Citric acid assisted one-step synthesis of highly dispersed metallic Co/SiO₂ without further reduction: as-prepared Co/SiO₂ catalysts for Fischer-Tropsch synthesis

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Abstract:

Highly dispersed metallic Co/SiO₂ 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. CH₄ and H₂ derived from the decomposition of metal-citric acid complexes act as reductants for synthesizing metallic Co⁰ from Co²⁺ in the chelating complexes. Thermogravimetry, differential thermal analysis, X-ray diffraction, transmission electron microscopy, temperature-programmed reduction, H₂-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 Co⁰ and highly dispersed on the SiO₂ 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 CO₂ 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.

Keywords: Reduction-free; High dispersion; Metallic catalysts; Citric acid; Co/SiO₂; Fischer-Tropsch synthesis

1. Introduction

Metallic catalysts are widely used in industrial catalytic processes, such as hydrogenation, dehydrogenation, isomerization, reforming, selective hydrocarbon oxidation catalysts [1] and so on. 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):

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 Co₃O₄ phase. However, Co₃O₄ crystallite sizes prepared from cobalt nitrates by these conventional methods become larger than 20 nm [6] on SiO₂ support. Chu et al. [10] used glow-discharge nitrogen and hydrogen plasma for the pretreatment of Co-based precursors to obtain 10 nm Co₃O₄ 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 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 Fischer-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 $C_{\text{sol-gel}}$ 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 $C_{\text{sol-gel}}$ (42.3%), the dispersion and activity of the as-prepared metallic Co/SiO₂ 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 CO₂ 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(NO₃)₂·6H₂O (≥ 99%), C₁₂H₁₀Co₃O₁₄·6H₂O (≥ 98%), citric acid, and a commercially available silica gel (Cariact Q-50, Fuji Silysia Co., specific surface area: 57 m²g⁻¹, pore volume: 1.2 mLg⁻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 Co²⁺/citric acid (noted as CA) = 1/1.5, noted as C_{N-C} . Following drying another 12 h, the precursor C_{N-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 $C_{N-C\text{-argon}}$. The as-prepared catalysts are directly used for FT synthesis without H₂

reduction. For reference 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 reference 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 $C_{N\text{-C-argon}}$), noted as $C_{C\text{-argon}}$. Reference 3 is our previously reported catalyst [14] prepared by a surface impregnation combustion method, noted as $C_{\text{sol-gel-argon}}$. 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 were 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, $T = 513\text{ K}$, $\text{CO}/\text{H}_2 = 1/2$, $\text{W/F} (\text{CO} + \text{H}_2 + \text{Ar}) = 10\text{ ghmol}^{-1}$ 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 ($\text{C}_1\text{-C}_5$) 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 $\text{C}_{\text{N-air-reduction}}$, $\text{C}_{\text{N-C-argon}}$, and $\text{C}_{\text{C-argon}}$ investigated by TG-DTA measurements in an argon atmosphere is compared in Fig. 2. As displayed in Figs. 2a-2c 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 reduced to metallic Co. The whole reduction process can be separated in two steps: 1) continual generation of CH_4 and H_2 by the decomposition of metal-citric acid complexes from 460 to 780 K; 2) the redox process between $\text{CH}_4\text{-H}_2$ and Co^{2+} at about 653 K. When using this novel citric acid assisted synthesis method, metallic Co/ SiO_2 catalysts are obtained, which are further demonstrated by XRD and TPR analysis.

Similarly, the exothermic peak at about 630 K in Fig. 2c corresponds to the redox process between $\text{CH}_4\text{-H}_2$ and Co^{2+} in cobalt citrate. As compared with the exothermic peak at 652 K in Fig. 2b, the shape of the exothermic peak in Fig. 2c is sharper (the DTA signal current in Fig. 2c is about $30\mu\text{V}$ rather than that in Fig. 2b about $20\mu\text{V}$) and the redox temperature is 22 K lower. During the catalyst preparation, a higher content of $\text{C}_6\text{H}_5\text{O}_7^{3-}$ is used to prepare the precursor of $\text{C}_{\text{N-C-argon}}$ than that of $\text{C}_{\text{C-argon}}$; therefore, more CH_4 and H_2 are generated during the decomposition of metal-citric acid complexes to take part in the redox process. As known, the redox process is strongly influenced by the ratio of reductants to oxidants. A lower content of reductant in the precursors makes the redox process more severe and easier to proceed.

3.2 XRD analysis and TEM images of the as-prepared catalysts

The XRD patterns of $C_{N\text{-reduction}}$, $C_{N\text{-C-argon}}$, $C_{C\text{-argon}}$, and the solid form of pure cobalt citrate burnt in argon without reduction are compared in Fig. 3. The diffraction peaks of $C_{N\text{-reduction}}$ in Fig. 3a which is after 10 h of reduction are indexed to metallic Co and SiO_2 phases. In Fig. 3b, the diffraction peaks of $C_{N\text{-C-argon}}$ prepared by citric acid assisted synthesis method and without further reduction exhibit only one broad peak, except for the diffraction peaks of SiO_2 , at about 45° , which is attributed to metallic cobalt. This result suggests that Co^{2+} in the metal-citric acid complexes is reduced to metallic Co^0 by H_2 and CH_4 from the continual decomposition of metal-citric acid complexes. As the diffraction peaks of metallic Co^0 in Fig. 3b are weak, this conclusion will be further proven by TPR analysis. However, the diffraction peaks of $C_{C\text{-argon}}$ in Fig. 3c and the products from direct burning of pure cobalt citrate in Fig. 3d are related to metallic Co, CoO and SiO_2 phases. As the diffraction peaks of Co and CoO phases in Figs. 3c and 3d are not well-resolved; the vertical axis are magnified and added in the Supporting Information, as compared in Fig. S2. In Fig. S2b, the peaks at about 38° and 62° are definitely attributed to CoO phase, which indicates that cobalt citrate can not be completely reduced by $\text{C}_6\text{H}_5\text{O}_7^{3-}$ supplied from itself.

Fig. 4 displays the TEM images of $C_{N\text{-reduction}}$, $C_{N\text{-C-argon}}$ and $C_{C\text{-argon}}$, respectively. For $C_{N\text{-C-argon}}$ in Fig. 4b, the particle-size distributions are rather narrow with standard deviations within 10% of the average sizes, indicating that this novel citric acid assisted synthesis method is a reliable way to prepare heterogeneous metallic catalysts with precise and desired compositions. The average sizes of metallic Co crystallites from Co size distributions are compared in Table 1. It is clear that the average sizes of Co crystallites obey the series: $C_{N\text{-C-argon}} < C_{C\text{-argon}} \ll C_N$. Compared with the conventional

impregnation method, the metallic Co^0 crystallite sizes of $\text{C}_{\text{N-C-argon}}$ are significantly decreased from 30 to 3 nm and highly dispersed on the SiO_2 support. However, for $\text{C}_{\text{C-argon}}$, which is prepared with cobalt citrate as precursors, the average sizes of Co or CoO are much larger, about 5.2 nm, and the particles in Figs. 4a and 4c, display more or less agglomerated state.

3.3 TPR analysis of the burnt catalysts

TPR profiles of the burnt precursor and catalysts $\text{C}_{\text{N-air}}$, $\text{C}_{\text{C-argon}}$ and $\text{C}_{\text{N-C-argon}}$ are compared in Fig. 5. In agreement with previous reports [7,17], the TPR peaks of the calcined catalyst $\text{C}_{\text{N-air}}$ at about 572 and 610 K are attributed to the two-step reduction of Co_3O_4 ($\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$).

For the as-prepared catalyst $\text{C}_{\text{N-C-argon}}$ without reduction, a continually increased TPR peak starting from about 490 K is displayed in Fig. 5b. This TPR peak might be caused by two reasons: 1) part of the cobalt is still in an oxidized state and can not be reduced by $\text{CH}_4\text{-H}_2$ released by the decomposition of metal-citric acid complexes; 2) reduction of surface cobalt species in an oxidized state because after the combustion process, surface active metallic Co is re-oxidized by 1% oxygen in argon, which is used as passivation gas at room temperature. Without the precautionary passivation step, the active cobalt species in the as-prepared catalysts $\text{C}_{\text{N-C-argon}}$ would be quickly and severely self-ignited at room temperature to form Co_3O_4 species. By continually increasing the reduction temperature, a broad peak at about 770 K is shown in Fig. 5b, which is assigned to the hydrogenation of amorphous carbon in the presence of metallic Co, because the TPR profiles of some carbon supported metal catalysts exhibit a broad peak having a similar shape at about 750-800 K [18,19], and TPR-MS is used to

identify the formation of methane [19]. The amorphous carbon left in the as-prepared catalysts is further identified and weighted by TG-DTA analysis in air. The extra smaller peak at higher temperature 1001 K in Fig. 5b is due to Co_xSiO_y species [20], which are quite difficult to reduce.

For $\text{C}_{\text{C-argon}}$ without reduction, a broad peak starting from 520 K is displayed in Fig. 5c. The peak in the region from 520 to 650 K is attributed to the reduction of CoO. The TPR peak at about 770 K also corresponds to the hydrogenation of amorphous carbon in the presence of metallic Co. It is notable that the area of the TPR peak at 770 K in Fig. 5b is about 1.5 times of that in Fig. 5c, which is similar to the molar ratio 9/4 of $\text{C}_6\text{H}_5\text{O}_7^{3-}$ used in the precursors for $\text{C}_{\text{N-C-argon}}$ ($\text{Co}^{2+}/\text{C}_6\text{H}_5\text{O}_7^{3-} = 1/9$) and $\text{C}_{\text{C-argon}}$ ($\text{Co}^{2+}/\text{C}_6\text{H}_5\text{O}_7^{3-} = 1/4$). For the preparation of $\text{C}_{\text{C-argon}}$, only Co^{2+} is the oxidant, while $\text{C}_6\text{H}_5\text{O}_7^{3-}$ acts as the reductant. However, for the synthesis of $\text{C}_{\text{N-C-argon}}$, NO_3^- in the metal-citric acid complexes offers extra oxygen for the oxidation of $\text{C}_6\text{H}_5\text{O}_7^{3-}$. Consequently, a lower molar ratio of amorphous is left in $\text{C}_{\text{N-C-argon}}$ than that in $\text{C}_{\text{C-argon}}$. The last TPR peak at about 1001 K is the same as previously discussed for Fig. 5b. It is noted that no reduction peaks are observed at about 520 K in Fig. 5c, suggesting that less surface active metallic cobalt are left in $\text{C}_{\text{C-argon}}$ than in $\text{C}_{\text{N-C-argon}}$.

The calculation methods of the reduction degree for $\text{C}_{\text{N-air}}$, $\text{C}_{\text{N-C-argon}}$ and $\text{C}_{\text{C-argon}}$ are demonstrated in the Experimental Section of the Supporting Information. As displayed in Fig. 5d, CuO was used to calibrate the TCD signal for H_2 consumption [21,22]. As compared in Table 1, the reduction degree of $\text{C}_{\text{N-air}}$ is about 82.0%, $\text{C}_{\text{C-argon}}$ about 63.2%, and $\text{C}_{\text{N-C-argon}}$ about 95.2%. It should be emphasized that the actual reduction degree of $\text{C}_{\text{N-C-argon}}$ is higher than 95.2% because part of surface active metallic Co is re-oxidized by 1% oxygen in argon during the passivation process. Compared with the reduction

degree of $C_{N-C-argon}$ and $C_{C-argon}$, it is testified that $C_6H_5O_7^{3-}$ from cobalt citrate itself is not enough for the reduction of cobalt species to form single metallic Co^0 phase.

3.4 TG-DTA analysis in air to study the content of amorphous carbon left in the as-prepared catalysts

According to the former report [14], oxidation of amorphous carbon and metallic cobalt happens at about 400-600 K in the presence of metallic cobalt, so the content of amorphous carbon left in the as-prepared catalysts $C_{N-C-argon}$ and $C_{C-argon}$ is mainly investigated by TG-DTA analysis in air from 400 to 600 K. As compared in Figs. 6a1 for $C_{N-C-argon}$ and in Fig. 6b1 for $C_{C-argon}$, a gradual weight increase is observed from 420 to 490 K, and the DTA curves in Fig. a2 display a small exothermic peak, which is attributed to the oxidation of metallic Co or CoO to Co_3O_4 . These experimental phenomena indicate that Co^{2+} in the chelated complexes could be reduced to metallic Co by H_2 and CH_4 from continual decomposition of metal-citric acid complexes. The main weight loss of the as-prepared catalysts in Figs. 6a1 and 6b1 is observed at about 510 K; simultaneously, the DTA plots exhibit a sharp exothermic peak. According to the experimental results reported by Zhang et al. [23] and Schüth et al. [24], the exothermic peak at about 510 K in Figs. 6a2 and 6b2 is attributed to the oxidation of amorphous carbon in the presence of metallic cobalt.

According to the TG plots in Figs. 6a1 and 6b1, the weight loss, which is attributed to the oxidation of amorphous carbon in the presence of cobalt [23], of $C_{N-C-argon}$ is about 4.0 wt%, and of $C_{C-argon}$ about 2.9 wt%. As the weight loss of the as-prepared catalysts in Fig. 6 is the combination of the weight loss of amorphous carbon and the weight increase from Co or CoO to Co_3O_4 , the calculation method of actual amorphous

carbon left in the catalysts is provided in the Supporting Information. After solving the equation, the weight of amorphous carbon left in $C_{N-C-argon}$ was about 8.13 wt% and $C_{C-argon}$ about 6.40 wt%, which is similar to the TPR results and DTA curves that show that the area of the DTA curve in Fig. 6a2 is about 1.5 times sharper than that of Fig. 6b2.

3.5. Hydrogen chemisorption

The chemisorption results of pure hydrogen on the catalysts $C_{N-reduction}$, $C_{N-C-argon}$, $C_{C-argon}$ and $C_{sol-gel-argon}$ are compared in Table 1. Uptakes of hydrogen on the support and amorphous carbon are negligible. The total H_2 uptake by catalysts followed the order: $C_{N-C-argon} > C_{sol-gel-argon} \gg C_{C-argon} \gg C_{N-reduction}$. Based on the reduction degree of the catalysts measured by TPR, the dispersion and the cobalt particle sizes are calculated and presented in Table 1. $C_{N-C-argon}$ prepared by this novel citric acid assisted method exhibits cobalt dispersions of about 20.9%. As compared with the dispersion (16.6%) of former reported $C_{sol-gel-argon}$ [14] and that (13.7%) of $C_{C-argon}$, metallic Co^0 dispersion of $C_{N-C-argon}$ is much higher. The calculated metallic cobalt particle sizes increase in the order: $C_{N-C-argon} \approx C_{sol-gel-argon} < C_{C-argon} \ll C_{N-reduction}$, which is in accordance with the results of TEM analysis.

3.6 Activity of the catalysts

The BET surface area, pore volume, and catalytic performance of $C_{N-reduction}$, $C_{N-C-argon}$, $C_{C-argon}$, and $C_{sol-gel-argon}$ are compared in Table 1. The BET surface area of silica (Q-50) is $57 \text{ m}^2\text{g}^{-1}$, whereas that of the catalyst $C_{N-reduction}$ is $65.5 \text{ m}^2\text{g}^{-1}$. The increase of BET surface area is derived from the metallic Co particles entering into the

pores of the support. For the as-prepared catalyst $C_{N-C-argon}$, the BET surface area is $78.6 \text{ m}^2\text{g}^{-1}$, about 13.1, 8.7 and $2.3 \text{ m}^2\text{g}^{-1}$ larger than those of the references $C_{N-reduction}$, $C_{C-argon}$, and $C_{sol-gel-argon}$. The increased BET surface area of $C_{N-C-reduction}$ comes from highly dispersed metallic Co^0 particles. Smaller Co particles contribute to larger BET surface area although 8.13 wt% of carbonic residues are left in the as-prepared catalysts.

On the catalytic performances of these FTS catalysts listed in Table 1, the reference $C_{N-reduction}$ exhibits only limited CO conversion as low as 16.7%, mainly determined by its largest cobalt crystallite sizes and lower cobalt dispersion. However, for the as-prepared catalyst $C_{N-C-argon}$ prepared by this novel citric acid assisted synthesis method and without further reduction, CO conversion is significantly high, about 64.5% (about fourfold higher than $C_{N-reduction}$ prepared by a conventional method), because of its smallest average Co particle size (highest metallic Co^0 dispersion). For $C_{C-argon}$ without reduction, CO conversion of $C_{C-argon}$ is about 33.1%. As compared with $C_{N-C-argon}$, its lower activity is mainly derived from its lower reduction degree.

Comparing with our previously reported [23] $C_{sol-gel-argon}$ (CO conversion: 42.3%; cobalt dispersion: 16.6%) prepared by a surface impregnation combustion method with the same content of citric acid as $C_{N-C-argon}$, the activity and dispersion is also remarkably increased. During the preparation process of $C_{sol-gel-argon}$, the sol precursors are viscous. When the viscous gels are supported on the surface of Q-50, the metal-citric acid complexes can not fully permeate into the pores. After combustion, a shell-like structure is formed, as indicated in Fig. 7a. A majority of metallic Co^0 particles stay on the surface of Q-50. However, for $C_{N-C-argon}$, it is no doubt that cobalt nitrate in the solution can completely permeate into the pores. Citric acid in the solution can also enter into the pores and covers cobalt nitrate to obtain metal-citric acid complexes. After

burning in an argon atmosphere, metallic Co^0 dispersed homogeneously throughout the support, as illustrated in Fig. 7b. In order to identify this blocking effect, the pore volume is determined by Shimadzu ASAP 2000 and the results are shown in Table 1. For Q-50 support, the pore volume is about 1.2 mLg^{-1} . The pore volume of $\text{C}_{\text{N-reduction}}$ catalyst is about 0.59 mLg^{-1} , because the metallic cobalt crystallites enter into the pores and take up some of the pore volume. For $\text{C}_{\text{C-argon}}$ and $\text{C}_{\text{N-C-argon}}$ catalysts, the pore volume is slightly smaller than that of $\text{C}_{\text{N-reduction}}$ catalyst. However for $\text{C}_{\text{sol-gel-argon}}$ catalyst, the pore volume is much smaller, only about 0.36 mLg^{-1} , indicating that parts of pores are blocked by carbonic residues.

It is notable that the methane selectivity of the as-prepared catalysts $\text{C}_{\text{N-C-argon}}$ and $\text{C}_{\text{C-argon}}$ is about 40.0%, much higher than that of conventional FTS catalysts. For $\text{C}_{\text{N-C-argon}}$, one reason is its smaller cobalt crystallite sizes, as finely dispersed metallic crystallite is not suitable for carbon chain growth, but methane formation is promoted. This observation is in agreement with the results reported by de Jong et. al [25] that smaller Co particles supported on carbon nanofiber exhibit much higher methane selectivity. For another reason, the metallic Co particles are embedded in the amorphous carbon. H_2 diffused more quickly than CO inside micropores of amorphous carbon, leading to the very higher H_2/CO ratio there than the original ratio at the cobalt surface, yielding excessive methane. For $\text{C}_{\text{C-argon}}$, the higher methane selectivity is due to its lower reduction degree of cobalt, because the formation of methane favors on the smaller Co surface surrounded by CoO. As compared in Table 1, the CO_2 selectivity of $\text{C}_{\text{N-C-argon}}$ is also very high, about 7.8%. According to the mechanism of FTS reaction, higher conversion of CO leads to much more generation of H_2O . Thus, water gas shift reaction is enhanced; more content of CO_2 is produced.

As displayed in Fig. 8, the hydrocarbon distribution of the burnt catalyst C_{N-C-argon} closely follows the Anderson–Schultz–Flory (ASF) distribution law. The yield of methane is large, followed by a minimum at C₂, a broad maximum from C₄ to C₈, and a gradual decrease to C₂₅.

4. Conclusions

Highly dispersed metallic Co/SiO₂ catalysts are directly prepared by a novel citric acid assisted synthesis method in an argon atmosphere without further reduction. During the combustion process, CH₄ and H₂ derived from the decomposition of metal-citric acid complexes act as reductants. Co²⁺ in the metal-citric acid complexes can be reduced to the metallic Co⁰. The as-prepared Co/SiO₂ catalyst is directly used in FTS and exhibits much higher activity, as compared with conventional cobalt nitrate and cobalt citrate impregnation methods. However, a tremendous amount of methane and lots of CO₂ are produced. This citric acid assisted synthesis method has the following features: 1) highly dispersed (cobalt dispersion: 20.9%) metallic Co/SiO₂ catalysts with smaller cobalt crystallite sizes (3.0 nm) can be directly synthesized without further reduction; 2) the activity of as-prepared Co/SiO₂ catalysts for FTS is significantly high; 3) the whole catalyst preparation process is easily-operated with inexpensive materials. This citric acid assisted synthesis method provides a new way to prepare highly dispersed metallic catalysts, especially for the catalysts which are difficult to reduce at high temperature.

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Figure captions

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

Fig. 2. TG-DTA analysis of the precursors for (a) $C_{N\text{-reduction}}$, (b) $C_{N\text{-C-argon}}$, and (c) $C_{C\text{-argon}}$ calcined in an argon atmosphere (The precursors were characterized at a heating rate 5 K/min from 293 to 873 K in the argon atmosphere).

3. XRD analysis of (a) $C_{N\text{-reduction}}$, (b) $C_{N\text{-C-argon}}$, (c) $C_{C\text{-argon}}$, and (d) the products from pure cobalt citrate directly burnt in argon at 723 K (■, SiO_2 ; ☆, Co; ▼, CoO; XRD patterns were obtained on a Rigaku RINT 2400 X-ray diffractometer, using monochromatic Cu K α radiation, scanning 2 θ from 20 to 80°, and at 40 kV and 40 mA).

Fig. 4. TEM images of (a) $C_{N\text{-reduction}}$, (b) $C_{N\text{-C-argon}}$, and (c) $C_{C\text{-argon}}$ (TEM images were obtained by TOPCON EM-002 B operated at 200 kV).

Fig. 5. TPR profiles of (a) $C_{N\text{-air}}$, (b) $C_{N\text{-C-argon}}$, (c) $C_{C\text{-argon}}$, and (d) CuO.

Fig. 6. TG-DATA analysis of (a) $C_{N\text{-C-argon}}$ and (b) $C_{C\text{-argon}}$ in air (The burnt catalysts were characterized at a heating rate 5 K/min from 293 to 873 K in air).

Fig. 7. Representation of (a) $C_{\text{sol-gel-argon}}$ and (b) $C_{N\text{-C-argon}}$ (•, metallic Co⁰).

Fig. 8. FT synthesis products distribution of the as-prepared catalyst $C_{N\text{-C-argon}}$ (Reaction conditions: T = 513 K, P = 1.0 MPa, catalyst weight: 1 g, Co loading: 15 wt%, n-hexadecane: 20 ml, stirring speed: 2000 rpm, TOS: 15 h, syngas: CO/H₂ = 1/2, W/F (CO + H₂ + Ar) = 10 g mol^{-1}).

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Table 1 Catalyst characterization results and catalytic performance for FTS.

Catalysts	H ₂ uptake ^a	Reduction degree ^b	Dispersion ^c	Co	Particle size (nm)	BET ^e	Pore vol.	CO conversion (%)	Selectivity (%)		
	μmol H ₂ /g	TPR (%)	Co (%)	H _{2(ad)} ^d	TEM	(m ² g ⁻¹)	mLg ⁻¹		CH ₄	CO ₂	C ₅₊
C _N -reduction	32.3	82	3.1	31	30	65.5	0.59	16.7	11.6	1.3	79.2
C _N -C-argon	252.6	95.2	20.9	4.6	3	78.6	0.47	64.5	40	7.8	43.5
C _C -argon	110.2	63.2	13.7	7	5.2	69.9	0.53	33.8	39.6	3.2	48.6
C _{sol-gel} -argon	200.6	95	16.6	5.8	3	76.3	0.36	42.3	42.3	3.9	44.4

Reaction conditions: T = 513 K, P = 1.0 MPa, catalyst weight: 1 g, Co loading: 15 wt%, n-hexadecane: 20 ml, stirring speed: 2000 rpm, TOS: 15 h, syngas: CO/H₂ = 1/2, W/F (CO + H₂ + Ar) = 10 ghmol⁻¹.

^a H₂-Chemisorption, adsorption temperature was 373 K.

^b Calculated by TPR profiles.

^c Assuming the stoichiometry H_{ad}/Co_s = 1.

^d Calculated by 96/Dispersion.

^e Determined by N₂ physical desorption at 77 K.