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The formation of cobalt silicates on Co/SiO_2 under hydrothermal conditions

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A Co/SiO_2 catalyst recovered after both gas and liquid phase Fischer–Tropsch synthesis exhibited significant decreases in the amount of reducible metal. Hydrothermal conditions similar to those occurring during Fischer–Tropsch synthesis were simulated in order to study compound formation in this Co/SiO_2 catalyst. Hydrothermal treatment at 220°C led to a catalyst with lower reducibility, attributable to the formation of both reducible and nonreducible (<900°C) Co silicates. The formation of these compounds occurred only when metallic Co was present, was more pronounced in the presence of hydrogen, and was inhibited by air.

Keywords: cobalt; silica; silicate; Fischer–Tropsch; hydrothermal

1. Introduction

Nickel, iron, and cobalt are relatively inexpensive metals which have been used as catalysts for the Fischer–Tropsch (FT) synthesis [1]. Among these, Co has been found to be very attractive due to its high FT activity, selectivity for linear hydrocarbons, and low activity for the competing water–gas shift reaction [2]. Dispersing the metal on a high surface area support, such as silica or alumina, is a common practice in order to make better use of the catalytically active component.

Various studies have shown that, for Co catalysts, the reduced metal, rather than its oxides or carbides, is the most active phase in CO hydrogenation [1]. Besides sintering and fouling through carbon deposition, compound formation between the Co metal and the support could be a possible source of catalyst deactivation due to a reduction in the amount of metallic Co in a catalyst. We have noted significant deactivation of a silica-supported Co catalyst during FT synthesis, accompanied by decreased reducibility after reaction. Since water is a byproduct of the FT synthesis, it is conceivable that Co silicate formation may occur under FT synthesis conditions, contributing to catalyst deactivation. Therefore, the condi-

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tions which lead to silicate formation or favor it are of great interest and warrant detailed investigation.

Silicate formation is of concern because Co silicates can only be reduced at temperatures above 550°C [3–5], where rapid sintering of the metal would also occur. Nevertheless, it seems to occur quite commonly judging from reports suggesting silicate formation for silica-supported Co catalysts depending upon the preparation method [3] and the type of metal salt used for the catalyst preparation [6]. Other studies have shown that for silica-supported Co catalysts prepared by aqueous incipient wetness, the pH of the solution and the drying temperature may also have a profound effect on silicate formation [4,7,8].

In this paper we report the results of a study of the effect of water vapor upon the structure of a silica-supported Co catalyst under controlled, reproducible conditions, simulating the hydrothermal reaction conditions occurring in FT synthesis. By variation of the water concentration, exposure time, and gas phase composition, the conditions which maximize or minimize Co silicate formation were determined.

2. Experimental

2.1. PREPARATION OF THE Co/SiO_2 CATALYST

The Co/SiO_2 catalyst that was used for all experiments was prepared by aqueous incipient wetness impregnation of silica (Davison, Grade 952) (surface area: 219 m^2/g, pore volume: 0.51 cm^3/g, impurities determined by ICP: 150 ppm Mg, 570 ppm Na, 750 ppm Ca, 120 ppm Ti, 220 ppm Al, 96 ppm Fe, 83 ppm P, 160 ppm K, and 30 ppm S) with an aqueous cobalt nitrate (Alfa Chemicals) solution to yield 20 wt% Co on SiO_2. The catalyst was calcined in a furnace at 300°C under air for 2 h. Then it was reduced under flowing hydrogen (99.999%, Liquid Carbonic Specialty Gases) by increasing the temperature at a rate of 1°C/min from ambient temperature to 250°C and holding for 10 h. The reduced catalyst was cooled under helium and passivated with 2% O_2/He (LCSG) at ambient temperature for 1 h.

2.2. FT SYNTHESIS EXPOSURE

For FT synthesis the catalyst samples were re-reduced in situ under flowing H_2 at 250°C for 10 h. One Co/SiO_2 catalyst sample was recovered after FT synthesis in a laboratory scale fixed-bed reactor. It had been on-stream for 24 h of reaction at atmospheric pressure, 220°C, H_2/CO ratio of 2, and an average CO conversion of about 4%. It will be designated by Co(FB). The other sample, Co(SBC), had seen 40 h of reaction in a slurry bubble reactor at 31 atm, 220–240°C, a feed composition of $H_2 : CO : N_2$ of 2 : 1 : 5, and an average CO conversion around 14%. The reduction behavior of both catalyst samples was investigated using H_2 TPR.

2.3. HYDROTHERMAL CATALYST TREATMENT

A 20 mm glass reactor equipped with an internal thermocouple and a fritted disk was used for the catalyst pretreatment. All gas flows (He, H_2, air) were controlled using mass-flow meters. Deionized, degassed water was introduced into the system as water vapor by bubbling helium through a jacketed saturator equipped with a thermocouple and connected to a recirculating, heatable water bath. Gas lines carrying water vapor were heated to ensure that there was no condensation of water prior to contact with the catalyst bed. The extent of saturation of the inert with water was calibrated by determining the amount of water collected in a downstream trap kept at −30°C. Typically, 0.3 g of catalyst was re-reduced in situ under flowing hydrogen by raising the temperature at a rate of 2°C/min to 250°C and maintaining this temperature for 10 h prior to hydrothermal treatment. Then the catalyst was allowed to cool under flowing helium. All catalyst treatment was carried out at 220°C and atmospheric pressure for a period of 2–115 h. The treatment stream contained water vapor (0–10 mol%) in helium, helium and hydrogen, or helium and air. Such a concentration of water vapor is typical for low conversion FT synthesis. Samples treated by these procedures will be referred to as $Co(X/Y)Z$, where X denotes the gas phase concentration of water during treatment (in mol%), Y denotes the exposure time (in h), and Z indicates if an additional gas besides helium was used for the treatment (A = air, H = hydrogen). Samples which had not been reduced before water treatment will be indicated by $Co_3O_4(X/Y)$. A detailed compilation of the various treatment conditions is given in table 1.

2.4. TEMPERATURE PROGRAMMED REDUCTION

After pretreatment or FT synthesis all samples were analyzed using an Altamira Instruments AMI-1 automated TPR system. Catalysts that had not been treated in air were first calcined using ultra-pure oxygen at 300°C for 90 min and then cooled under argon flow for 1 h to remove any residual gas phase oxygen. Subsequently, the catalyst was ramped at 5°C/min to 900°C under 30 cm^3/min of 5% H_2/Ar. A thermal conductivity detector at the reactor outlet was used to measure hydrogen consumption as a function of temperature.

3. Results

The results of H_2 TPR of the catalyst samples investigated are compiled in table 1. The reduction behaviors of the catalyst samples recovered after FT synthesis are compared to the original catalyst in fig. 1. The untreated catalyst, Co/SiO_2, showed two distinct reduction peaks at 300 and 350°C, typical for the two-step reduction of Co_3O_4 to Co^0 [9]. The catalyst sample recovered after 40 h of

Table 1
Compilation of H_2O-treatment conditions and TPR results of Co/SiO_2

Catalyst	Reduction[a] in situ	Vapor-phase composition		Exposure time (h)	TPR[b] peak temp. (°C)	Reducibility up to 900°C (%)[c]
		H_2O	balance			
Co/SiO_2[d] after prep.	–	–	–	–	302, 355	90
Co(5/2)[d]	yes	5%	95% He	2	291, 357	74
Co(10/18)[d]	yes	10%	90% He	18	377	76
Co(10/92)[d]	yes	10%	90% He	92	363, 508, 604	45
Co_3O_4(5/2)[e]	no	5%	95% He	2	317, 362	83
Co_3O_4(5/115)[e]	no	5%	95% He	115	359, 611	88
Co(5/18)A[d]	yes	5%	47.5% air, 47.5% He	18	380, 525	76
Co(5/72)A[d]	yes	5%	47.5% air, 47.5% He	72	375, 539	83
Co(10/18)H[d]	yes	10%	10% H_2, 80% He	18	380	50
Co(FB)[d]	yes	1%[f]	CO/H_2	24	334	62
Co(SBC)[d]	yes	5%[f]	$CO/H_2/N_2$	40	339	71

[a] In situ reduction was carried out by heating the catalyst under flowing H_2 at 250°C for 10 h.

[b] Calcined in O_2 at 300°C for 2 h prior to TPR, except for Co_3O_4 samples which were not re-calcined before TPR.

[c] The accuracy of the determination of the reducibility was ±4%.

[d] After preparation, calcined at 300°C, reduced at 250°C, and passivated at ambient temperature with 2% O_2/He prior to these treatments.

[e] After preparation, only calcined at 300°C.

[f] Estimated based on average conversions of 4 and 14%, respectively, during the runs.

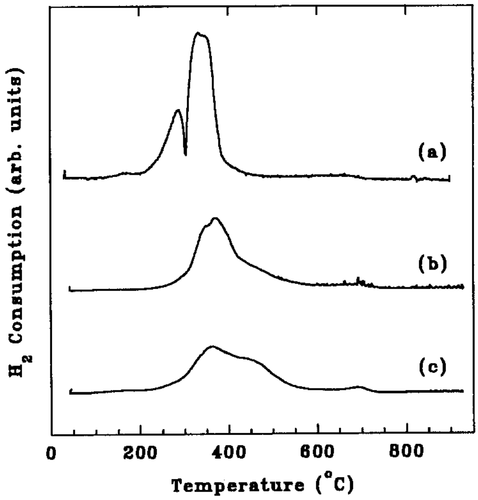

Fig. 1. Comparison of the TPR of Co/SiO_2 after preparation with samples recovered after FT reaction: (a) Co/SiO_2 (original), (b) Co(SBC), (c) Co(FB).

FT synthesis in a slurry-bubble column reactor, Co(SBC), exhibited a broad peak at 380°C with clearly discernible shoulders at ca. 350 and 500°C. Its total reducibility of 71% was notably lower than that for Co/SiO_2 prior to reaction (90%). The catalyst sample recovered after fixed-bed FT synthesis, Co(FB), showed an even greater decrease in reducibility to 62%. The intensity of the low temperature peak during TPR was smaller and that of the peak at 500°C was higher compared to those for the Co(SBC) sample.

Fig. 2 shows the effects on TPR behavior of increased water vapor exposure (time and concentration) for reduced Co/SiO_2. Co(5/2) exhibited only one clear reduction peak at around 370°C. Co(10/18) showed one broad peak of significantly lower intensity at 375°C stretching out to 550°C. Co(10/92) reduced in a broad, not well structured feature with two small peaks at 360 and 600°C. Generally, the reduction maxima of the in situ reduced and hydrothermally treated catalysts shifted to higher temperatures with increasing water vapor exposure. In parallel, the total reducibility of these catalysts decreased in the same manner from 90 to 45% (see table 1).

A similar result was obtained for Co(10/18)H, a reduced sample that had been exposed to water and H_2, simultaneously (see fig. 2e). The maximum in the rate of reduction was found at 380°C with a low temperature shoulder. No significant reduction of the catalyst was observed at higher temperatures. The total reducibility was found to be 50% after only 18 h of hydrothermal treatment in the presence of H_2.

Treating reduced samples in a gas flow also containing air (Co(5/18)A and Co(5/92)A) resulted in only a small decrease in reducibility compared with the untreated Co/SiO_2 catalyst (see table 1) with similar peak patterns (fig. 3), notably the emergence of a small peak around 530°C typical for Co silicate reduction.

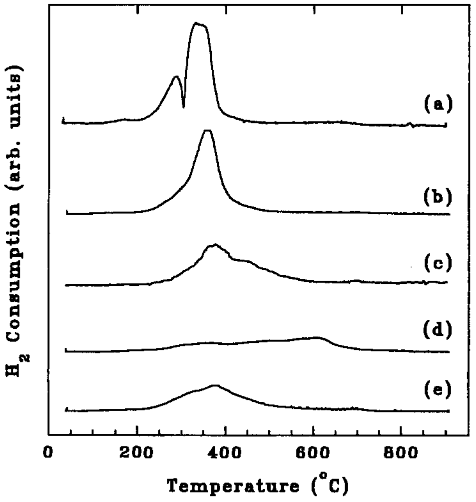

Fig. 2. TPR of the original and the hydrothermally treated, reduced Co/SiO_2: (a) Co/SiO_2 (original), (b) Co(5/2), (c) Co(10/18), (d) Co(10/92), (e) Co(10/18)H in the presence of H_2.

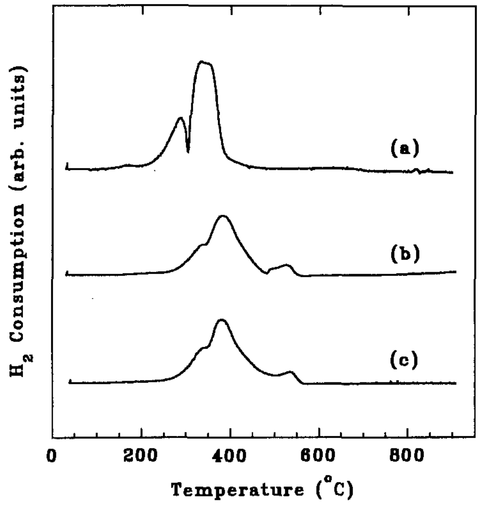

Fig. 3. Effect of hydrothermal treatment in the presence of air upon the TPR of reduced Co/SiO$_2$: (a) Co/SiO$_2$ (original), (b) Co(5/18)A, (c) Co(5/72)A.

In fig. 4, the effects of hydrothermal treatment of the calcined catalyst are depicted. The reduction pattern for Co$_3$O$_4$(5/2), a calcined sample which was not in situ reduced before water treatment, resembled that of the untreated catalyst Co/SiO$_2$ and the reducibility was only marginally less. Increasing the exposure time of the calcined catalyst to 115 h did not induce any significant changes.

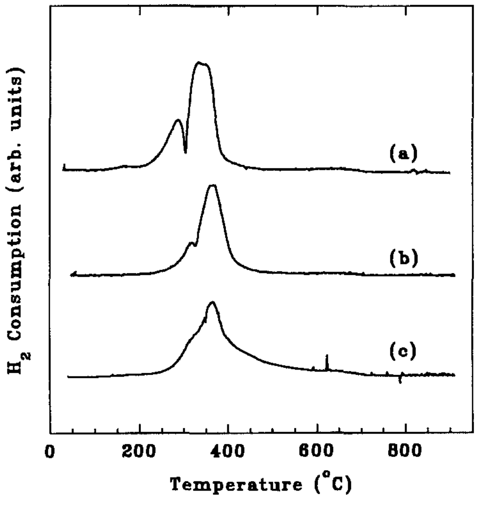

Fig. 4. Effect of hydrothermal treatment upon the TPR of calcined Co/SiO$_2$: (a) Co/SiO$_2$ (original), (b) Co$_3$O$_4$(5/2), (c) Co$_3$O$_4$(5/115).

4. Discussion

Analysis of the TPR behavior of metal catalysts provides useful information about the structure and nature of a particular catalyst. When cobalt is in the oxide form, Co_3O_4 or Co_2O_3, passing hydrogen over the catalyst at temperatures in the range between 250 and 450°C will usually reduce the cobalt to Co^0 [9]. Two steps are required for this process, first Co_3O_4 and Co_2O_3 are reduced to CoO; then this Co^{2+} oxide is reduced to cobalt metal [10,11]. The two reduction peaks observed for the original Co/SiO_2 after preparation can, thus, be attributed to the two step reduction of Co_3O_4 to CoO (ca. 300°C) and the subsequent reduction of CoO to Co^0 (ca. 360°C). The TPR results for the catalysts recovered after FT synthesis revealed the absence of a separated low temperature reduction peak at ca. 300°C. For bulk cobalt oxide, the separation of the two reduction steps into two discernible reduction peaks during H_2 TPR is not always possible, and it has been proposed that it is the interaction of cobalt oxide with the support that leads to a more pronounced splitting of these two reduction peaks [9]. Thus, the absence of the low temperature TPR peak could indicate a decreased interaction of cobalt oxide with the support and behavior of the supported oxide more like bulk oxide [9]. Along the same lines, for silica-supported vanadia, a low temperature TPR peak has been assigned to the reduction of surface species as compared to bulk vanadia using results of a variety of experimental techniques [12]. In any case, a decrease or absence of this low temperature TPR peak for Co/SiO_2 probably indicates less available surface Co and more bulk oxide behavior of the reducible Co oxide. Simultaneous with this decrease in the low temperature TPR peak after FT synthesis was a decrease in overall reducibility.

The most pronounced result found in this study was the clear decrease in the overall reducibility of Co/SiO_2 with increasing extent of hydrothermal treatment of the catalyst in its reduced state. This would indicate that some form of Co, most likely a compound with silica, was formed that was not reducible during TPR to 900°C. There is a substantial number of reports in which Co phases on Co/SiO_2 reducible only above 700°C have been identified as Co silicates or hydrosilicates [5,8,13]. Certain Co silicates were reported to be reducible under hydrogen flow but they can be easily distinguished from Co oxide since they reduce at temperatures between 500 and 800°C [3–5]. Based on the broadening of the reduction peaks and their shift to higher temperatures, we conclude that there was formation of "reducible" Co silicate. Note, however, that this Co silicate phase was not detectable by XRD, a result also observed previously [4], suggesting a highly dispersed silicate phase. Using XPS, Coulter and Sault [14] have recently demonstrated the formation of highly dispersed surface silicates on vacuum-dried silica-supported Co catalysts. Since bulk Co oxide reduces completely below 500°C [9] and Co silicates should be reducible under our conditions, the apparent loss of reducible cobalt indicates that part of the cobalt is in a "nonreducible" form (<900°C) either due to the formation of a nonreducible Co compound (bulk Co silicate) or due to the presence of diffusional barriers or both of these effects. Coulter and Sault [14] attributed the formation of an irreducible Co phase to the migration of Co^{2+} into the silica framework at elevated temperatures. It is also known that silica is mobile under hydrothermal conditions [15]. Thus, this could lead to the enclosure of part of the Co or Co silicate in a silica matrix, perhaps making it less accessible for hydrogen reduction during TPR. On the other hand, the surface silicate formed during hydrothermal treatment, perhaps only a few layers thick, may serve as a solid-state diffusional barrier during the TPR process, thus, making part of the Co irreducible under our experimental conditions. The broadening and shift of the TPR peaks to higher temperature would be consistent with such an explanation.

The presence of air during hydrothermal treatment had a substantial effect upon the catalyst, especially for long exposure times. Compared to the treatment only with water vapor in inert gas, treatment in air–water mixture resulted in less loss of reducibility of the catalyst. This degree of reducibility was not greatly affected by exposure time. Also, the reduction pattern was more characteristic of the untreated catalyst, as seen from the two low temperature peaks (fig. 3). The small peaks at ca. 540°C, however, indicate the formation of some small amounts of reducible Co silicate. As was the case for the overall reducibility, the intensity of these peaks did not vary with increasing exposure time. These observations suggest that the presence of air strongly inhibits the formation of both reducible and "non-reducible" silicates. Since air at 220°C re-oxidizes Co metal, it is reasonable to assume that the formation of silicates is linked to the presence of metallic Co rather than Co oxide. This supposition is supported by the reduction behavior of calcined Co/SiO_2 without in situ reduction prior to hydrothermal treatment ($Co_3O_4(5/2)$ and $Co_3O_4(5/115)$). Only minor changes in the reducibility and the reduction pattern of these catalysts were observed even after exposure times of 115 h.

Additional strong evidence for the role of Co metal in the formation of Co silicate comes from the reduction behavior of Co(10/18)H, which had been exposed to water and hydrogen simultaneously. A drastic reduction in the reducibility to 50% together with the usual broadening of the reduction peaks indicates significantly faster formation of silicates than with a comparably treated sample without hydrogen being present (Co(10/18)).

5. Conclusions

The formation of Co silicates in Co/SiO_2 has been found to occur during FT synthesis, in both the gaseous and the liquid phase. In order to explore the role of water vapor in causing this formation, the Co/SiO_2 catalyst was studied using conditions simulating those present during FT synthesis. It was found that, depending upon exposure time and gas phase concentration, a loss of the catalytically active metal phase and the formation of Co silicates occurred. The Co silicates formed were not completely reducible even during TPR to 900°C. The formation of silicates occurred rapidly for the in situ reduced catalyst and even more rapidly in the presence of hydrogen. The presence of air retarded this effect. On the contrary, when the cobalt was present as the oxide, hydrothermal treatment had little effect. It is concluded that the presence of Co metal is necessary for Co–silica reactions to occur forming both "reducible" and "nonreducible" (<900°C) Co silicate. The results point out a type of catalyst change which can occur during reaction.

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