to 210 °C. Other approaches could be used for achieving a better performance, like plasma enhanced preparation, increasing the reaction pressure.

#### IV. CONCLUSION

For the four alumina-supported nano-cobalt catalysts with different thermal treatment (200-500 °C), XRD and XPS results illustrated that there were mainly nano  $\text{Co}_3\text{O}_4$  crystalite phases of 9-10 nm and the size of cobalt nano-particles did almost not change with the different temperature of thermal treatment. This was different from that of silica-supported cobalt catalysts.

The supported cobalt catalyst (CoAp340 sample) calcinated at 340 °C presented a better activity for FT synthesis to clean fuels, at mild conditions like atmospheric pressure (100 kPa), 1800 mL/g/h and 190 °C; rather than high pressure ( $2 \times 10^6$  Pa or more). Its CO conversion was 5.91% with a  $\text{C}_{5+}\text{HC}$  selectivity of 77.1%.

The TPR results illustrated an easier reducibility of nano-particles for CoAp340 sample among the four cobalt catalysts, and that the reduction peak temperature for the formation of metallic cobalt was shifted to a lower temperature at 431°C, compared to 540°C of the CoAp200 catalyst.

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TABLE V Catalytic performances of four supported nano-cobalt catalysts under condition with 100 kPa,  $T$ -Rn of 190 °C, GHSV=1800 mL/g/h,  $H_2/CO$  of 2, TOS of 24 h and reduction temperature of 400 °C

Catalyst	Conv. CO/%	Selectivity/%			
		CH <sub>4</sub>	C <sub>2</sub> -HC	C <sub>3-4</sub> -HC	C <sub>5+</sub> -HC
CoAp200	3.28	8.32	4.25	13.71	75.72
CoAp340	5.91	8.28	3.93	10.65	77.13
CoAp400	4.59	8.15	3.90	10.33	77.62
CoAp500	2.66	6.52	3.56	10.16	79.76

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