



Effect of pretreatment temperature on catalytic performance of the catalysts derived from cobalt carbonyl cluster in Fischer-Tropsch Synthesis

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Abstract: The monometallic cobalt-based catalysts were prepared by pretreating the catalysts derived from carbonyl cluster precursor $(\text{CO})_6\text{Co}_2\text{CC}(\text{COOH})_2$ supported on $\gamma\text{-Al}_2\text{O}_3$ with hydrogen at 180, 220, and 260°C respectively. The temperature effect of the pretreatments on the structure evolution of cluster precursors and the catalytic performance of the Fischer-Tropsch (F-T) synthesis was investigated. The pretreated catalyst at 220°C with unique phase structure exhibited best catalytic activity and selectivity among three pretreated catalysts. Moreover, the catalysts exhibited high dispersion due to the formation of hydrogen bonds between the cluster precursor and $\gamma\text{-Al}_2\text{O}_3$ support.

Keywords: Cobalt carbonyl cluster; Co-based catalyst; pretreatment temperature; F-T synthesis

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INTRODUCTION

It is well known that metal carbonyl clusters are able to play unusual roles in catalytic activity and selectivity for a variety of reactions [1, 2]. Many homo- and heterogeneous catalysts have been prepared by using the clusters as catalyst precursors [3, 4]. Among them, the heterogeneous catalysts prepared by metallic carbonyl cluster precursors loaded on solid supports exhibited distinct characteristics and activities in heterogeneous catalyst system [5, 6]. The published studies indicated that the carbonyl precursors, such as $\text{Co}_2(\text{CO})_8$, $\text{Co}_4(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ [7-9], are excellent precursors due to their small metallic particles, which possibly emerge from the bonds between metal atoms in their zero oxidation state in these complexes. Moreover, these complexes were assumed to mimic small metallic particles covered with CO ligands [10]. Potential advantages of carbonyl based catalysts are the following: greater metal dispersion, higher number of zero valence cobalt species available, well defined organometallic cluster structure. Thus, the catalysts synthesized using these precursors would be more interesting by removing the ligands of the clusters to gain coordinative unsaturation in cluster catalysis [11-13]. The activation of supported metal carbonyl catalysts has generally been done by thermal decomposition in an inert atmosphere [14]. Siani et al. [15] investigated the pretreatment atmosphere effect on the active metal species over the bimetallic cluster derived PtFe/SiO₂ catalyst for the oxidation of CO, and found that the surface species formed on the support have different structure after the removal of organic ligands when the

catalyst is treated in either He or H₂ flow. Furthermore, the activity depends strongly on the structure of the surface species. On the other hand, the pretreatment temperature can also be considered as an important factor to influence the structure of the surface species. For example, the cluster $[\text{Ir}_4(\text{CO})_{12}]$ loaded on $\gamma\text{-Al}_2\text{O}_3$, upon treatment in H₂ at 300°C, gives no disruption of the tetrahedral metal frame [16]. However, when $\text{H}_3\text{Re}_3(\text{CO})_{12}$ was adsorbed onto $\gamma\text{-Al}_2\text{O}_3$, and was treated in H₂ at 400°C, the average Re-Re distance was contracted and a new structure was formed though the surface structure is still predominantly trirhenium [17]. Literature data [18] indicated that the optimum pretreatment temperature helps to obtain more active sites by releasing CO ligands without decomposing the frameworks of clusters. To date, the detailed study of the relationship between the structure evolution of cluster precursor and the catalytic performance of catalyst is still challenging.

In the present study, cobalt-based catalysts were prepared by using cobalt carbonyl cluster containing carboxyl groups $(\text{CO})_6\text{Co}_2\text{CC}(\text{COOH})_2$ as catalyst precursor. The precursor was loaded on $\gamma\text{-Al}_2\text{O}_3$ support and further pretreated under H₂-Ar flow at various temperatures respectively. The carbonyl and carboxyl ligands removal process and structure evolution of the precursor and pretreated catalysts were examined by TG and IR techniques. The catalytic performance of the catalysts was also investigated for the F-T synthesis.

EXPERIMENTAL

General details: Dicobalt octacarbonyl $\text{Co}_2(\text{CO})_8$ and acetylenedicarboxylic acid HOCCCCOOH were purchased from Alfa Aesar and used as received. $(\text{CO})_6\text{Co}_2\text{CC}(\text{COOH})_2$ was prepared under dry N₂ using

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standard Schlenk techniques as previous description with minor modification [19]. We have modified the Schlenk method that liquid nitrogen was replaced in the port of solvent coming down, which prevent to volatile the solvent. All the solvents were dehydrated with an appropriate drying agent and deoxidized by distilling under Nitrogen atmosphere before use. Schlenk techniques were employed in the synthesis and handling of all air-sensitive materials.

Catalyst preparation: The γ - Al_2O_3 support (40-60 mesh) was calcined in air at 500°C for 10h prior to use to remove impurities of the surface. The catalyst was prepared as follows (10 wt% Co): The pretreated γ - Al_2O_3 support was impregnated with $(\text{CO})_6\text{Co}_2\text{CC}(\text{COOH})_2$ in THF kept for 24 hours in the room temperature with nitrogen flow. Then the excess solvent THF was removed under nitrogen flow. Subsequently, the dry solid catalyst was obtained, and labeled as $\text{Co}_2/\text{Al}_2\text{O}_3$. The freshly prepared $\text{Co}_2/\text{Al}_2\text{O}_3$ was in situ pretreated respectively at 180 , 220 , and 260°C for 10h under hydrogen flow, labeled as $\text{Co}_2(180^\circ\text{C})/\gamma\text{-Al}_2\text{O}_3$, $\text{Co}_2(220^\circ\text{C})/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co}_2(260^\circ\text{C})/\gamma\text{-Al}_2\text{O}_3$.

Fischer-Tropsch synthesis catalytic evaluation: The F-T synthesis was performed in a stainless steel fixed-bed reactor (i.d. 10 mm). The catalyst (4.0 g, 40–60 mesh) was mixed with the same-sized quartz in order to improve the temperature distribution within the reactor. Prior to the F-T reaction, as comfortable catalytic condition the catalysts were pretreated at 180 , 220 , and 260°C for 10h with H_2 under atmospheric pressure and cooled down to room temperature in the corresponding atmosphere. Then the reaction pressure was increased up to 2.0 MPa before switching to a flow mixture gas of CO, H_2 and Ar (volume ratio of $\text{H}_2:\text{CO}:\text{Ar} = 20:10:1$). The gas flow was set at a space velocity of 500 h^{-1} and the reaction temperature was slowly increased to 220°C at a ramp rate of $1^\circ\text{C}/\text{min}$. CO, CH_4 , Ar and CO_2 in the gas effluent were analyzed on-line by a Shimadzu GC-8A gas chromatograph equipped with a thermal conductivity detector (TCD) using TDX-01 column. And the light hydrocarbons ($\text{C}_1\text{--}\text{C}_5$) were analyzed by a Shimadzu GC-8A gas chromatograph on-line equipped with a flame ionization detector (FID) using a Porapak-Q column.

Catalyst characterization:

Infrared spectroscopic analysis

IR spectra were recorded with a NEXUS-670 FTIR spectrometer equipped with an MCT (Mercury cadmium telluride) detector, and the spectral resolution was 2 cm^{-1} . The samples are typically examined in KBr pellets after thorough mixing by pestling and tableting.

Differential thermal gravimetric analysis:

Thermogravimetric-differential scanning calorimetry (TG-DSC) measurements were carried out on a NETZSCH STA 449F3 thermogravimetric analyzer from room temperature to 800°C with a rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

RESULTS AND DISCUSSION

TG analysis: Figure 1 showed TG curve of the $(\text{CO})_6\text{Co}_2\text{CC}(\text{COOH})_2$ precursor from room temperature to 800°C under nitrogen atmosphere. There are two steps of weight loss for the sample. The first weight loss of 41.5% from 73°C to 257°C was corresponded to the removal of carbonyl ligands (calculated: 42.0%), and

the next weight loss of 21.4% from 257°C to 418°C was attributed to the decomposition of two $-\text{COOH}$ groups of the cluster (calculated: 22.5%) (No further reading about the data available so far). In addition, a small plateau was observed during the first step of weight loss.

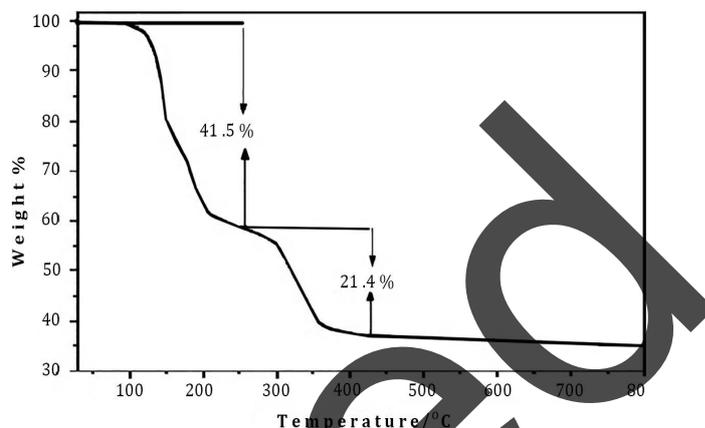


Fig. 1. TG curve of the $(\text{CO})_6\text{Co}_2\text{CC}(\text{COOH})_2$ precursor

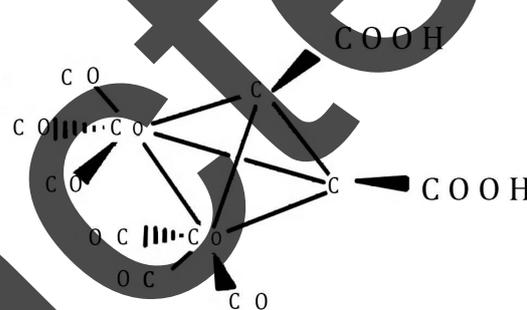


Fig. 2. The structural scheme of the cluster precursor

From the available structural scheme of the complex (Figure 2), we could suppose that this plateau corresponded to a phase where the volatile carbonyl groups have been removed first. (There is a TG analysis explanation in the Figure 1)

IR analysis: Infrared spectra of the pure crystalline precursor $(\text{CO})_6\text{Co}_2\text{CC}(\text{COOH})_2$, the fresh $\text{Co}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst and $\gamma\text{-Al}_2\text{O}_3$ support are presented in Figure 3. The set of bands at 2118 , 2090 , and 2038 cm^{-1} in ν_{CO} region and at 1656 , 1526 , 1395 , 1203 cm^{-1} in ν_{COO^-} region represented characteristics of the $(\text{CO})_6\text{Co}_2\text{CC}(\text{COOH})_2$ cluster precursor (Figure 3 (a)). The absorption frequencies at 2979 , 881 , and 751 cm^{-1} were assigned to the coordinated acetylene $\text{C}\equiv\text{C}$ stretching bands, which were slightly shifted to lower frequencies compared to those of coordinated acetylene without carboxyl groups [20]. For the $\text{Co}_2/\gamma\text{-Al}_2\text{O}_3$ sample, the profile and location of the carbonyl bands remained unchanged (Figure 3 (b)), implicating that the impregnated cluster precursor retains the structural feature of the cobalt core. However, the location and intensity for the carboxyl group stretching ν_{COO^-} and the ν_{OH} stretching (3421 cm^{-1}) changed significantly compared to pure crystalline precursor, suggesting that hydrogen bonds were formed between the carboxyl groups of cluster framework and the hydroxyl groups of support (It is a hydroxyl group from $-\text{OH}$). Anchoring the carbonyl cluster to the support via hydrogen bonds would make the cobalt clusters on support surface immobile and to congregate, which would be favorable for improving cobalt dispersion and should contribute to catalytic activity

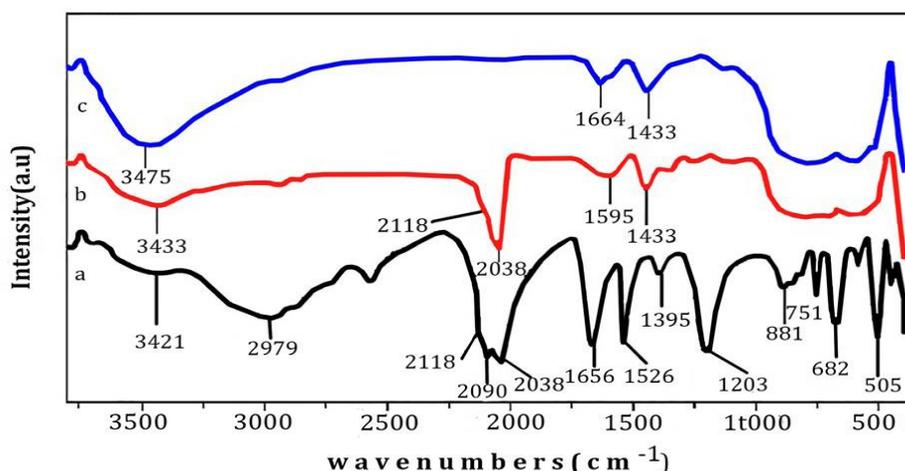


Fig. 3. IR spectra (KBr pellet) of the samples: (a) pure crystalline precursor $(\text{CO})_6\text{Co}_2\text{CC}(\text{COOH})_2$; (b) $\text{Co}_2/\text{Al}_2\text{O}_3$; (c) $\gamma\text{-Al}_2\text{O}_3$

Table 1. Catalytic performance of the catalysts for F-T synthesis reaction, %

Catalysts	CO Conv.	S_{CH_4}	$S_{\text{C}_2\text{-C}_4}$	$S_{\text{C}_5^+}$
$\text{Co}_2(180^\circ\text{C})/\gamma\text{-Al}_2\text{O}_3$	76	26	1	73
$\text{Co}_2(220^\circ\text{C})/\gamma\text{-Al}_2\text{O}_3$	89	16	3	81
$\text{Co}_2(260^\circ\text{C})/\gamma\text{-Al}_2\text{O}_3$	86	22	1	77
$\text{Co}_2/\gamma\text{-Al}_2\text{O}_3$	60	26	1	73

(Clearly, the unique catalytic behavior depended on the bond formation via reaction between the cluster and surface hydroxyl groups.)

Catalytic performance analysis: The catalytic performance of the cobalt carbonyl cluster catalysts pretreated at various temperatures was performed. The CO conversion and product selectivity were measured after 10 h on stream. The results are shown in Table 1 and the $\text{Co}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst without pretreatment was used as reference. It can be seen that all the pretreated catalysts exhibited enhanced catalytic performance than the reference catalyst. Furthermore, the $\text{Co}_2(220^\circ\text{C})/\gamma\text{-Al}_2\text{O}_3$ catalysts exhibited the highest activity among three pretreated catalysts. The $\text{Co}_2(260^\circ\text{C})/\gamma\text{-Al}_2\text{O}_3$ catalyst showed comparable activity and the $\text{Co}_2(180^\circ\text{C})/\gamma\text{-Al}_2\text{O}_3$ catalyst had the lowest activity for F-T reaction. Similar trend was observed for selectivity of C_5^+ . On the basis of TG result, the reason for the lowest activity for $\text{Co}_2(180^\circ\text{C})/\gamma\text{-Al}_2\text{O}_3$ catalyst was that the amount of active sites existed around the cobalt core was significantly less, since the coordinated CO still occupied the active sites when the catalyst was decarbonylated at 180°C in H_2 flow. In contrast, the cleaner cobalt particle surface and specific phase structure can be obtained by using 220 and 260°C as pretreated temperature. It can provide more active sites than the catalysts prepared at lower temperature. In the case of the $\text{Co}_2(260^\circ\text{C})/\gamma\text{-Al}_2\text{O}_3$ catalyst, the weak bonds between the cobalt center and the CO molecules located at specially active sites directly led to the lower abundance of activated CO molecules, resulting in the lower catalytic activity and selectivity.

CONCLUSIONS

In this work, cobalt-based catalysts were prepared by using $(\text{CO})_6\text{Co}_2\text{CC}(\text{COOH})_2$ precursor loaded on $\gamma\text{-Al}_2\text{O}_3$ support. The catalysts exhibited high dispersion by anchoring

the cluster precursor to $\gamma\text{-Al}_2\text{O}_3$ support via hydrogen bonds between them, and most of the cobalt particles dispersed as amorphous phase on the support. The catalysts were further pretreated in-situ in H_2 flow at 180 , 220 , and 260°C respectively. The precursor clusters on the support passed through an interesting procedure of structure evolution during pretreatment process. Different pretreatment temperature resulted in different structure of cobalt species. The unique structure that corresponded to producing more activated CO, such as the structure produced in $\text{Co}_2(220^\circ\text{C})/\gamma\text{-Al}_2\text{O}_3$, was favorable for the F-T synthesis and could exhibit high catalytic performance.

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