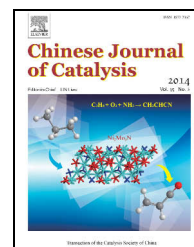


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## Article

# Cobalt-based catalysts derived from cobalt carbonyl clusters for Fischer-Tropsch synthesis

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## ABSTRACT

Co catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were prepared using Co<sub>2</sub>(CO)<sub>8</sub>HCCCOOH, Co<sub>3</sub>(CO)<sub>9</sub>CCH<sub>2</sub>COOH, and Co<sub>4</sub>(CO)<sub>10</sub>HCCCOOH as precursors. Co(NO<sub>3</sub>)<sub>2</sub> was used as the precursor for preparing the reference catalyst. The results of Fischer-Tropsch synthesis tests and characterization by transmission electron microscopy, NH<sub>3</sub> temperature-programmed desorption, and infrared showed that the different precursors have significant effects on the dispersion of the Co, which affect their catalytic behavior. CO conversion and C<sub>5+</sub> selectivity over these catalysts prepared from different precursors decreased in the order Co<sub>3</sub>(CO)<sub>9</sub>CCH<sub>2</sub>COOH > Co<sub>2</sub>(CO)<sub>8</sub>HCCCOOH > Co<sub>4</sub>(CO)<sub>10</sub>HCCCOOH > Co(NO<sub>3</sub>)<sub>2</sub>.

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## 1. Introduction

Fischer-Tropsch (F-T) synthesis is one of the most promising alternative routes for converting natural gas and coal into liquid fuels. Cobalt-based catalysts are the preferred catalyst due to high activity and selectivity toward linear hydrocarbons, and low activity for the water-gas shift (WGS) reaction [1]. It is known that the product distribution from F-T synthesis usually follows the Anderson-Schultz-Flory (ASF) law, and it is difficult to obtain specific hydrocarbons in high selectivity from F-T synthesis. Thus, it is a critical issue to rationally design new Co-based catalysts with enhanced higher liquid hydrocarbon selectivity in F-T synthesis [2,3]. Many studies showed that the cobalt sources had a significant effect on the metal-support interaction, reduction properties and dispersion, and the activity and selectivity of the catalysts prepared by impregnation [4,5]. Co(NO<sub>3</sub>)<sub>2</sub> is often used as the Co salt in the catalyst preparation, however, other compounds such as Co<sub>2</sub>(CO)<sub>8</sub>,

Co<sub>4</sub>(CO)<sub>12</sub>, Co-EDTA, Co(acac)<sub>3</sub>, and Co(CH<sub>3</sub>COO)<sub>2</sub> can also be used. Kraum et al. [6] systematically studied the correlation between catalytic activity and the cobalt source for TiO<sub>2</sub>-supported catalysts using different Co precursors, and found that the catalytic activity decreased in the order Co(COO)<sub>2</sub> > Co(CH<sub>3</sub>COO)<sub>2</sub> > Co(acac)<sub>3</sub> > Co(NO<sub>3</sub>)<sub>2</sub> > Co-EDTA > Co(acac)<sub>2</sub>. Niemela et al. [7] reported on the performance of 5% Co/SiO<sub>2</sub> catalysts prepared from different cobalt sources for F-T synthesis. They found that the dispersion of the active components followed the order of Co<sub>2</sub>(CO)<sub>8</sub> > Co<sub>4</sub>(CO)<sub>12</sub> >> Co(NO<sub>3</sub>)<sub>2</sub>. Compared to the traditional Co catalyst, cobalt carbonyl clusters can provide zero valent metal particles and do not need to be reduced at high temperature. Moreover, multi-metallic carbonyl clusters have a potential more efficient metal synergy. In this work, we prepared a series of Co-based catalysts using carbonyl clusters as the cobalt precursors. Their catalytic performance for F-T synthesis was investigated, and was also compared with the catalyst prepared using Co(NO<sub>3</sub>)<sub>2</sub>.

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## 2. Experimental

### 2.1. Materials

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was purchased from a domestic supplier.  $\gamma\text{-Al}_2\text{O}_3$  was purchased from Alfa Aesar.  $\text{Co}_4(\text{CO})_{10}\text{HCCCOOH}$  and  $\text{Co}_2(\text{CO})_6\text{HCCCOOH}$  were prepared according to published procedures [8]. The molecular structures are shown in Fig. 1.  $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{COOH}$  was obtained by the reaction of  $(\text{CO})_{10}\text{Co}_4\text{HCCCOOH}$  and  $\text{Eu}(\text{OCCF}_3)_3$  dissolved in freshly distilled tetrahydrofuran (THF). The crystal structural parameters and data are given in Table 1. Selected bond lengths and angles are given in Table 2. The structure and the atom numbering scheme is shown in Fig. 1(c). X-ray single crystal analysis revealed  $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{COOH}$  is a triclinic system with the centro-symmetrical space group  $P\bar{1}$  (see Table 1).

### 2.2. Catalyst preparation

The  $\gamma\text{-Al}_2\text{O}_3$  support was calcined at 500 °C for 10 h to dehydroxylate the surface prior to use. The Co catalysts were prepared by conventional incipient wetness impregnation of  $\gamma\text{-Al}_2\text{O}_3$  (40–60 mesh) using THF solution of  $\text{Co}_2(\text{CO})_6\text{HCCCOOH}$ ,  $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{COOH}$ , or  $\text{Co}_4(\text{CO})_{10}\text{HCCCOOH}$  under  $\text{N}_2$  atmosphere. Excess solvent was removed by  $\text{N}_2$  flow. The solids obtained were dried in  $\text{N}_2$  atmosphere for 24 h at room temperature, and named as  $\text{Co}_n/\gamma\text{-Al}_2\text{O}_3$  ( $n = 2, 3, 4$ ; the same below). The  $\text{Co}(\text{N})/\gamma\text{-Al}_2\text{O}_3$  catalyst was prepared by incipient wetness impregnation with  $\text{Co}(\text{NO}_3)_2$  and dried in air at 120 °C for 12 h. Then, the sample was calcined in air at 350 °C for 6 h. Co contents in these samples were 10 wt%.

### 2.3. Catalyst pretreatment

The catalysts with the two types of precursors were pretreated under different pretreatment conditions. The temperature-programmed hydrogen reduction experiment of  $\text{Co}(\text{N})/\gamma\text{-Al}_2\text{O}_3$  catalyst showed the typical reduction behavior of  $\text{Co}/\text{Al}_2\text{O}_3$  with the peak at 347 °C attributed to the reduction of bulk  $\text{Co}_3\text{O}_4$  ( $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ ) in the catalyst and the high temperature peak (396–470 °C) attributed to the reduction of  $\text{Co}^{2+} \rightarrow \text{Co}^0$  [9,10]. Since the  $\text{Co}_3\text{O}_4$  species can interact with  $\text{Al}_2\text{O}_3$  at high temperature to form the irreducible  $\text{CoAlO}_4$  species [11], the  $\text{Co}(\text{N})/\gamma\text{-Al}_2\text{O}_3$  catalyst was reduced at 400 °C in a hydrogen

**Table 1**

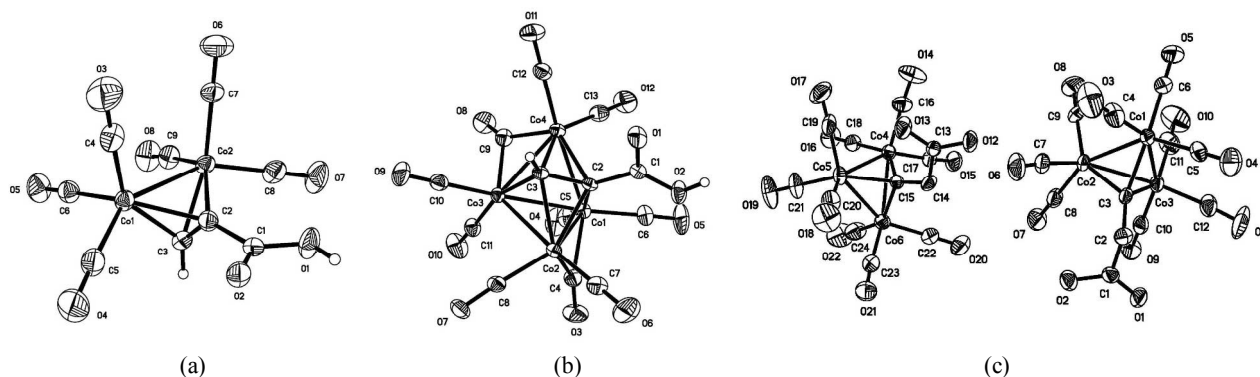
Crystal and structural data of  $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{COOH}$ .

Empirical formula	$\text{C}_{12}\text{H}_3\text{Co}_3\text{O}_{11}$
Formula weight	499.76
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a$ (Å) = 8.2074(7) $b$ (Å) = 13.5852(12) $c$ (Å) = 15.9065(14) $\alpha$ (°) = 95.6430(10) $\beta$ (°) = 101.035(2) $\gamma$ (°) = 92.4500(10)
$Z$	4
Dcalc (g/cm <sup>3</sup> )	1.917
Absorption coefficient (mm <sup>-1</sup> )	2.898
F(000)	972
Crystal size	0.31 mm × 0.12 mm × 0.10 mm
$\theta$ range for data collection (°)	1.51–25.02
Reflections collected / unique	8900 / 5962 [ $R(\text{int}) = 0.0301$ ]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7604 and 0.4669
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	5962/0/469
Goodness-of-fit on $F^2$	1.018
Final $R$ indice [ $I > 2\sigma(I)$ ]	$R_1 = 0.0556$ , $\omega R_2 = 0.1470$
$R$ indice (all data)	$R_1 = 0.0885$ , $\omega R_2 = 0.1787$
Largest diff. peak and hole (e Å <sup>-3</sup> )	1.826 and -0.585
Temperature (°C)	25(2)

flow. However, the  $\text{Co}_n/\text{Al}_2\text{O}_3$  catalysts with zero valent cobalt were only flushed with  $\text{H}_2$  flow at 200 °C.

### 2.4. Catalytic activity test

F-T synthesis was carried out in a fixed-bed stainless steel reactor ( $\phi$  18 mm × 700 mm). The catalyst (4 g) was loaded into the reactor, flushed with high purity  $\text{H}_2$  at 200 °C ( $\text{Co}(\text{NO}_3)_2/\text{Al}_2\text{O}_3$  at 400 °C) for 10 h, and then the catalyst was slowly cooled to 180 °C under  $\text{H}_2$  flow. The inlet gas was switched to syngas ( $\text{H}_2/\text{CO} = 2$ ), the pressure was increased to 2.0 MPa and the reactor temperature was raised to 220 °C in 1 h. Ar was used as an internal standard for the calculation of CO conversion. The gas hourly space velocity (GHSV) was kept constant at 500 h<sup>-1</sup>. The outlet gases containing  $\text{H}_2$ , CO,  $\text{CH}_4$ , and  $\text{CO}_2$  were analyzed by online gas chromatography on a Shimadzu GC-8A equipped with a TDX-01 carbon molecular sieve column and a TCD detector. Hydrocarbon products with carbon



**Fig. 1.** Molecular structures of  $\text{Co}_2(\text{CO})_6\text{HCCCOOH}$  (a),  $\text{Co}_4(\text{CO})_{10}\text{HCCCOOH}$  (b), and  $\text{Co}_3(\text{CO})_9\text{CCH}_2\text{COOH}$  (c).

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