Effects of coaltar carbide on Fischer–Tropsch synthesis with MnO supported Co-based catalysts

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A B S T R A C T
Coaltar carbide (Co2C) was considered as potential catalysts available for large-scale industrialization of transforming syngas (H2 and CO) to clean fuels. Herein, we successfully synthesized Co-based catalysts with MnO supported, to comprehend the effects of Co2C for Fischer–Tropsch synthesis (FTS) under ambient conditions. The huge variety of product selectivity which was contained by different active sites (Co and Co2C) has been found. Furthermore, density functional theory (DFT) shows that Co2C is efficacious of CO adsorption, whereas is weaker for H adsorption than Co. Combining the advantages of Co and Co2C, the catalyst herein can not only obtain more C5 products but also suppress methane selectivity. It can be a commendable guide for the design of industrial application products in FTS.

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1. Introduction

Fischer–Tropsch synthesis (FTS), a significant step in the transformation of syngas (a mixture of H2 and CO) to clean fuels or value-added chemicals, is of both industrial and fundamental importance [1–4]. The challenge of selective formation of available hydrocarbons through FTS lies in precisely controlling C–C coupling by adjusting hydrogenation and suppressing methane formation under reaction [5]. To this end, catalysts with both high activity and selectivity are highly desirable to obtain products on-demand.

Transitional metal carbides (TMC) have been emerged as a promising class of catalytic materials in FTS because their metallic-like properties [6–11]. Among TMC, iron carbide represents a leading catalyst to afford long-chain hydrocarbons due to its high stability, per pass conversion and hydrocarbon selectivity [12,13]. In contract, its analog, coaltar carbide, has long been considered as an unwanted byproduct which results in the activity loss of the metallic Co active center during FTS [14]. Quite recently, the role of Co2C has been turned. For example, Zhong et al. revealed a high relevancy among the particle size, the exposed facets of Co2C and catalytic performance [15]. The specific Co2C surface exhibited excellent selectivity towards the formation of lower olefins with low selectivity towards methane production [16]. Ding et al. synthesized stable and efficient Co–Co2C catalysts [17] and proposed that Co–Co2C interfaces have synergistic effects and are responsible for the formation of alcohols [18]. Although tremendous efforts have been made to understand the effect of the coaltar carbide, due to the tanglesome reactions in FTS, it is rather difficult to elucidate the formation process of the active site and the characterization of the catalysts [17,19–23].

Herein, we used co-precipitation method to successfully synthesize Co2C@MnO catalyst which performed different selectivities with Co/MnO and Co2C@MnO catalysts under ambient reaction conditions (250 °C, 0.1 MPa), TEM and in-situ XRD experiments

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confirmed the formation of coexisted Co and Co$_2$C. The atomic structure of the Co/Co$_2$C@MnO catalyst was studied by X-ray absorption fine structure (XAFS). Based on the DFT analysis of the Co-based catalysts, we further understood the catalytic mechanism of the cobalt carbide and provided guidance for the molecular design of the catalytic performance of the Co-based catalysts in FTS.

2. Experimental

2.1. Synthesis of catalyst

CoMnO$_2$ catalyst was synthesized by co-precipitation method refer to our previous work [14]. In a typical synthesis, an aqueous solution containing cobalt nitrate (Co(NO$_3$)$_2$·6H$_2$O; Sinopharm) and manganese nitrate (50 wt% Mn(NO$_3$)$_2$, Sinopharm) was prepared (2 M, (mol/mol)=2/1), and Na$_2$CO$_3$ aqueous solution (2 M) was added. The mixed solution was vigorously stirring at RT. Following, the formed suspension went through a procedure of filtration, repeated washing process and dried overnight at 100 °C. Finally, we calcined the dried powder at 330 °C for 3 h in the air. When the solution precipitant was replaced by the mix of (NaH$_2$O)$_2$ Co and Na$_2$CO$_3$ solution (Na/Na (mol/mol)=1/1), we obtained Co/Co$_2$C@MnO. If the solution precipitant was replaced by only Na$_2$CO$_3$ solution, Co$_2$C@MnO was obtained.

2.2. Characterization

2.2.1. In situ X-ray diffraction (XRD) analysis

In situ powder X-ray diffraction measurement and analysis for Fischer–Tropsch reaction were referred to our previous work [24]. The phase transformation of the calcined samples was monitored during reduction process at 0.1 MPa in a H$_2$ flux of 20 mL/min with a thermal rate of 1 °C/min from RT to 350 °C and the XRD patterns were collected every 20 °C. Then, the samples were kept at 350 °C about 5 h, and the XRD spectra were collected every 30 min at 350 °C (Fig. S1). Afterwards, the cell temperature was cooled down to 250 °C, at which the catalytic behavior was monitored under 0.1 MPa syngas (H$_2$/CO=2/1) at a flux rate of 20 mL/min (Fig. 1). We collected the XRD spectra every 30 min during the FT process. Each scan was performed at 40 kV and 40 mA with a scanning angle range of 30°–80° at a rate of 2°/min. All the XRD spectra were carried out by the X'pert HighScore Plus software package with the PDF library.

2.2.2. Transmission electron micrograph (TEM)

The morphology of the spent catalysts was observed by Tecnai G$^2$S-TWIN instrument with an accelerating voltage of 200 kV [25].

2.2.3. X-ray absorption fine spectroscopy (XAFS)

Co K-edge XAFS data were measured in transmission mode at beamline BL14W1 of Shanghai Synchrotron Radiation Facility (SSRF) [26]. The extended X-ray absorption fine structure (EXAFS) data analyses were carried out by using the Demeter software package [27,28]. The Fourier transformation of the $k^2$-weighted functions was applied to the EXAFS data. The fitting of the EXAFS data was calculated by Artemis program in Iffleff.

2.3. Catalytic test

Catalysts were tested in a fixed-bed stainless steel plug-flow reactor with inner diameter 9 mm refer to our previous work [14]. In a typical test, ca. 2 mL catalyst and 2 mL SiO$_2$ were mixed to obtain isothermal plug flow conditions. The reactor was filled with 0.1 MPa H$_2$ at RT and heated to 175 °C at a rate of 5 °C/min and then the gas atmosphere was changed into syngas (H$_2$/CO=2). The temperature was further increase into 250 at a heating speed of 0.5 °C/min. At the outlet of the reactor, we use a condenser to separate the gas and liquid products. The catalytic performances were analyzed after stabilization for 12 h. Agilent 6890N GC gas chromatograph with a HP-5 capillary column and a flame ionization detector (FID) was used to analyze products. The water-bearing products and oil-bearing products were analyzed by butyl with internal standard method and area normalization method, respectively.

2.4. DFT calculations

Spin-polarized plane-wave basis set density functional theory (DFT) as implemented in the Vienna ab initio Simulation Package (VASP) [29], Perdew–Burke–Ernzerhof (PBE) [29] generalized gradient approximation (GGA) [30] functional was used to evaluate the exchange-correlation energy. The energy and force convergence were $10^{-5}$ eV and 0.02 eV, respectively. The energy cut off was 400 eV. A 16 × 16 × 16 Monkhorst–Pack k-point mesh was employed in the calculations of bulk properties. The lattice volume was fitted with the third-order Birch–Murnaghan isothermal equation of state [31]. The resulted lattice parameters of FCC Co and Co$_2$C are $a=b=c=3.457\AA$ and $a=2.850\AA$, $b=4.361\AA$ and $c=4.345\AA$, respectively. For the calculation of Co and H$_2$ molecule, a 20 × 20 × 20 unit cell and 1 × 1 × 1 k-point mesh were employed.

A 15 Å vacuum region was applied to separate slabs in the calculation of slab model. We only investigate the most stable surface of Co$_2$C, which is Co$_2$C (101) as is reported previously [32]. A p(2 × 2) unit cells for Co$_2$C (101) were utilized in our calculation, which contains 4 layers of Co and 2 layers of C. The bottom 2 Co layers and one C layer were fixed, and outer layers were fully relaxed. A p(3 × 3) unit cell for FCC Co (111) was also applied in the calculation. It contained three Co layers with the bottom layer one fixed. (Scheme S1) Monkhorst-Pack mesh k-points of (3 × 3 × 1), (3 × 4 × 1) were used for FCC Co (111), Co$_2$C (101)-C-terminated and Co$_2$C (101)-Co-terminated surface calculations, respectively. Dipole corrections have been applied in the calculations to avoid artificial dipole effects. Since CO and H adsorptions on Co (111) were well studied, we only consider the most stable adsorption site. H was on the 3-fold-fcc-hollow site and CO was on the top of Co atom. In the case of adsorption on Co$_2$C-C-terminated, four sites were taken into consideration, as was shown in Scheme S1. However, some of them were not favorable for CO/H adsorption. There were only three distinguishable configurations for CO adsorption (Scheme S2) and two for H adsorption (Scheme S3). The most stable adsorption site for H and CO on Co$_2$C (101)-Co-terminated was shown in Scheme S4.

The adsorption energy was defined as:

$$E_{ad}(H) = E_{slab+H} - E_{slab} - E_{H2}/2$$

$$E_{ad}(CO) = E_{slab+CO} - E_{slab} - E_{CO}$$

$E_{ad}(H)$ was the adsorption energy of H. $E_{slab}$ was the energy of Co (111) or Co$_2$C(101) slab model. $E_{H2}$ was the energy of H$_2$. $E_{slab+H}$ was the energy of slab model with one H atom. $E_{ad}(CO)$ was the adsorption energy of CO. $E_{CO}$ was the energy of CO. $E_{slab+CO}$ was the energy of slab model with CO adsorbed on it.

3. Results and discussion

3.1. In situ XRD

Despite of different preparing methods, the in-situ XRD results recorded during H$_2$ reduction suggest that all the three catalysts
are composed by a mixture of MnO, metallic Co and Co$_2$Mn$_{1-x}$O after the pre-treatment process (Fig. S1). Fig. 1 shows the in-situ XRD patterns of the catalysts in syngas. For Co@MnO catalyst, the peaks belonging to face center cubic (FCC) Co and MnO existing in the whole 6 h syngas reaction and Co$_2$C phase cannot be observed (Fig. 1(a)). For Co/Co$_2$C@MnO catalyst, in addition to the FCC Co peak, Co$_2$C peaks were shown in a syngas flow at 250 °C (Fig. 1(b)), which can be assigned as 2θ = 37.0°, 41.3°, 42.6°, 45.8°, and 56.6° corresponding to the crystalline plane of Co$_2$C (110), (002), (111), and (112) according to PDF 01-072-1369, respectively. The formed Co$_2$C was very stable even after a 10 h syngas reaction (Fig. S2). It suggests the co-existence of FCC Co and Co$_2$C in Co/Co$_2$C@MnO catalyst. As for Co$_2$C@MnO catalyst, after the syngas feed was introduced, the cobalt metal gradually turned into Co$_2$C with time on-stream. Meanwhile, the single phase (Co$_2$Mn$_{1-x}$O) segregated into FCC Co and MnO, respectively. After 4 h of reaction, the structure was stable and the metallic cobalt completely transformed into Co$_2$C. It can be clearly seen that Co$_2$C formed in Co/Co$_2$C@MnO and Co$_2$C@MnO, which suggests the importance role of Na$_2$CO$_3$ in the formation of Co$_2$C.

3.2. TEM

TEM and HRTEM images of the three spent catalysts are shown in Fig. 2. All are near spherical aggregated nanoparticles with quite a similar average particle size approximating 10 nm (Fig. 2(a)-(c)). The plane distance with ca. 1.53 Å can be assigned as [220] plane of MnO, which is observed in all three samples. A plane distance of ca. 2.01 Å and ca. 2.40 Å corresponds to [111] plane of Co and [101] plane of Co$_2$C, respectively. As shown in Fig. 2(d) and (f) only Co was observed in Co@MnO and only Co$_2$C existed in Co$_2$C@MnO. While, in the Co/Co$_2$C@MnO catalyst, the coexistence of the FCC cobalt metal and the cobalt carbide phase was revealed (Fig. 2(e)). The TEM measurements correspond to the result of in-situ XRD analysis and suggest that the active center in three catalysts might be different, that is, Co, Co/Co$_2$C, and Co$_2$C, respectively.
3.3. Catalytic performance

In order to understand catalytic mechanism, the catalytic activity of Co-based catalysts is presented. The hydrocarbons and alcohols are all possible products through FTS. The catalytic performances of the prepared catalysts during FT reaction were performed at 250°C, 0.1 MPa, and GHSV = 3000 mL·g<sub>cat</sub>·h<sup>-1</sup> with H<sub>2</sub>/CO = 2 in a fixed-bed reactor. The variations in CO conversion and product selectivity for the spent catalysts are listed in Table 1. The CO conversion is similar for all the catalysts. However, we observed diverse product selectivities over these catalysts. Specifically, the selectivities of methane for Co@Co/C@MnO and Co@Co/C@MnO are only 18.1% and 18.3%, respectively, which are much lower than that for Co@MnO (37.5%). Moreover, the production of lower olefins is 39.2% on Co@Co/C@MnO which is higher than those of Co@MnO (18.6%) and Co@Co/C@MnO (22.9%). These results suggest that the Co<sub>2</sub>C also can activate CO like metallic cobalt, however, it suppresses methane formation by suppressing the over-hydrogenation. Nevertheless, the highest C<sub>5</sub> selectivity is observed on Co@Co/C@MnO (42.5%), while the other two catalysts show only around half of the value that is 25.9% and 22.3% for Co@MnO and Co@Co/C@MnO, respectively. This result suggests that a higher C-C coupling is favored in the presence of both Co and cobalt carbide. In addition, the effect of MnO is removed by catalytic performance (Table S3) and water gas shift reaction (Table S4) in this FTS condition.

3.4. XAFS measurement

X-ray Absorption Near Edge Spectroscopy (XANES) analysis is used to distinguish the structure and valence state of the Co-based catalysts in Fig. 3. Fig. 3(a) shows the Co K-edge normalized XANES spectra of the calcined Co-based catalysts and a comparison of Co, Co<sub>2</sub>O<sub>4</sub> and Co<sub>2</sub>C [14] reference compounds. As the ion charge corresponds to the transition energy, the edge position shifts toward lower energies with oxidation states: 7709.8 eV and 7729.0 eV for Co and Co<sub>2</sub>O<sub>4</sub>, respectively. All the spectra of the calcined Co-based catalysts exhibit oxidation states similar to the Co<sub>2</sub>O<sub>4</sub> reference. Fig. 3(c) exhibits the Co K-edge XANES profile in the spent catalysts and reference compounds for comparison. A peak can be found at the pre-edge at 7712 eV for Co@Co/C@MnO and Co@Co/C@MnO, due to the consist of the non-centrosymmetric Co<sub>2</sub>C in catalysts. The absorption edge around in the spent Co-based catalysts sample showed a medium signal between the Co reference and Co<sub>2</sub>O<sub>4</sub>, which revealed that the valence state is lower than +2 in the spent catalysts. Moreover, the ratio of Co<sub>2</sub>C to Co of Co@Co/C@MnO catalyst is 1.68 (calculated by linear combination fitting (LCF) listed in Table S2), which impacts methane and C<sub>5</sub> selectivity on the Co-based catalysts.
To evaluate the local geometry around Co atoms, both the calcined and the spent catalysts were collected by extended X-ray Absorption Fine Structure Spectroscopy (EXAFS). The k^2-weighted EXAFS Fourier transform magnitude spectra of the calcined and spent Co-based catalysts are provided in Fig. 3(b) and (d). In Fig. 3(b), there are two peaks at 1.60 Å and 2.42 Å (without phase-corrected), which respectively represents the first Co-O coordination shell and the second Co-Co coordination shell for cobalt oxide. It is consistent with the XRD patterns. The R space spectra of the spent Co-based catalysts are shown in Fig. 3(d). The EXAFS fitting results and the fitted Fourier transforms spectra are given in Table S1 and Figs. S3–S5. For the Co@MnO spent catalyst, the first peak with the coordination number of ~3.0 at 1.92 Å corresponded to the Co-O contribution. The coordination number of the peak at 2.48 Å which should be assigned to the Co-Co coordination shell for metallic Co is 5.9, indicating that Co nanoparticles dominate in the Co@MnO spent catalyst. The peak at 1.90 Å is the Co-Co coordination shell of CoO. It can be observed that the peak at 1.90 Å of Co/CoO@MnO is around 0.03 Å bigger than that of CoO@MnO and the coordination number increases from 1.0 to 4.0, which further confirms that Co and CoO coexist for Co/CoO@MnO-spent catalyst.

These data were also consistent with the in-situ XRD, TEM and XANES measurements.

3.5. DFT calculations

Density functional theory (DFT) was used to investigate the adsorption of H and CO on both Co and CoO2C surface. The most stable configurations were shown in Fig. 4. H prefers to be adsorbed on the 3-fold-fcc-hollow site on the Co (111) surface with an adsorption energy of −2.723 eV which is similar previous research [33]. The most stable adsorption site for H on CoO2C (101) was Co-bridge site (Fig. 4, Schemes S1 and S3) with an adsorption energy of −2.091 eV which is much weaker than the adsorption on Co. Furthermore, we invested the most stable adsorption site for H and CO on Co-terminated CoO2C (101) with the adsorption energy of −0.669 eV and −2.130 eV (Scheme S4), respectively. Thus, the activation of hydrogen would be much easier on Co compared to CoO2C. However, the CO-adsorption energies were −2.106 eV and −1.629 eV on CoO2C and Co, respectively, that is, CO preferred to be adsorbed on CoO2C rather than Co.
4. Conclusions

In summary, Co@MnO, Co/Co2C@MnO and Co2C@MnO catalysts were synthesized by co-precipitation method and characterized by in situ XRD, TEM, XANES, and EXAFS. The formation of Co2C is a new active site of activating CO and essential for suppressing over-hydrogenation and methane formation as revealed by both experimental data and DFT calculations. On the other hand, the Co metal is preferable for C–C coupling. A higher C–C coupling (C5+) is favored in the presence of both Co and cobalt carbide. We hypothesized that the different ratios between Co and Co2C have a direct influence on the light olefins and C5+. Selectivity during FT synthesis. This finding opens the door for further investigation of the industrial products selectivity of the Co-based catalysts in FTS.

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Supplementary materials

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