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Citric acid assisted one-step synthesis of highly dispersed metallic Co/SiO_2 without further reduction: As-prepared Co/SiO_2 catalysts for Fischer–Tropsch synthesis

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ABSTRACT

Highly dispersed metallic Co/SiO_2 catalysts are prepared by a novel citric acid assisted synthesis method in an argon atmosphere and directly used in Fischer–Tropsch synthesis without further reduction. CH_4 and H_2 derived from the decomposition of metal–citric acid complexes act as reductants for synthesizing metallic Co^0 from Co^{2+} in the chelating complexes. Thermogravimetry, differential thermal analysis, X-ray diffraction, transmission electron microscopy, temperature-programmed reduction, H_2-chemisorption, and Brunauer–Emmett–Teller methods are used to identify the catalysts, proving that cobalt species are almost completely reduced (reduction degree: 95%) to metallic Co^0 and highly dispersed on the SiO_2 support with small cobalt crystallite sizes (about 3 nm). The activity of this proposed catalyst is about 4-times of that prepared by the conventional incipient-wetness impregnation method. However, a tremendous amount of methane and lots of CO_2 are produced. This novel citric acid assisted synthesis method herein is promising for preparing highly dispersed supported metallic catalysts, especially for the catalysts which are difficult to reduce.

1. Introduction

Metallic catalysts are widely used in industrial catalytic processes, such as hydrogenation, dehydrogenation, isomerization, reforming, and selective hydrocarbon oxidation catalysts [1]. To obtain higher concentrations of, and efficient utilization of, surface metallic active sites, supported nano or subnano-structured metallic catalysts [2–5] with higher dispersion and smaller particle sizes have received widespread interest in recent years.

For Fischer–Tropsch synthesis (FTS):

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \qquad (1)$$

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O \qquad (2)$$

Co-based catalysts are conventionally prepared by aqueous impregnation methods [6–9] on different supports. Next, the precursors are calcined in an oxidizing atmosphere to produce the Co_3O_4 phase. However, Co_3O_4 crystallite sizes prepared from cobalt nitrates by these conventional methods become larger than 20 nm [6] on SiO_2 support. Chu et al. [10] used glow-discharge nitrogen and hydrogen plasma for the pretreatment of Co-based precursors to obtain 10 nm Co_3O_4 particles. De Jong et al. decomposed cobalt nitrate in the NO/He atmosphere to obtain supported Co_3O_4 particles with a diameter of 4–5 nm [11]. Co-based catalysts prepared by these methods [6–11] are all in Co_3O_4 phases, which should be reduced with pure hydrogen at high temperature for at least 6 h. It is noted that the smaller particles of Co_3O_4 should be reduced at much higher temperature (higher than 723 K) to partially obtain metallic Co. For Al_2O_3 support which has the strong support interaction with the cobalt oxides, the particle sizes of Co_3O_4 are much smaller than SiO_2 support, but the cobalt oxides state is more difficult to be reduced [12,13] as compared with SiO_2 support.

Here, a novel citric acid assisted synthesis method is proposed to prepare highly dispersed metallic Co/SiO_2 (Co crystallite sizes: 3 nm) catalysts directly without further reduction. Cobalt-based catalysts are first conventionally prepared by an aqueous impregnation method with cobalt nitrate and SiO_2 (Q-50). After drying, the as-prepared precursors are treated by citric acid solution. Then, the metal–citric acid precursors are calcined in an argon atmosphere to obtain metallic Co/SiO_2 catalysts, which are directly used for FT synthesis without further reduction. In this catalyst preparation process, citric acid acts both as a chelating agent to provide complexing ligands, forming a homogeneous precursor, and as a

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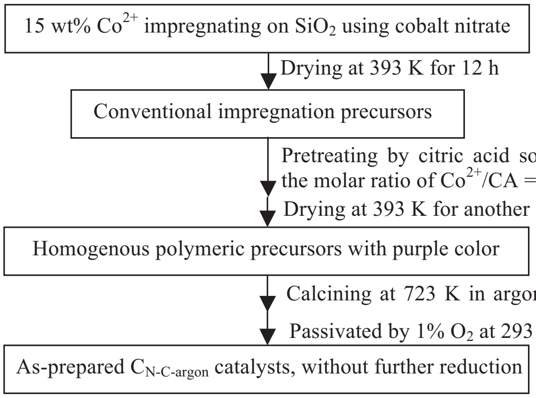

Fig. 1. A schematic flow chart of the catalysts prepared by citric acid assisted synthesis method.

reductant source to obtain metallic Co from Co^{2+}. This citric acid assisted synthesis method has the following features: (1) highly dispersed metallic Co/SiO_2 catalysts can be directly synthesized without further reduction; (2) the activity of as-prepared Co/SiO_2 catalysts for FTS is significantly high; (3) the whole catalysts preparation process is easily operated with inexpensive materials. This citric acid assisted synthesis method can open a new methodology to prepare highly dispersed metallic catalysts, especially for the catalysts which are difficult to reduce.

In this study, the activity of the as-prepared catalysts is investigated for slurry-phase Ficher–Tropsch synthesis (FTS) at 513 K and 1.0 MPa for 15 h. Three catalysts, $C_{N\text{-reduction}}$ and C_C prepared by an aqueous impregnation method with cobalt nitrate and citrate as precursors, respectively, as well as our previously reported catalysts $C_{sol\text{–}gel}$ prepared by a surface impregnation combustion method [14], are used as the reference catalysts. Compared with the dispersion and the activity of $C_{N\text{-reduction}}$ (CO conversion: 16.7%), C_C (33.8%) and $C_{sol\text{–}gel}$ (42.3%), the dispersion and activity of the as-prepared metallic Co/SiO_2 catalysts (CO conversion: 64.5%) prepared by this novel citric acid assisted synthesis method are significantly promoted. However, a tremendous amount of methane and lots of CO_2 are produced.

2. Experimental

2.1. Preparation of catalysts

A schematic flow chart of the catalyst prepared by a citric acid assisted synthesis method is illustrated in Fig. 1. $Co(NO_3)_2 \cdot 6H_2O$ (≥99%), $C_{12}H_{10}Co_3O_{14} \cdot 6H_2O$ (≥ 8%), citric acid, and a commercially available silica gel (Cariact Q-50, Fuji Silysia Co., specific surface area: 57 $m^2 g^{-1}$, pore volume: 1.2 $mL g^{-1}$) are used as raw materials. First, cobalt-based catalysts with 15 wt% metal loading are conventionally prepared by a wetness aqueous impregnation method using cobalt nitrate, noted as C_N. After drying at 393 K for 12 h, the as-prepared precursor is pretreated by citric acid solution with the molar ratio of Co^{2+}/citric acid (noted as CA) = 1/1.5, noted as $C_{N\text{–}C}$. Following drying another 12 h, the precursor $C_{N\text{–}C}$ is calcined in an argon atmosphere at 723 K for 3 h, and subsequently passivated by 1% oxygen in argon at room temperature for 4 h, noted as $C_{N\text{–}C\text{-argon}}$. The as-prepared catalysts are directly used for FT synthesis without H_2 reduction. For Ref. [1], the precursor C_N is calcined in air at 723 K for 3 h, and subsequently reduced at 723 K for 10 h in pure hydrogen, noted as $C_{N\text{-air-reduction}}$. For Ref. [2], cobalt citrate ($C_{12}H_{10}Co_3O_{14} \cdot 6H_2O$) is used instead of cobalt nitrate. The precursor is directly burnt in argon without further reduction (the combustion condition is the same as that of $C_{N\text{–}C\text{-argon}}$), noted as $C_{C\text{-argon}}$. Ref. [3] is our previously reported catalyst [14] prepared by a surface impregnation combustion method, noted as $C_{sol\text{–}gel\text{-argon}}$. All of the reference catalysts were also investigated for FT synthesis.

2.2. Characterization of catalysts

The characterization conditions and methods of thermogravimetry differential thermal analysis, X-ray diffraction, Brunner–Emmett–Teller, and transmission electron microscopy, and H_2-chemisorption were the same as those reported in our previous work [14,15].

The reduction behavior of the supported metal oxide phases was studied by hydrogen temperature-programmed reduction (H_2-TPR) in a Catalyst Analyzer (BELCAT-B, BEL. Japan Co., Ltd.), using 0.030 g burnt catalysts with 5% hydrogen diluted by argon at atmospheric pressure. The reduction degree corresponding to the TPR curves were calculated from the area of the peaks from 298 to 723 K, assuming Co_3O_4 is the main component being reduced.

2.3. Catalytic activity tests

Catalytic testing was carried out using a semi-batch slurry-phase reactor with an inner volume of 85 mL. One gram of the catalyst was loaded into the reactor with 20 mL n-hexadecane as the liquid medium. The reaction conditions were: P(total) = 1.0 MPa, T = 513 K, CO/H_2 = 1/2, W/F ($CO + H_2 + Ar$) = 10 g h mol^{-1} for TOS 15 h. The effluent gas from the reactor was analyzed by an online gas chromatography. A thermal conductivity detector (TCD) was used to analyze gaseous products (CO, CO_2 and CH_4). 3% argon is used as inner standard. Light hydrocarbons (C_1–C_5) were analyzed on-line by a flame ionization detector (FID) with a Porapak-Q column. The analysis of hydrocarbons dissolved in the solvent and cooled in the trap was carried out by FID with a silicone SE-30 column.

3. Results and discussion

3.1. TG–DTA analysis of the precursors calcined in an argon atmosphere

The thermal behavior of the precursors for $C_{N\text{-air-reduction}}$, $C_{N\text{–}C\text{-argon}}$, and $C_{C\text{-argon}}$ investigated by TG–DTA measurements in an argon atmosphere is compared in Fig. 2. As displayed in Fig. 2a–c for all the precursors, two endothermic peaks at about 320 and 380 K are observed. The first endothermic peak at about 320 K is assigned to the evaporation of the remaining water in the precursors. The second endothermic peak at about 380 K arises from the desorption of the chemically adsorbed water.

As shown in Fig. 2a, two other endothermic peaks at about 460 and 485 K are attributed to the two-step decomposition of cobalt nitrate with the TG plots exhibiting the main weight loss, which is consistent with many reports. Finally, Co_3O_4 is obtained and no significant variation is observed when the temperature is higher than 573 K, indicating that decomposition of cobalt nitrate is virtually complete at about 573 K. Concerning Fig. 2b, as compared with the TG–DTA analysis of pure citric acid (Supporting Information, Fig. S1) and the decomposition process of cobalt nitrate in Fig. 2a, the endothermic peak at about 485 K in Fig. 2b is assigned to the decomposition of cobalt nitrate and free citric acid (not chelating with Co^{2+}). With increasing temperature, TG plots show a continual weight loss from 460 to 780 K. During this process, a large amount of gases such as H_2, H_2O, CH_4, NO, CO_2, NH_3, NO_2 are liberated [14,15]. For the broad exothermic peak at about 652 K in Fig. 2b with the TG plots illustrating an abrupt weight loss, the metal–citric acid complexes undergo a redox reaction, wherein H_2 and CH_4 act as reductants, while Co^{2+} in the metal–citric acid complexes performs as an oxidant. After combustion, Co^{2+} in the chelated complexes is