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Article

Fischer-Tropsch synthesis: Characterizing and reaction testing of $\text{Co}_2\text{C}/\text{SiO}_2$ and $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ catalysts

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ABSTRACT

SiO_2 - and Al_2O_3 -supported Co_2C catalysts were prepared by carburizing supported Co precursors with CO. The catalysts were characterized by N_2 physisorption, X-ray diffraction and H_2 temperature-programmed reduction techniques, and evaluated by the Fischer-Tropsch (F-T) reaction. The results showed that SiO_2 - and Al_2O_3 -supported Co_2C catalysts could be successfully obtained but sufficient carburization time was required. All of the as-prepared supported Co_2C catalysts exhibited activity and selectivity towards alcohols. It is considered that surface metallic Co species contributed to the activity, surface Co_2C species were responsible for the formation of alcohols, and bulk Co_2C species were inert during the F-T reaction.

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1. Introduction

Because of the depletion of petroleum resources and the deterioration of the environment, Fischer-Tropsch (F-T) synthesis has attracted great attention because it can be used to produce clean liquid fuels from coal, natural gas, and biomass by catalytic conversion of a synthesis gas intermediate. Many metals, such as Fe, Co, Ni, and Ru, can be used as active catalysts for F-T synthesis, and Fe and Co are the most commonly used [1–4]. One interesting phenomenon that occurs on the supported Fe- and Co-based catalysts is the formation of iron and cobalt carbide during the reaction. The formation of iron carbides is easy, because the apparent activation energy of carbon diffusion in iron (43.9–69.0 kJ/mol) is substantially lower than for the F-T reaction (89.1 ± 3.8 kJ/mol), which makes it difficult to identify whether iron carbides or iron metal are the real active sites for F-T synthesis [3,4]. In contrast,

the consensus is that the real active site for Co catalysts is metallic Co, and the formation of the Co_2C phase would result in deactivation of the Co catalysts [1,5–8]. However, Volkova et al. [9] suggested that the appearance of cobalt carbide on Cu-Co catalysts was responsible for the formation of alcohols during the F-T reaction and it followed a CO insertion mechanism. Liu et al. [10] attributed the synthesis of higher alcohols from syngas over LaFeO_3 -supported Co-Cu catalysts to nano-sized Co_2C . We have reported that the synthesis of C_1 – C_{18} linear alcohols could be achieved over activated carbon-supported Co catalyst in the presence of Co and Co_2C species [11–13]. Recently, we showed that linear alcohols can be directly synthesized from syngas over unsupported Co_2C catalysts, and found that the reactivity and selectivity of the catalysts were closely related to surface Co and Co_2C active sites [14,15].

Some density functional theory (DFT) studies have given a better understanding of the relationship between the structure

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and catalytic properties of Co₂C in F-T synthesis and alcohol formation [16–18]. However, understanding of the Co₂C phase is still inadequate and the following question remains to be answered in the field: why is the appearance of Co₂C responsible for the deactivation of the supported Co catalysts? To the best of our knowledge, supported Co₂C as catalysts for F-T synthesis has not been reported. In this paper, we report the synthesis and performance of SiO₂- and Al₂O₃-supported Co₂C catalysts. We also discuss the role that Co₂C species play in supported Co catalysts.

2. Experimental

2.1. Sample preparation

Two types of SiO₂ supports were purchased from Qingdao Haiyang Chemical Co., Ltd. (Qingdao, China), and are denoted as SiO₂(1) and SiO₂(2). The Al₂O₃ support was obtained from Qingdao Meigao Chemical Co., Ltd. (Qingdao, China). The supports were impregnated using an incipient wetness impregnation method with an appropriate Co(NO₃)₂·6H₂O solution. Co loading was kept constant at approximately 15 wt.% (as metal Co). Following drying at 100 °C for 6 h, the catalyst precursors were calcined in flowing Ar at 350 °C for 4 h. All of the samples were then reduced at 250 °C in flowing H₂ (60 mL/min) for 24 h and carburized with CO (1 atm, 60 mL/min) at 220 °C. The SiO₂(1), SiO₂(2), and Al₂O₃ supported catalyst precursors were carburized for 140, 145 and 120 h, and are denoted as Co₂C/SiO₂(1), Co₂C/SiO₂(2), and Co₂C/Al₂O₃, respectively. For comparison, a SiO₂(1) supported Co₂C sample carburized for 72 h was prepared and is denoted as Co₂C*/SiO₂(1).

2.2. Catalyst characterization

The surface area, average pore diameter, and pore volume of the supports and catalysts were measured with nitrogen physisorption at –196 °C using a Micromeritics instrument (Autosorb-1). Prior to the measurements, the samples were degassed in flowing He at 200 °C for 2 h. The average pore diameter and pore volume were determined with the BJH method, and the specific surface area was estimated with the BET method.

The crystalline phases of the catalysts were examined by X-ray diffraction (XRD) with Cu K_{α1} radiation on a PANalytical X'Pert PRO diffractometer at 40 kV and 40 mA. The spectra were recorded from 30° to 60° at a scanning rate of 10°/min.

For the measurements, the catalysts were ground into a fine powder and placed inside a dish.

H₂ temperature-programmed reduction (H₂-TPR) experiments were conducted on an Altamira Instruments AMI-300 unit. The sample (150 mg) was treated with a 10% H₂/Ar gas mixture at a flow rate of 50 mL/min, and the reduction temperature was increased from room temperature to 900 °C at a heating rate of 10 °C/min. The desorbed exit-gases were continuously monitored using an online mass spectrometer (MS) (Oministar, Pfeiffer Vacuum).

2.3. F-T synthesis

The F-T reaction was performed in a stainless-steel fixed-bed microreactor (9 mm i.d. and 450 mm length). The catalyst (4 mL) was diluted with quartz sand to a volume ratio of 1:1 in the reactor. After loading the catalysts into the reactor, the gas was switched from air to syngas (H₂/CO = 1, GHSV = 500 h^{–1}) at 3.0 MPa and the temperature was increased at a 0.3 °C/min heating rate to 220 °C. The reaction effluent passed through a condenser to collect the liquid products. The moment when the reactor reached the designed temperature was taken as the starting time. After 24 h stabilization, the liquid organic products and the aqueous products for another 24 h were off-line analyzed on an HP-6890 gas chromatograph (GC) with 5% PH ME capillary columns and a flame ionization detector after being carefully separated. The outlet gas was on-line analyzed using a HP-6890 GC with a Parapack-Q column and thermal conductivity detector.

3. Results and discussion

3.1. Performance of the F-T reaction

The activity and selectivity results of F-T synthesis over the supported Co₂C catalysts are listed in Table 1. Normal hydrocarbons, CO₂, and linear α-alcohols in the range of C₁–C₁₈ were produced over all the catalysts, which is in agreement with our previous results [11,12]. The Co₂C/SiO₂(1) catalyst showed the highest CO conversion (43.9%) and alcohol selectivity (65.6%). The Co₂C/SiO₂(2) catalyst had only 8.8% CO conversion, but 61.0% alcohol selectivity. The Co₂C/Al₂O₃ catalyst exhibited considerable CO conversion (16.4%) but negligible alcohol selectivity (8.2%).

The alcohols obtained on these catalysts were all linear, and their distribution is in agreement with an Anderson-Schulz

Table 1

Performance of the F-T reaction over the supported Co₂C catalysts^a.

Catalyst	CO conversion (C %)	Selectivity (C %)				Alcohol distribution (C %)		
		C ₁ –C ₄ ^b	CO ₂	C ₅ + ^c	Alcohols	Methanol	C ₂ –C ₅ ^d	C ₆ + ^e
Co ₂ C/SiO ₂ (1)	43.9	13.3	4.0	17.1	65.6	19.3	76.5	4.2
Co ₂ C/SiO ₂ (2)	8.8	21.5	1.6	15.8	61.1	23.1	74.9	2.0
Co ₂ C/Al ₂ O ₃	16.4	12.0	1.7	78.1	8.2	20.9	59.4	19.7

^a Reaction conditions: H₂/CO = 1/1, P = 3.0 MPa, GHSV = 500 h^{–1}, T = 220 °C.

^b Hydrocarbons with 1–4 carbon atoms.

^c Hydrocarbons with more than four carbon atoms.

^d Mixed α-alcohols with 2–5 carbon atoms.

^e Mixed α-alcohols with more than five carbon atoms.

-Flory (ASF)-type distribution (not shown here). This agrees with our previous results [11,12]. Additionally, from Table 1, the proportion of C_{6+} alcohols in the alcohol fraction for the Co_2C/Al_2O_3 catalyst was 19.7%, while for the $Co_2C/SiO_2(1)$ and $Co_2C/SiO_2(2)$ catalysts it was only 4.2% and 2.0%, respectively. It is worth mentioning that the maximum alcohol carbon numbers for the $Co_2C/SiO_2(1)$ and $Co_2C/SiO_2(2)$ catalysts were eight and seven, respectively, while for the Co_2C/Al_2O_3 catalyst the number reached 18. We will further discuss the performance of all the catalysts in the later sections.

3.2. Nitrogen physisorption measurements

The BET surface area, average pore diameter, and pore volume data of the supports and catalysts are listed in Table 2. The BET surface areas, average pore diameters, and pore volumes of the supported Co_2C catalysts were considerably smaller than those of the corresponding supports, which is mainly because of pore blockage [19,20].

3.3. XRD results

Fig. 1 shows the XRD patterns of the $Co_2C/SiO_2(1)$, $Co_2C/SiO_2(2)$, Co_2C/Al_2O_3 , and $Co_2C^*/SiO_2(1)$ samples after preparation. The peaks at $2\theta = 37.0^\circ$ and 42.5° for all the samples can be attributed to the (110) and (111) planes of hexagonal Co_2C , and the peak at $2\theta = 45.7^\circ$ for Co_2C/Al_2O_3 can be assigned to the Co_2C (021) plane (PDF 01-072-1369). No peaks corresponding to cobalt were observed in the patterns of the $Co_2C/SiO_2(1)$, $Co_2C/SiO_2(2)$, and Co_2C/Al_2O_3 samples. However, for the $Co_2C^*/SiO_2(1)$ sample, a peak at $2\theta = 47.5^\circ$ was observed, which can be ascribed to the (101) plane of hcp cobalt (PDF 00-001-1278). It is known that unsupported Co_2C can be obtained by carburizing metallic Co with CO at $220^\circ C$, but more than 500 h carburization time is required [21]. In the present work, the XRD results revealed that supported Co_2C catalysts can be successfully prepared by carburizing supported Co precursor after reduction and significantly less carburization time was spent than for unsupported Co_2C , but considerable carburization time was still necessary.

Fig. 2 shows the XRD patterns of the $Co_2C/SiO_2(1)$, $Co_2C/SiO_2(2)$, and Co_2C/Al_2O_3 catalysts after reaction. The used $Co_2C/SiO_2(1)$ and $Co_2C/SiO_2(2)$ catalysts showed XRD peaks that can only be attributed to Co_2C . However, for the used Co_2C/Al_2O_3 catalyst, the characteristic Co_2C peaks at 37.0° and 45.7° were observed, but the characteristic Co_2C peak at 42.5° almost disappeared and new peaks at 44.3° and 47.5° ap-

Fig. 1. XRD patterns of supported Co_2C samples after preparation.

peared, which can be attributed to the (111) plane of fcc cobalt (PDF 00-00-1259) and the (101) plane of hcp cobalt (PDF 00-001-1278), respectively. It has been reported that Co_2C species readily react with H_2 to form CH_4 and Co ($Co_2C + 2H_2 \rightarrow 2Co + CH_4$) even at a low temperature of $150^\circ C$ [22]. Under real F-T reaction conditions, Co_2C would be partially decomposed by H_2 into cobalt, although the CO partial pressure would ensure the existence of Co_2C species, as we previously reported [15]. Therefore, the metallic cobalt species that were present on the used Co_2C/Al_2O_3 catalyst were derived from the partial decomposition of Co_2C . Moreover, the disparate behavior of Co_2C species on the SiO_2 and Al_2O_3 supports indicated that, as expected, there may be a support effect that can influence the Co_2C phase transition during the reaction. We will discuss this topic more extensively with the findings of the H_2 -TPR analyses in the next section.

3.4. H_2 -TPR-MS results

As mentioned in Section 3.3, Co_2C species can react with H_2 to form CH_4 and Co. Based on this, we attempted to use CH_4 formed in situ during the catalysts' H_2 -TPR process as a probe to investigate the state of Co_2C species in contact with the supports. Fig. 3 shows the CH_4 formation signals during the H_2 -TPR

Fig. 2. XRD patterns of supported Co_2C catalysts after reaction.

Table 2

Textural properties of the supports and the supported Co_2C catalysts.

Catalyst	BET surface area (m^2/g)	Total pore vol- ume (cm^3/g)	Average pore diameter (nm)
$SiO_2(1)$	203.2	0.98	19.3
$SiO_2(2)$	337.5	1.05	12.5
Al_2O_3	104.7	0.55	21.0
$Co_2C/SiO_2(1)$	175.5	0.77	17.6
$Co_2C/SiO_2(2)$	245.8	0.74	12.0
Co_2C/Al_2O_3	92.8	0.39	17.1

Fig. 3. H₂-TPR profiles of the supported Co₂C catalysts after preparation.

process of the supported Co₂C catalysts after preparation. Three CH₄ peaks appeared at 343, 407 and 556 °C for Co₂C/SiO₂(1), two CH₄ peaks appeared at 343 and 814 °C for Co₂C/SiO₂(2), and two CH₄ peaks appeared at 442 and 662 °C for Co₂C/Al₂O₃. We suggest that the peak at 343 °C for Co₂C/SiO₂(1) and Co₂C/SiO₂(2) is because of hydrogenation of surface carbon, the peaks at 407 °C for Co₂C/SiO₂(2) and 442 °C for Co₂C/Al₂O₃ are because of hydrogenation of subsurface carbon, and the peaks above 509 °C for all the catalysts are because of the hydrogenation of lattice carbon of Co₂C strongly interacting with the supports. Based on this characterization and XRD results, we believe that the supported Co₂C catalysts can be successfully prepared not only in bulk but also on the surface.

Fig. 4 shows the H₂-TPR results of the three catalysts after reaction. CH₄ peaks at 343 and 423 °C (probably because of hydrogenation of surface or subsurface carbon) were observed for the used Co₂C/SiO₂(1) and Co₂C/SiO₂(2) catalysts, respectively, but no such peaks were observed for the used Co₂C/Al₂O₃ catalyst. This indicated that there were more surface or subsurface Co₂C sites on the SiO₂ supported catalysts than on the Al₂O₃-supported catalysts. Additionally, the CH₄ formation peaks because of the hydrogenation of the lattice carbon of Co₂C strongly interacting with the supports were

Fig. 4. H₂-TPR profiles of the supported Co₂C catalysts after reaction.

observed on all the samples, but the temperature greatly differed compared with those on the fresh samples. This indicated that reconstruction of the bulk Co₂C phase of all the catalysts may be induced during the reaction. Correlating the H₂-TPR characterization with the performance of the supported Co₂C catalysts, the alcohol selectivity was closely related to surface Co₂C species. On one hand, for the used Co₂C/SiO₂(1) and Co₂C/SiO₂(2) catalysts, considerable Co₂C species existed at the surface or subsurface and resulted in high alcohol selectivities, whereas nearly no Co₂C species existed at the surface of the used Co₂C/Al₂O₃ catalyst, leading to negligible alcohol yield. On the other hand, the areas of the CH₄ formation peaks for the used Co₂C/SiO₂(1) and Co₂C/SiO₂(2) catalysts were similar, which indicated that there were almost the same amounts of surface or subsurface Co₂C species on the catalyst surface, resulting in similar alcohol selectivity for both catalysts. It is well known that CO conversion of cobalt-based catalysts is mainly related to the number of Co⁰ active sites. We previously reported that the activity of unsupported Co₂C catalysts originated from the partial transition of the Co₂C phase to the Co⁰ phase [15]. By comparing Figs. 3 and 4, for the Co₂C/SiO₂(1) catalyst, the CH₄ peak at 343 °C decreased and the peak at 407 °C completely disappeared after the reaction. In contrast, for the Co₂C/SiO₂(2) and Co₂C/Al₂O₃ catalysts, the CH₄ peak attributed to surface or subsurface carbon did not significantly change. This indicated that a high number of Co⁰ active sites appeared on the Co₂C/SiO₂(1) catalyst, which was responsible for the high activity, whereas the low activity of the Co₂C/SiO₂(2) and Co₂C/Al₂O₃ catalysts could be because of a low number of Co⁰ active sites, even though metallic Co phase was present on the used Co₂C/Al₂O₃ catalyst. In the present paper, we only obtained a qualitative relationship between the catalyst activity and the number of Co⁰ active sites. Thus, more studies have to be carried out to quantitatively determine the number of Co⁰ active sites of Co₂C catalysts under real F-T conditions. Note that, for the used Co₂C/SiO₂(2) and Co₂C/Al₂O₃ catalysts, the bulk Co₂C species that were in contact with the supports did not contribute to the catalyst activity, because both catalysts did not have high CO conversion. Therefore, we suggest that bulk Co₂C species are inert. In addition, from Table 1, the production of long-chain alcohols (i.e., C₆₊ alcohols) was inhibited when the Co₂C/SiO₂(1) and Co₂C/SiO₂(2) catalysts exposed more Co₂C sites on the surface compared with the Co₂C/Al₂O₃ catalyst. According to the literature [9,11], alcohol formation on Co-based catalysts follows a CO insertion mechanism, Co⁰ is the active species for the C chain growth, and Co₂C species can activate CO without rupture and insert CO into C chain intermediates, which leads to alcohol synthesis. Our results indicate that alcohol chain termination was favored when too many surface Co₂C species were exposed on the catalyst surface. Of course, not only the role of Co₂C but also the reasons for alcohol chain propagation need further study.

4. Conclusions

SiO₂- and Al₂O₃-supported Co₂C catalysts for F-T synthesis were successfully prepared by carburizing the corresponding

Graphical Abstract

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Fischer-Tropsch synthesis: Characterizing and reaction testing of $\text{Co}_2\text{C}/\text{SiO}_2$ and $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ catalysts

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SiO_2 - and Al_2O_3 -supported Co_2C catalysts for alcohol synthesis were prepared by carburizing the corresponding supported Co precursors with CO. All of the as-prepared supported Co_2C catalysts exhibited activity and selectivity for alcohols.

supported Co precursors with CO, although more than 100 h carburization time was necessary. All of the as-prepared supported Co_2C catalysts exhibited activity and selectivity for alcohol formation. It is considered that surface metallic Co originating from the decomposition of surface Co_2C under reaction conditions contributed to the catalyst activity, surface or sub-surface Co_2C species were responsible for the formation of alcohols, and bulk Co_2C species that interacted with the supports were inert during the F-T reaction.

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费托合成： SiO_2 和 Al_2O_3 负载的 Co_2C 催化剂的表征和评价

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摘要: 采用CO碳化SiO₂和Al₂O₃负载的Co(NO₃)₂的方法制备了SiO₂和Al₂O₃负载的Co₂C催化剂, 采用N₂物理吸附、X射线衍射和H₂-程序升温还原技术对催化剂进行了表征, 并用于催化费托合成反应中. 结果显示, 需要较长碳化时间才可合成负载的Co₂C催化剂; 所制催化剂表现出CO加氢生成高碳醇的催化性能, 其原因可能在于催化剂表面存在的金属Co物种使CO解离, 表面Co₂C物种有利于CO插入, 从而导致醇的生成, 但体相Co₂C则不具有催化活性.

关键词: 负载型碳化钴; 费托合成; 醇; 表面活性位

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1. 前言

由于石油资源的减少和自然环境的恶化, 将煤、天然气和生物质经合成气催化转化为洁净燃料的费托合成引起了广泛关注. 许多金属, 比如Fe, Co, Ni和Ru都可以用于费托合成反应, 其中Fe和Co是最常用的^[1–4]. 有趣的是, 负载型Fe和Co基催化剂在反应过程中可以形成Fe和Co的碳化物. Fe的碳化物很容易形成, 这是由于C在Fe晶格内的扩散活化能(43.9–69.0 kJ/mol)显著低于费托反应活化能(89.1 ± 3.8 kJ/mol), 因而不利于区别Fe和Fe的碳化物在费托反应中的作用^[3,4]. 相比之下, 人们普遍认为金属Co是费托合成Co基催化剂的活性中心, 而Co₂C的形成会导致催化剂失活^[1,5–8]. 然而, Volkova等^[9]报道了Cu-Co催化剂上醇的生成可能与Co₂C的出现有关, 其且遵循CO插入机理. Liu等^[10]将LaFeO₃负载的Co-Cu催化剂上CO加氢生成醇的性能归因于纳米形态的Co₂C物种. 我们报道了活性炭负载的Co基催化剂在反应过程中可以原位生成Co₂C物种, 可导致C₁–C₈线性混合醇的生成^[11–13]. 随后, 我们发现线性混合醇可以在非负载的Co₂C催化剂上生成, 而且催化剂的活性和选择性与表面Co和Co₂C物种有关^[14,15].

密度泛函理论计算结果给出了Co₂C结构与其催化性能的关系^[16–18], 但是对Co₂C的研究仍然不足, 特别是如下问题仍未解决: 为什么负载型Co基催化剂上出现的Co₂C物种会导致催化剂失活. 另一方面, 据我们所知, 目前没有关于负载型Co₂C作为费托合成催化剂的报道. 本文报道了SiO₂和Al₂O₃负载的Co₂C催化剂的合成及其催化费托反应结果, 并讨论了Co₂C物种在负载型Co基催化剂上的作用.

2. 实验部分

2.1. 样品制备

本文选用两种SiO₂作为载体(青岛海洋化工有限公司), 分别记为SiO₂(1)和SiO₂(2), 一种Al₂O₃作为载体(青岛美高化工有限公司). 首先将Co(NO₃)₂·6H₂O浸渍到载

体上, 使Co含量为15%, 然后将样品在100 °C干燥6 h, 在350 °C于Ar气氛中焙烧4 h. 之后, 将样品在250 °C于氢气流(60 mL/min)中还原24 h, 然后采用CO (0.1 MPa, 60 mL/min)于220 °C碳化. SiO₂(1), SiO₂(2)和Al₂O₃负载的样品分别碳化140, 145和120 h, 记为Co₂C/SiO₂(1), Co₂C/SiO₂(2)和Co₂C/Al₂O₃. 为了比较, 制备了SiO₂(1)负载的、碳化72 h的样品, 记为Co₂C*/SiO₂(1).

2.2. 催化剂表征

样品的比表面积、平均孔径和孔体积在Micromeritics Autosorb-1型物理吸附仪上进行. N₂吸附前, 样品先在200 °C脱气处理2 h. 样品比表面积由N₂吸附等温线结合BET方程求得, 孔体积和平均孔径由BJH模型计算而得.

采用PANalytical公司的X'Pert PRO型X射线粉末衍射(XRD)仪测定样品的晶相组成. 选用Cu K_{α1}靶, 管流40 mA, 管压40 kV, 扫描范围30°–60°, 扫描速度为10°/min. 测试前, 样品经粉碎研磨后压入玻璃片内.

H₂程序升温还原(H₂-TPR)实验在Altamira公司的AMI-300型化学吸附仪器上进行. 样品装填量为150 mg, 以10% H₂/Ar为还原气, 流量为50 mL/min, 以10 °C/min的升温速率升温至900 °C, 同时用瑞士Oministar Pfeiffer Vacuum型质谱仪跟踪测定程序升温过程中的气体产物.

2.3. 费托合成反应

费托反应在内径为9 mm的不锈钢固定床反应器(长度为450 mm)中进行. 催化剂装填量为4 mL, 并采用体积比为1:1的石英砂稀释. 将催化剂置于反应器内后, 引入合成气(H₂/CO = 1, GHSV = 500 h⁻¹), 将压力设为3.0 MPa, 然后以0.3 °C/min的速率升温至220 °C. 反应器温度达到设定值时开始计时. 经24 h稳定后, 液相产物每24 h放样一次. 液相产物经水浴冷阱收集, 静置至油相和水相分层后, 用分液漏斗分离, 采用HP-6890型气相色谱仪(5% PH ME柱和FID检测器)离线分析, 以仲丁醇为内标物, 采用内标法分析水相中含氧化合物含量; 尾气采用HP-6890 GC型气相色谱仪(Parapack-Q柱和TCD检测器)在线分析.

3. 结果与讨论

3.1. 费托反应结果

表1为所制负载型 Co_2C 催化剂上费托反应结果. 可以看到, 所有催化剂上均生成烃类、 CO_2 和 $\text{C}_1\text{--C}_{18}$ 线性混合醇, 与我们以前的结果^[11,12]类似. $\text{Co}_2\text{C}/\text{SiO}_2(1)$ 催化剂具有最高的CO转化率(43.9%)和醇的选择性(65.6%); $\text{Co}_2\text{C}/\text{SiO}_2(2)$ 催化剂的CO转化率只有8.8%, 但醇的选择性达到了61.0%; $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ 催化剂具有一定的CO转化率, 但醇选择性仅为8.2%.

我们发现, 所得的醇类产物都是线性的, 且遵循ASF分布, 与我们之前的研究结果^[11,12]一致. 还可以看到, $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ 催化剂上 C_{6+} 醇占总醇的19.7%; 而对于 $\text{Co}_2\text{C}/\text{SiO}_2(1)$ 和 $\text{Co}_2\text{C}/\text{SiO}_2(2)$ 催化剂, C_{6+} 醇分别只占4.2%和2.0%, 且最大碳数的醇分别为正辛醇和正庚醇; 而对于 $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ 催化剂, 最大碳数的醇是正十八醇.

3.2. N_2 物理吸附表征结果

载体及各催化剂的比表面积、平均孔径和孔体积结果列于表2中. 负载的 Co_2C 催化剂的比表面积、平均孔径和孔体积明显小于相应的载体, 这可能是由于载体的孔堵塞所导致的^[19,20].

3.3. XRD结果

图1为新鲜 $\text{Co}_2\text{C}/\text{SiO}_2(1)$, $\text{Co}_2\text{C}/\text{SiO}_2(2)$, $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ 和 $\text{Co}_2\text{C}^*/\text{SiO}_2(1)$ 样品的XRD谱. 所有样品均在 $2\theta = 37.0^\circ$ 和 42.5° 出现对应于 Co_2C 的(110)和(111)面的衍射峰, 同样, $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ 样品在 $2\theta = 45.7^\circ$ 出现对应于 Co_2C 的(021)面(PDF 01-072-1369)的衍射峰. 另外, $\text{Co}_2\text{C}/\text{SiO}_2(1)$, $\text{Co}_2\text{C}/\text{SiO}_2(2)$ 和 $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ 样品均未出现Co的特征峰. 而在 $\text{Co}_2\text{C}^*/\text{SiO}_2(1)$ 样品上, 在 $2\theta = 47.5^\circ$ 出现对应hcp Co的(101)面(PDF 00-001-1278)的衍射峰. 研究发现, 需碳化500 h以上才可得到非负载的 Co_2C ^[21]. 本文则可以通过碳化负载金属 $\text{Co}(\text{NO}_3)_2$ 的方式得到负载型 Co_2C , 虽然碳化时间大幅减少, 但仍需足够的时间才可保证碳化完全.

图2为反应后的 $\text{Co}_2\text{C}/\text{SiO}_2(1)$, $\text{Co}_2\text{C}/\text{SiO}_2(2)$ 和 $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ 催化剂的XRD谱. 由图可见, $\text{Co}_2\text{C}/\text{SiO}_2(1)$ 和 $\text{Co}_2\text{C}/\text{SiO}_2(2)$ 催化剂上只出现 Co_2C 的特征衍射峰; 而在 $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ 催化剂上可以观察到位于 37.0° 和 45.7° 的 Co_2C 特征峰, 但是位于 42.5° 的 Co_2C 特征峰几乎消失, 同时在 44.3° 和 45.7° 出现了新的衍射峰, 分别对应fcc Co的(111)面(PDF 00-00-1259)和hcp Co的(101)面(PDF 00-001-1278). 研究表明^[22], Co_2C 很容易与 H_2 反应转化

为金属Co, 同时生成 CH_4 (反应温度可低至 150°C). 我们也发现^[15], 在真实费托反应条件下, Co_2C 会与 H_2 作用而部分分解成金属Co, 同时由于CO分压的作用, 一部分 Co_2C 又得以稳定存在. 因此, 反应后 $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ 催化剂上出现的金属Co峰源于 Co_2C 的分解. 这明显不同于 SiO_2 负载的 Co_2C 性质, 说明载体可以影响 Co_2C 在反应条件下的转变.

3.4. H_2 -TPR-MS结果

如前所述, Co_2C 可与 H_2 反应而转化为金属Co和 CH_4 . 因此, 我们以 Co_2C 在 H_2 -TPR过程中生成的 CH_4 为探针, 考察了 Co_2C 物种与载体的接触状态. 图3给出了各新鲜催化剂在 H_2 -TPR过程中生成 CH_4 的信号图. 可见, $\text{Co}_2\text{C}/\text{SiO}_2(1)$ 在 343 , 407 和 556°C 出现了3个峰; $\text{Co}_2\text{C}/\text{SiO}_2(2)$ 在 343 和 814°C 出现了2个峰; $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ 在 442 和 662°C 也出现了2个峰. 我们认为, $\text{Co}_2\text{C}/\text{SiO}_2(1)$ 和 $\text{Co}_2\text{C}/\text{SiO}_2(2)$ 在 343°C 出现的 CH_4 峰是由于样品表面 Co_2C 物种加氢而形成的; $\text{Co}_2\text{C}/\text{SiO}_2(2)$ 在 407°C 和 $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ 在 442°C 出现的 CH_4 峰归因于样品次表面 Co_2C 物种的加氢, 而各催化剂上高于 509°C 出现的 CH_4 峰是由于样品体相 Co_2C 物种(与载体接触)加氢形成的. 综合 H_2 -TPR和XRD结果可认为, 负载型 Co_2C 催化剂的合成是成功的, 不仅催化剂体相由 Co_2C 构成, 而且表面也存在 Co_2C 物种.

图4为反应后各催化剂的 H_2 -TPR谱. 可见, $\text{Co}_2\text{C}/\text{SiO}_2(1)$ 和 $\text{Co}_2\text{C}/\text{SiO}_2(2)$ 分别在 343 和 423°C 出现 CH_4 峰, 可能源于催化剂表面或次表面 Co_2C 物种的加氢. 然而 $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ 催化剂上没有明显地观察到此类峰的出现. 这意味着 SiO_2 负载的催化剂比 Al_2O_3 负载的催化剂在反应中存在着更多的表面或次表面 Co_2C 物种. 另外, 所有反应后的催化剂均出现体相 Co_2C 物种加氢而形成的甲烷峰, 但是与反应前的相比, 峰温存在明显差别. 这意味着催化剂的体相 Co_2C 结构可能在反应过程中发生重构. 将 H_2 -TPR结果与催化剂性能相关联, 可以看出, 醇的选择性与表面 Co_2C 物种紧密相关. 一方面, 在反应后 $\text{Co}_2\text{C}/\text{SiO}_2(1)$ 和 $\text{Co}_2\text{C}/\text{SiO}_2(2)$ 催化剂上存在着大量的 Co_2C 物种, 从而导致了高的醇的选择性, 而 $\text{Co}_2\text{C}/\text{Al}_2\text{O}_3$ 催化剂上几乎没有表面 Co_2C 物种, 因而醇的选择性非常低; 另一方面, $\text{Co}_2\text{C}/\text{SiO}_2(1)$ 和 $\text{Co}_2\text{C}/\text{SiO}_2(2)$ 催化剂上 CH_4 形成峰的面积几乎相同, 说明这两种催化剂的表面 Co_2C 物种数量几乎相等, 因而醇的选择性相近. 众所周知, Co基催化剂上 Co^0 是催化活性中心. 我们之前报道了非负载的 Co_2C 催化剂的活性源于费托反应中 Co_2C 部

分分解而形成的金属Co相^[15]。比较图3和图4可以发现, 对于Co₂C/SiO₂(1)催化剂, 343 °C出现的CH₄峰面积显著减小, 而407 °C处的峰几乎消失; 对于Co₂C/SiO₂(2)和Co₂C/Al₂O₃催化剂, 由表面Co₂C加氢形成的CH₄峰没有显著的变化。这可能说明反应中Co₂C/SiO₂(1)催化剂上Co⁰物种较多, 从而导致高的催化活性, 而Co₂C/SiO₂(2)和Co₂C/Al₂O₃催化剂上Co⁰的数量少, 因而催化剂活性低。我们仅定性地分析了催化剂活性与Co⁰数量的关系, 定量研究仍需大量的工作。我们也注意到, 对于Co₂C/SiO₂(2)和Co₂C/Al₂O₃催化剂, 与载体接触的体相Co₂C的存在并未导致催化剂有高的活性, 因此可推断体相Co₂C是惰性的。另外, 由表1可见, Co₂C/SiO₂(1)和Co₂C/SiO₂(2)催化剂上长链醇(即C₆₊醇)的形成被抑制, 这可能是由于这两个表面暴露了过多的Co₂C活性位。

根据文献[9,11]报道, Co基催化剂上醇的生成可能遵循CO插入机理, 并且Co⁰是碳链增长的中心, 而Co₂C是非解离吸附CO使其插入到碳链中间体中生成醇的中心。我们的结果显示, 过多的表面Co₂C物种可以起到终止醇类碳链增长的作用。当然, 不仅Co₂C的催化作用, 而且影响醇的碳链增长因素均值得深入考察。

4. 结论

采用CO碳化SiO₂和Al₂O₃负载Co(NO₃)₂的方法, 成功制备了用于费托合成的相应负载型Co₂C催化剂, 但是制备过程需要100 h以上。所制催化剂显示出了催化CO加氢生成醇的能力。Co₂C部分分解而形成的表面金属Co物种使催化剂具有活性, 而表面Co₂C物种是醇的生成中心, 但与载体接触的体相Co₂C没有催化活性。