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Article

One-step production of C₁–C₁₈ alcohols via Fischer-Tropsch reaction over activated carbon-supported cobalt catalysts: Promotional effect of modification by SiO₂

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ABSTRACT

The promotional effect of SiO₂ on the catalytic synthesis of mixed C₁–C₁₈ alcohols from syngas using the Fischer-Tropsch reaction over activated carbon-supported cobalt catalysts was investigated. X-ray diffraction, H₂ temperature-programmed reduction, pulsed CO chemisorption and N₂ physisorption techniques were all employed to assess the catalyst. Although the addition of SiO₂ decreased the reducibility of the Co component, Co dispersion was significantly increased and its aggregation during reaction was inhibited, resulting in greatly enhanced reaction activity. Appropriate amounts of SiO₂ also promoted the formation of Co₂C, leading to an increased selectivity for C₁–C₁₈ alcohols. More importantly, the addition of SiO₂ favored the formation of higher molecular mass alcohols (C₆–C₁₈) by suppressing Co reduction, thus producing an abundance of Co(II) species capable of facilitating CO insertion.

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1. Introduction

To reduce the demand for declining petroleum reserves, the selective conversion of syngas (CO + H₂) derived from coal, natural gas or biomass feed-stocks into value-added products is currently of significant importance [1,2]. One promising route involves the catalytic conversion of syngas to hydrocarbons and oxygenates, normally referred to as Fischer-Tropsch (FT) synthesis [3]. Supported cobalt catalysts are favored in this reaction because of their high activity, high selectivity for long-chain hydrocarbons and low water gas shifts [1,4]. When these catalysts are applied to the FT synthesis of hydrocarbons, the cobalt metal sites are thought to be the sole active sites [5]. However, the production of higher molecular mass alcohols via FT synthesis typically requires synergy between proximate

catalytic sites having different functionalities and acting as locations for both the dissociation and non-dissociative insertion of CO. As an example, bimetallic catalysts such as CuCo, CuFe and RuMo have been proposed as materials capable of providing the necessary synergistic interactions [6–8].

In a previous study, we demonstrated that activated carbon (AC)-supported cobalt catalysts are able to produce linear C₁–C₁₈ alcohols from syngas via the FT reaction because of the synergy between active Co₂C sites formed *in situ* during the reaction and active cobalt sites [9–11]. More importantly, we found that the incorporation of Al₂O₃ as a promoter improves the C₆–C₁₈ fraction in the alcohols because of an Al₂O₃-induced effect on the ratio of adsorbed H₂ and CO [12]. The direct synthesis of longer-chain (>C₆) linear alcohols makes this catalytic process of particular interest, owing to the usefulness of these

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compounds as reagents in the syntheses of plasticizers, detergents and lubricants.

SiO₂ is one of the most commonly employed supports or binders in FT synthesis catalysts. For instance, the incorporation of SiO₂ into Fe-based catalysts helps to hinder the growth of iron particles due to agglomeration, while the strong Fe-SiO₂ interactions in the catalysts effectively stabilize the active phases [13]. The addition of SiO₂ to Al₂O₃-supported cobalt catalysts has also been shown to significantly improve the extent of reduction of supported cobalt catalysts, resulting in enhanced catalytic activity for FT synthesis [14].

The present study attempted to improve the FT reaction activity and the fraction of C₆–C₁₈ alcohols in the total alcohols by modifying AC-supported cobalt (Co/AC) catalysts with SiO₂. To this end, a series of Co/AC catalysts having different SiO₂ contents were prepared by an impregnation method. These catalysts were subsequently characterized by N₂ adsorption, powder X-ray diffraction (XRD), H₂ temperature-programmed reduction (H₂-TPR) and pulsed CO chemisorption. The performance of the various catalysts during FT synthesis was also assessed using a fixed-bed reactor, and the performance data were correlated with the characterization results.

2. Experimental

2.1. Catalyst preparation

The AC employed in this study was obtained from the Tangshan Union Activated Carbon Co., Ltd. and was made from coconut shells. The AC was washed first with a HCl solution (10 wt%) and then several times with deionized water to remove impurities, and was then crushed to a particle size of 80 to 100 mesh prior to use. The Co/AC catalyst was prepared by the incipient wetness impregnation of the AC with an aqueous solution of cobalt nitrate (Sinopharm Chemical Reagent Co., Ltd.). The resulting wet samples were dried at 323 K for 6 h in air and then calcined at 623 K for 4 h under pure Ar. The SiO₂-promoted catalysts were prepared by impregnating the AC with both an aqueous solution of cobalt nitrate and an ethanol solution of tetraethoxysilane (TEOS, Si(OC₂H₅)₄). The resulting material was dried and calcined under the same conditions described above. The un-promoted and SiO₂-promoted catalysts are denoted herein as 15Co/AC and 15Co-*x*SiO₂/AC, respectively, where *x* indicates the mass percentage of SiO₂ relative to the initial mass of the support material in the dried catalysts (*x* = 0.2, 2.1, 4.2 and 6.3). The cobalt loading was 15 wt% for all catalysts.

2.2. Evaluation of the FT reaction

The FT reaction was performed in a fixed-bed stainless micro-reactor (9 mm i.d. and 450 mm length). In each trial, a 4-mL portion of the catalyst was diluted with quartz sand at a 1:1 volume ratio in the reactor. Prior to the reaction, the catalyst was reduced *in situ* at 703 K under a H₂ flow at atmospheric pressure for 4 h. The catalyst was subsequently cooled to 373 K, at which point the gas flow was switched to syngas (H₂/CO =

2) at 3.0 MPa and the temperature was increased at a rate of 0.3 K/min to 493 K. The reaction effluent was passed through a condenser to collect the liquid products. The point in time at which the reactor reached the designated reaction temperature was taken as the starting time. After 24 h stabilization, the liquid organic products and the aqueous products were collected for a further 24 h and analyzed off-line using an HP-6890 GC with a 5% phenyl-methyl capillary column and an FID detector. The outlet gas was analyzed on-line using an HP-6890 GC with a Porapack-Q column and a TCD detector.

2.3. Catalyst characterization

The textural properties of the activated carbon and catalysts following calcination were determined using N₂ physisorption at 77 K, employing a Quantachrome Instruments Autosorb-IQ unit. Each sample (200 mg) was degassed under vacuum at 523 K for 2 h prior to the measurement. The pore size distribution, average pore diameter and pore volume were determined by the BJH method and the specific surface area was estimated by the BET method.

The crystalline phases of catalysts both after reduction and reaction were examined by XRD with Cu K α 1 radiation, using a PANalytical X'Pert PRO diffractometer at 40 kV and 40 mA. The patterns were recorded from 20° to 60° at a scanning rate of 10°/min. Prior to these measurements, the catalysts were ground to a fine powder and placed inside a specimen dish.

H₂-TPR was carried out using an Altamira Instruments AMI-300 unit. Each sample (50 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 ambient to 1123 K at a heating rate of 10 K/min. The hydrogen consumption was recorded using an on-line mass spectrometer (MS, Oministar, Pfeiffer Vacuum).

Pulsed CO chemisorption data were obtained with an Altamira Instruments AMI-300 U. A 50-mg sample of each catalyst precursor was used for each test. Prior to analysis, each precursor was pre-reduced *in situ* under 10% H₂/Ar (99.999%) at 703 K for 4 h, then purged with Ar (99.999%) at the same temperature for 15 min to remove adsorbed species from its surface, and subsequently cooled to 373 K. Desorbed CO was detected by TCD. The precursors were repeatedly dosed with 526- μ L portions of 10% CO/He until the TCD signal reached a constant value.

3. Results and discussion

3.1. Performance during the FT reaction

Table 1 shows the results obtained from the FT reaction over 15Co-*x*SiO₂/AC catalysts, from which it is evident that the CO conversion monotonically increased from 30.2% to 76.6% as the SiO₂ doping increased from 0 to 6.3%. The CH₄ selectivity decreased from 24.0% to 13.7% as the SiO₂ content was initially increased from 0 to 0.2% and was ultimately reduced to 10.7% at a SiO₂ content of 6.3%. The selectivity for C₂–C₄ hydrocarbons decreased from 22.5% to 2.3%, while that for C₅+

Table 1FT reaction results employing 15Co/AC catalysts with different SiO₂ loadings.

Catalyst	CO conversion (C%)	Selectivity (C%)					Alcohol distribution (C%)		
		CH ₄	C ₂ –C ₄ ^a	CO ₂	C ₅₊ ^b	Total alcohol	C ₁	C ₂ –C ₅	C ₆ –C ₁₈
15Co/AC	30.2	24.0	22.5	2.1	32.8	18.5	6.5	54.2	39.3
15Co-0.2SiO ₂ /AC	38.0	13.7	8.0	1.0	49.3	28.0	4.3	42.9	52.8
15Co-2.1SiO ₂ /AC	52.7	12.3	5.5	0.9	55.4	25.9	4.2	37.3	58.5
15Co-4.2SiO ₂ /AC	67.2	12.8	3.7	1.1	62.8	19.6	4.2	33.3	62.5
15Co-6.3SiO ₂ /AC	76.6	10.7	2.3	1.2	65.9	19.9	6.3	39.1	54.6

Reaction conditions: $p = 3.0$ MPa, GHSV = 500 h⁻¹, $t = 493$ K.^a Hydrocarbons with carbon numbers from 2 to 4.^b Hydrocarbons with carbon numbers more than 4.

hydrocarbons increased from 32.8% to 65.9% as the SiO₂ content was increased from 0 to 6.3%. The total alcohol selectivity increased to a maximum value of 28.0% at a 0.2% SiO₂ loading and then dropped to a minimum value of 19.6% at a 4.2% SiO₂ loading. With respect to alcohol distribution, it can be seen that the methanol proportion was consistently below 6.5% while, surprisingly, the proportion of linear C₆–C₁₈ alcohols was increased from 39.3% to 62.5% by increasing the SiO₂ content from 0 to 4.2%, and was subsequently reduced when an excess of SiO₂ was added.

The Anderson-Schulz-Flory (ASF) product distributions for the formation of alcohols, olefins and paraffins over representative 15Co-0.2SiO₂/AC catalyst are presented in Fig. 1 (showing data for alcohols and olefins up to C₁₈ and paraffins up to C₂₄). There are slight deviations in the case of paraffins with fewer than seven carbons (such as methane and butane), olefins with fewer than five carbons (such as ethylene and butylene) and alcohols with more than 16 carbons that we believe may be attributed to an acceptable level of experimental error. In general, though, the product distributions all generated linear ASF plots. Table 2 lists the chain-growth probability factors (α) for paraffin, olefin and alcohol products as a function of SiO₂ content. The α values for each type of product are seen to pass through a maximum value at approximately 4.2% SiO₂, again demonstrating that higher molecular mass alcohols and hydrocarbons were produced by SiO₂-modified Co/AC catalysts. It is worth noting that the α value for the alcohols is slightly different from those obtained for the paraffins and olefins over the 15Co/AC. However, remarkably, this difference was mini-

mized when the SiO₂ promoter was added, possibly as a result of the promotional effect of the SiO₂. The very similar α values obtained for alcohols, paraffins and olefins over each catalyst suggest that these products were likely produced via sequential insertion of carbonaceous intermediates during growth of the carbon chain.

3.2. Textural properties of catalysts

The textural properties of the AC support and the AC-supported Co catalysts with or without SiO₂ addition are compared in Table 3, while the pore size distributions for the support and catalysts are shown in Fig. 2. It has been reported that although AC supports contain large quantities of micro-pores, the metal precursors tend to be present predominantly inside the wider pores [15]. Thus, the pore size distributions of the support and catalysts were only compared over the range of 10 to 50 nm. It can be seen that there were no significant differences in the average pore diameter and the pore size distribution between the support and the catalysts. However, the BET surface area and pore volume of the 15Co/AC catalyst were considerably smaller than those of the support, primarily resulting from the pore blockage that occurred when cobalt was loaded on the support [16,17]. The addition of SiO₂ evidently had little effect on the BET surface area and pore volume of the 15Co/AC cata-

Fig. 1. The ASF product distribution over the 15Co-0.2SiO₂/AC catalyst.**Table 2**Effect of the SiO₂ promoter on chain-growth probability factors for alcohols and hydrocarbons.

SiO ₂ loading (%)	α_{alcohols}	$\alpha_{\text{paraffins}}$	α_{olefins}
0	0.61	0.72	0.59
0.2	0.67	0.78	0.73
2.1	0.72	0.78	0.75
4.2	0.76	0.79	0.77
6.3	0.73	0.80	0.75

Table 3Textural properties of the AC support and 15Co/AC catalysts with different SiO₂ loadings.

Catalyst	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
AC	1001	0.55	2.2
15Co/AC	736	0.40	2.2
15Co-0.2SiO ₂ /AC	832	0.46	2.2
15Co-2.1SiO ₂ /AC	763	0.41	2.1
15Co-4.2SiO ₂ /AC	738	0.41	2.2
15Co-6.3SiO ₂ /AC	719	0.37	2.1

Fig. 2. Pore size (D) distributions calculated from nitrogen desorption isotherms for the AC support and various catalysts.

lyst and therefore the improved performance of the modified catalysts may be attributed to the chemical effects of the SiO_2 .

3.3. TPR analysis

The reduction behavior of the $15\text{Co}-x\text{SiO}_2/\text{AC}$ catalysts was assessed by H_2 -TPR, and the corresponding reduction profiles are presented in Fig. 3. For each catalyst, three H_2 consumption peaks were generated within the temperature ranges from 480 to 571 K, from 571 to 684 K, and above 684 K. The broad peak above 684 K could be attributed to hydrogenation of surface oxygen-containing groups on the AC support in the presence of Co metal [13,18], while the other two reduction peaks could be assigned to the consecutive reduction of Co_3O_4 through CoO to Co^0 . The area of the CoO to Co reduction peak was reduced as the SiO_2 loading was increased from 0 to 0.2%, possibly due to the formation of Co-Si species that could not be reduced at the temperatures applied during TPR. As the SiO_2 content was further increased to 4.2%, the area of the CoO to Co reduction peak continuously decreased, probably indicating that more irreducible Si-O species were formed with increasing SiO_2 content. When an excess of SiO_2 was added, the area of the CoO to Co reduction peak was slightly increased but was still less than that of the CoO to Co reduction peak for the un-promoted catalyst, presumably because this level of SiO_2 doping was insufficient to ensure the formation of a large quantity of irreducible Si-O species. The position of the CoO to Co reduction peak shifted to a lower temperature when a small amount of SiO_2 was added (0.2%), but shifted back to a higher temperature when at 2.1% of SiO_2 , and then moved gradually to much higher temperatures as the SiO_2 loading was further increased to 6.3%. These results demonstrated that SiO_2 might have been acting to increase the interaction between Co and the AC support only when added at high concentrations. It is believed that the Si-O species assumed to be present might not contribute to the interaction between Co species and the support, since otherwise the CoO to Co reduction temperature would have increased when 0.2% of SiO_2 content was added. Previous studies [14] on the reduction behavior of Al_2O_3 -supported cobalt cata-

Fig. 3. TPR profiles of the $15\text{Co}-x\text{SiO}_2/\text{AC}$ catalysts. (1) $15\text{Co}/\text{AC}$; (2) $15\text{Co}-0.2\text{SiO}_2/\text{AC}$; (3) $15\text{Co}-2.1\text{SiO}_2/\text{AC}$; (4) $15\text{Co}-4.2\text{SiO}_2/\text{AC}$; (5) $15\text{Co}-6.3\text{SiO}_2/\text{AC}$.

lysts with SiO promoters concluded that the doping of SiO_2 promoted the reduction of these catalysts because the strong interactions between cobalt metal and the Al_2O_3 support were reduced by adding SiO_2 . In the present study, the interactions between cobalt metal and the AC support should have been weakened compared with the interactions in Al_2O_3 -supported cobalt catalysts. Therefore the obvious decrease in the area of the CoO to Co reduction peak when SiO_2 was added, as well as the increased reduction temperature at high SiO_2 levels compared with that of the $15\text{Co}/\text{AC}$ catalyst, allow us to conclude that the incorporation of SiO_2 inhibited the reduction of cobalt species, although a very low SiO_2 concentration decreased the CoO to Co reduction temperature.

3.4. CO chemisorption

CO chemisorption results for the $15\text{Co}-x\text{SiO}_2/\text{AC}$ catalysts are shown in Table 4. The amount of adsorbed CO increased slightly, from 71.2 to 75.4 $\mu\text{mol/g}$, when the SiO_2 content was increased from 0 to 0.2% and then continuously decreased as the SiO_2 content was further increased. These results suggest that the addition of SiO_2 to the $15\text{Co}/\text{AC}$ catalyst produced SiO_2 -covered surfaces and modified the surface morphology of the Co sites, resulting in changes in their CO adsorption capacity. The addition of small amounts of SiO_2 (0.2%) to the $15\text{Co}/\text{AC}$ catalyst increased CO uptake, indicating that the Co sites on the $15\text{Co}-0.2\text{SiO}_2/\text{AC}$ had increased surface irregulari-

Table 4

CO uptake and reducibility data for $15\text{Co}/\text{AC}$ catalysts with different SiO_2 loadings.

SiO_2 loading (%)	CO uptake ^a ($\mu\text{mol/g}$)	Co reduction degree ^b (%)
0	71.2	85.4
0.2	75.4	70.6
2.1	66.2	68.2
4.2	49.2	63.1
6.3	30.9	70.1

^aBased on CO chemisorptions.

^bBased on H_2 consumption in TPR using CuO as reference.

ties. These data suggest that high concentrations of SiO₂ provide an effective radius around the Co metal sites in terms of blocking CO adsorption, and consequently decrease the CO uptake.

3.5. XRD characterization

The phase compositions of catalysts with different SiO₂ loadings after reduction and reaction were investigated by XRD, with the results presented in Figs. 4 and 5, respectively. From Fig. 4 it is evident that, in all catalysts, CoO diffraction lines at 36.5° and 42.5° were present after reduction in addition to a line at 44.3° resulting from metallic cobalt. These data confirm that some CoO remained unreduced in all the catalysts in this work, in agreement with the TPR results. In addition, the intensity of the Co peak decreased when the SiO₂ loading was increased from 0 to 0.2%, and disappeared when the SiO₂ loading was further increased, demonstrating that the dispersion of Co was enhanced after SiO₂ was added to the 15Co/AC catalyst.

Fig. 5 shows that the used catalysts all exhibited obvious peaks resulting from metallic cobalt. In addition, peaks corresponding to cobalt carbide can be clearly observed for the 15Co-0.2SiO₂/AC and 15Co-2.1SiO₂/AC catalysts. However, no peaks corresponding to CoO were generated by any of the catalysts, likely indicating that unreduced Co species were highly dispersed during the reaction via migration into the micro-pore system of the activated carbon. A similar phenomenon was reported by Díaz *et al.* [19], who observed the migration of unreduced NiO species during reactions on AC-supported Ni-Ca catalysts. The intensity of the metallic Co peaks for all the spent catalysts was greater than those for the corresponding reduced catalysts. Thus the Co nano-particles apparently undergo aggregation during the FT reaction. However, the metallic Co peak intensity also decreased monotonically as the SiO₂ content was increased, demonstrating that larger amounts of SiO₂ were more likely to inhibit the aggregation of metallic Co species. The activity of the cobalt catalysts during the FT synthesis depends solely on the number of cobalt active sites, a characteristic that is determined by the Co particle size, loading

Fig. 4. XRD patterns of 15Co/AC catalysts with different SiO₂ loading after reduction.

Fig. 5. XRD patterns of 15Co/AC catalysts with different SiO₂ loadings after the FT reaction.

amount and extent of reduction [20]. In the present study, the Co loading was constant for all the catalysts. The reduction degree (see Table 4) determined from TPR characterization was considerably smaller in the case of the SiO₂-promoted catalysts compared with the 15Co/AC catalyst, indicating that the quantity of Co sites available for the FT reaction was decreased in the SiO₂-promoted catalysts. Although SiO₂ doping decreased the cobalt particle sizes in the reduced catalysts, as shown in Fig. 4, the cobalt particles will grow during the reaction. Since the cobalt particle size in the spent catalysts decreased monotonically as the SiO₂ content increased, we may speculate that there was a linear increase in the number of Co sites with increasing SiO₂ content in the spent catalysts. This hypothesis readily explains the steady increase observed in CO conversion with increasing SiO₂ loading. Moreover, based on this hypothesis, we can conclude that the CO conversion over AC-supported Co catalysts depends solely on the number of Co sites available during the reaction, irrespective of the extent of Co dispersion or the degree of reduction.

One feature of supported cobalt catalysts on activated carbon made from coconut or apricot shells during the FT reaction is that cobalt carbide is formed *in situ*, documented by XRD characterization during our studies [9,10,12]. However, in the present work, a cobalt carbide phase could not be clearly observed in the XRD patterns of the used 15Co/AC catalyst, and thus the present results are quite different from those of our previous studies. This discrepancy likely results from the pre-treatment of the activated carbon with a concentration of acid sufficient to inhibit Co₂C formation. By careful examination of the literature, we have identified many factors capable of affecting the formation of Co₂C on AC-supported Co catalysts, including the presence of promoters [9,10,12,21] and variations in Co particle sizes [22]. As an example, Lü *et al.* [23] reported that treatment of the AC with suitably concentrated nitric acid inhibits Co₂C formation on the AC-supported Co catalysts during the FT reaction, which agrees with our present observations. Additionally, we note that considerable amounts of alcohols could still be produced over the 15Co/AC catalyst, suggesting that highly dispersed cobalt carbide might still be

present on the catalyst surface, although not identifiable by XRD. Upon doping with 0.2% SiO₂, the cobalt carbide peak was clearly seen, in contrast to the lack of this peak in the XRD pattern of the 15Co/AC catalyst. The cobalt carbide peak intensity gradually decreased and almost disappeared as the SiO₂ content was further increased. This indicated that the addition of an optimal amount of SiO₂ promoted the formation of Co₂C, while an excessive amount inhibited Co₂C formation. Correlating the intensity of the cobalt carbide XRD peak with the alcohol selectivity, a qualitative relationship between the cobalt carbide content and the alcohol selectivity is readily identified. Increased Co₂C formation and increased alcohol selectivity could be simultaneously observed, while the opposite is also true. In future, a more thorough, quantitative analysis of this relationship will be carried out.

3.6. Effect of the SiO₂ promoter on the alcohol distribution over the 15Co/AC catalyst

Many reasons can be advanced to explain the shift in the hydrocarbon distribution of the FT reaction towards high molecular mass. As we noted in a previous report [12], this could result from a higher extent of re-adsorption of short α -olefins (followed by further chain growth) [24,25], Co particle size effects [26,27], or pore size effects of the support material [28], as well as an effect of the high intrinsic chain-growth probability of cobalt [29]. However, none of these reasons suitably explains the data for our AC-supported Co catalyst systems, including the present case. It is well recognized that with regard to alcohol formation over these AC-supported Co catalysts, the CO insertion mechanism is the most plausible reaction route [9,10,12,30]. It has also been reported that unreduced Co(II) species could act as non-dissociative CO adsorption sites, meaning CO insertion sites [31–33]. Based on the TPR results in Fig. 3 and the reduction degree data in Table 4, we can determine that the amount of unreduced Co(II) species increased

as the SiO₂ loading was increased until a maximum value was reached, and that this trend was also correlated with the variations in the C₆–C₁₈ alcohols generated. Thus, we speculate that the SiO₂ doping resulted in an abundance of Co(II) species capable of facilitating CO insertion, thereby favoring the formation of C₆–C₁₈ alcohols.

4. Conclusions

Doping AC-supported Co catalysts with a SiO₂ promoter significantly improved catalytic activity during the FT reaction by increasing the Co metal dispersion, but more importantly by inhibiting Co particle aggregation during the reaction, resulting in a large number of Co active sites. Addition of the optimal amount of SiO₂ promoted the formation of Co₂C, leading to improved selectivity for alcohols. SiO₂ addition favored the formation of higher molecular mass alcohols (C₆–C₁₈), likely because it suppressed the reduction of Co and thus generated an abundance of the Co(II) species that facilitate CO insertion.

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Graphical Abstract

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One-step production of C₁–C₁₈ alcohols via Fischer-Tropsch reaction over activated carbon-supported cobalt catalysts: Promotional effect of modification by SiO₂

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The addition of SiO₂ to activated carbon-supported cobalt catalysts favors the formation of higher molecular mass alcohols (C₆–C₁₈). SiO₂ suppresses the reduction of Co, resulting in an abundance of Co(II) species and thus facilitating CO insertion.

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活性炭负载的钴基催化剂催化费托合成反应一步合成C₁–C₁₈混合醇: 二氧化硅助剂的作用

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摘要: 采用费托合成反应以及X射线衍射、H₂程序升温还原、CO脉冲化学吸附和N₂物理吸附表征手段研究了SiO₂助剂对活性炭负载的钴基催化剂上生成C₁–C₁₈混合醇的影响。结果表明, SiO₂的添加抑制了钴物种的还原, 但提高了钴物种的分散度, 同时抑制了金属钴颗粒在反应过程中的团聚, 从而显著提高了催化剂的活性。适量SiO₂的添加促进了碳化钴的生成, 从而提高了总醇选择性。重要的是, 通过SiO₂抑制钴物种的还原, 导致大量二价钴物种的生成, 从而有助于CO插入到碳链中间体中而使高碳醇容易生成。

关键词: 钴催化剂; 高碳醇; 二氧化硅助剂; 费托合成; 碳化钴

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