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Cobalt aluminate formation in alumina-supported cobalt catalysts: effects of cobalt reduction state and water vapor

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This research was focused at getting deeper insight into the circumstances of "cobalt aluminate" formation in alumina-supported cobalt catalysts. It was desired to determine which state(s) of cobalt (i.e. reduced or oxidized) and what reaction conditions play a significant role in the aluminate formation at the relatively mild conditions used for reduction or Fischer–Tropsch synthesis. Reduction and hydrothermal pretreatments were applied to influence the formation of nonreducible Co-support compounds. Temperature-programmed reduction (TPR) was used to measure the amount of reducible cobalt compounds formed in 20 wt% Co/Al_2O_3 catalyst. The results reveal that the presence of partially reduced cobalt in a well-dispersed form is required for the formation of cobalt aluminate. The presence of water vapor promotes cobalt aluminate formation probably by hydrating the alumina and possibly by partially reoxidizing highly dispersed cobalt.

KEY WORDS: cobalt aluminate formation; hydrothermal treatment; Co/Al_2O_3; cobalt reducibility.

1. Introduction

Cobalt metal is an excellent catalyst for the Fischer–Tropsch synthesis (FTS) [1]. It has high selectivity for linear hydrocarbons and a low activity for the water gas shift reaction [2,3]. By dispersing cobalt particles on a support, an increase in the catalytically active metal surface can be achieved. However, compound formation between cobalt and the support may occur during pretreatment and/or reaction. Catalysts forming such compounds lose some part of the active cobalt metal phase resulting in lower activities in FTS.

Water vapor has been found to facilitate the formation of Co-support compounds [4–7]. This can constitute a serious problem since water is a by-product of both metal catalyst reduction and FTS. In previous studies in our laboratory [6,8], water vapor was suggested to affect the reducibility of $CoRu/\gamma\text{-}Al_2O_3$ in two possible ways: (1) by increasing the cobalt-support interaction and (2) by facilitating the migration of cobalt ions into the tetrahedral sites of $\gamma\text{-}Al_2O_3$ to form nonreducible cobalt aluminate. It is well known that in $CoAl_2O_4$, Co^{2+} ions sit in a spinel structure. The term "nonreducible" is applied because this cobalt aluminate can only be reduced above 800–900 °C [9]. It was shown by Arnoldy and Moulijn [10] that calcination at 600 °C or higher appears to cause Co^{2+} ions to diffuse gradually into the alumina structure resulting in an expansion of the alumina lattice and, thus, in the formation of a "diluted" cobalt aluminate compound.

In order to better understand the circumstances of "cobalt aluminate" formation at relatively mild reaction/reduction conditions, a study of alumina-supported cobalt catalysts was undertaken to determine the effect of cobalt state (i.e. oxidized versus reduced) and water vapor presence on Co-support compound formation.

2. Experimental

2.1. Catalyst preparation

The $Co/\gamma\text{-}Al_2O_3$ catalyst was prepared by incipient wetness impregnation of $\gamma\text{-}Al_2O_3$. The support precursor (Al_2O_3, Vista B) was calcined at 500 °C for 10 h before impregnation in order to put it into the form of $\gamma\text{-}Al_2O_3$ as evidence by XRD (BET surface area $= 209\,m^2/g$, average particle size ca. $60\,\mu m$, pore volume $= 0.5\,cc/g$, specific gravity $= 2.4$). A suitable amount of cobalt nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$) was dissolved in distilled water and impregnated into the support to incipient wetness in a single step to give 20 wt% cobalt in the reduced catalyst. The catalyst was then dried at 110 °C overnight and calcined in air at 300 °C for 2 h.

2.2. Catalyst pretreatments

2.2.1. Reduction

The calcined catalysts were reduced in flowing H_2 at 150 °C, 250 °C, or 350 °C for 10 h at high space velocity ($16\,000\,h^{-1}$).

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2.2.2. *Hydrothermal treatment*

Catalyst samples were treated under a stream of helium with 3% by volume of water vapor at 350 or 450 °C for 10 h (space velocity was 900 h^{-1}). In some cases, water vapor was introduced during the reduction step as well.

2.2.3. *Recalcination*

Prior to TPR measurement, the catalyst samples were reoxidized under a stream of dry air at 300 °C for 2 h.

2.3. *Catalyst nomenclature*

The nomenclature used in this study to designate different catalyst pretreatments is the following:

C: (re)calcination treatment
R(*T*): reduction at *T* °C
He*W*(*T*) or *RW*(*T*): hydrothermal treatment in 3% H_2O/He or in 3% H_2O/H_2 at *T* °C.

Thus, for example, Co_C was a catalyst sample after preparation and initial calcination. A catalyst sample that had been calcined, reduced at 450 °C, and then recalcined is denoted as Co_C_R(450){}_C.

2.4. *Temperature-programmed reduction (TPR)*

Reducibility of the catalyst samples was determined by TPR carried out in an Altamira AMI-1 system. The TPR measurements were conducted using approximately 50 mg of catalyst, a temperature ramp from 40 to 900 °C at 5 °C/min, and a gas flow of 5% H_2 in argon (25 cc/min). A thermal conductivity detector (TCD) was used to determine the amount of hydrogen consumed during temperature ramping. A water trap was placed between the catalyst and the TCD detector to remove water produced during reduction. Hydrogen consumption was calibrated using TPR of silver oxide under the same conditions. The reducibilities corresponding to the TPR curves were calculated from the area of the peaks assuming Co_3O_4 as a main component to be reduced.

3. Results and discussion

After calcination (Co_C), a catalyst sample was sent to Galbraith lab to determine the actual amount of cobalt. It was found to be 18.4 wt%. The XRD patterns of this catalyst have been given elsewhere [8].

3.1. *TPR peak identification*

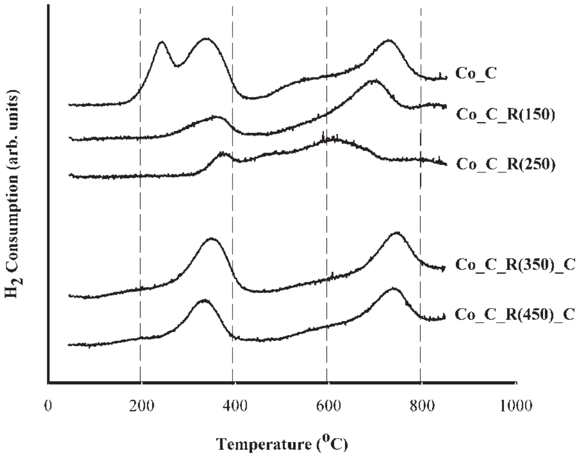

Figure 1. TPR profiles of catalyst samples reduced at different temperatures.

All TPR profiles of the alumina-supported cobalt catalyst pretreated at the various conditions used in this study show two major peaks: a lower-temperature peak located between 200–400 °C and a higher-temperature one located between 500–800 °C (see figure 1). The position of the actual TPR peak is influenced by the kinetics of reduction that involves the effects of the valency and dispersion of cobalt oxide and the strength of its interaction with the support, the reduction gas composition, etc. The number of Al^{3+} ions surrounding the cobalt ions is suggested to influence the TPR peak temperature by some kind of polarization effect [10]. It would appear to be difficult to perfectly assign the broad TPR peaks to the reduction of the well-defined cobalt species. However, the following generally accepted assignment can be applied for the above-mentioned peaks. The TPR peak between 200–400 °C is related to the two-step reduction of $Co_3O_4 \rightarrow CoO \rightarrow Co^\circ$, while the peak between 500–800 °C is related to the reduction of cobalt oxide species (Co^{2+} and Co^{3+}) strongly interacting with the support (Co_XO_Y-$Al_2O_3 \rightarrow$ Co metal) [4,10–13]. The two-step reduction of Co_3O_4 usually exhibits only one TPR peak [10,11]. The additional peak at around 220 °C in the TPR curve of the calcined sample (Co_C in figure 1) can be attributed to the reductive decomposition of some cobalt nitrate remaining on the catalyst after initial calcination [10]. Our previous study showed that a prolonged treatment up to 14 h is necessary to remove the incompletely decomposed nitrate if only calcination is applied [6].

One has to be very cautious when analyzing TPR data for supported cobalt because of the following reasons. As it was stated in the experimental section, the reducibilities are calculated assuming the reduction of Co_3O_4; thus, any discrepancy in the real composition of cobalt oxide may lead to some error in the calculated results. It is obvious that the higher-temperature peak of the Co_C sample does not represent Co_3O_4 particles, but rather surface Co^{3+}/Co^{2+} species whose reduction stochiometry is unknown. In addition, as stated previously, the first peak reflects the decomposition of cobalt nitrate residue (equivalent to ca. 12.3% of the cobalt present) resulting in CoO that in turn reduces to cobalt metal during the TPR [14]. This process consumes more H_2 per mole cobalt than the reduction of cobalt oxide spinel, and consequently, the degree of reduction for Co_C is clearly overestimated. Furthermore, the exothermic reductive decomposition is suggested to produce metal species strongly interacting with alumina. Finally, as different cobalt oxide species are contacted with hydrogen at increasing temperature during TPR, diffusion of surface cobalt species into the bulk may occur, resulting in the formation of a nonreducible cobalt phase. These facts can make the results of TPR measurements on cobalt catalysts more difficult, but not impossible to interpret.

3.2. *Effect of calcination*

TPR of the catalyst calcined in air at 300 °C (table 1, Entry 1) shows that this low calcination temperature transformed some cobalt oxide (ca. 25%) into a form that is in strong interaction with the support (see the peak between 500–800 °C in figure 1). Furthermore, some cobalt species (ca. 18%) were also formed that were not reducible up to 900 °C. This latter result could suggest that the formation of cobalt species that are nonreducible during TPR (behaving like cobalt aluminate) might be linked to the calcination treatment at 300 °C. This, however, is probably not the case as will be discussed later.

3.3. *Effect of reduction temperature*

The optimum reduction temperature for Co/Al_2O_3 catalysts is usually 350 °C, since it provides large amounts of the catalytically active metal surface. To study the effect of reduction temperature on the degree of reduction of cobalt, reduction temperatures were varied from 150 to 350 °C. Performing TPR right after catalyst reduction, the amount of additional reducible cobalt was found to vary depending on the reduction temperature previously applied (see table 1, entries 2–4), as would be expected. Reduction at temperatures equal to or higher than 150 °C completely converted any residual cobalt nitrate, as evident from the TPR results in figure 1.

The recalcination of the catalyst previously reduced at 350 °C (Co_C_R(350){}_C) resulted in a 31.4% reducibility in the range of 45–400 °C. Taking this value as a reference, since the nitrate peak is absent and the cobalt has been reoxidized, we can estimate that the reduction carried out at 150 and 250 °C produces 70 and 90% of the amount of cobalt reducible during the standard H_2 treatment (related to the reducibility of Co_C_R(350){}_C during TPR up to 400 °C) respectively. Investigating the corresponding TPR curves in figure 1, we can see a change in the position of the high-temperature peak with increasing reduction temperature, which means that the presence of hydrogen at 250/350 °C causes a broader distribution of strongly interacting cobalt species, while recalcination makes them rather "uniform" again (see Co_C_R(350){}_C in figure 1).

Considering the samples recalcined prior to TPR (see the two lower TPR curves in figure 1 and entries 5–6 in table 1), we can conclude that the R(350) treatment compared to the simple calcination did not influence the position and the area of the higher-temperature peak significantly. The reduction carried out at 450 °C, however, converted a larger portion of cobalt into the nonreducible form. This nonreducible cobalt was formed mainly at the expense of reducible metal related to that in the lower-temperature peak (i.e. related to the

Table 1
Reducibilities of catalyst samples after different pretreatments

Entry	Sample	Reducibility (%)			Nonreducible Co (<900 °C) (%)
		Overall (45–900 °C)	(45–400 °C)	(400–900 °C)	
1	Co_C	81.8	56.6	25.2	18.2
2	Co_C_R(150)	34.7	9.3	25.4	n.a.
3	Co_C_R(250)	26.8	3.3	23.5	n.a.
4	Co_C_R(350)	24.5	0.0	24.5	n.a.
5	Co_C_R(350)_C	54.0	31.4	22.6	46.0
6	Co_C_R(450)_C	42.9	22.3	20.7	57.1
7	Co_dried_HeW(350)_C	74.7	26.2	48.4	25.3
8	Co_C_HeW(350)	60.8	29.6	31.2	39.2
9	Co_C_R(150)_HeW(350)_C	60.6	27.9	32.7	39.4
10	Co_C_R(250)_HeW(350)_C	47.4	23.1	24.3	52.6
11	Co_C_R(350)_HeW(350)_C	40.5	15.7	24.8	59.5
12	Co_C_R(450)_HeW(350)_C	33.9	17.2	16.7	66.1
13	Co_C_R(350)_HeW(450)_C	42.3	19.4	22.9	57.7
14	Co_C_RW(350)_C	47.0	22.0	25.0	53.0

Note: n.a.: not available.

reduction of Co_3O_4). The higher-temperature peak (400–900 °C) did not vary significantly, indicating that the amount of cobalt ions strongly interacting with O-Al ligands was apparently not influenced by a 100 °C increase in reduction temperature. The TPR analysis indicated that 46.0 and 57.1% of the cobalt were nonreducible species for Co_C_R(350){}_C and Co_C_R(450){}_C respectively. The major cobalt phase in the Co_C sample can be considered to be Co_3O_4, whereas the partially reduced catalysts consisted of Co_3O_4, CoO, and Co^0. Co_3O_4 can be considered to be completely reduced by 400 °C [8]. With an increase in reduction temperature, an increased amount of Co^{2+} ions and strongly held Co^{2+} surface species had to be present in addition to metallic cobalt. It is possible that the support surface acts to keep the amount of surface Co^{2+} ions constant, while excess ions diffuse into the alumina structure during reduction and subsequent calcination and TPR, resulting in an increased amount of the nonreducible phase (subsurface or surface nonstochiometric cobalt aluminate). The more severe the reduction condition is, the more Co_3O_4 transforms to a form that cannot form oxide particles again upon recalcination.

TPR by its nature involves reduction. Thus, based on the influence of reduction temperature, it is highly likely that the nonreducible cobalt aluminate determined for a calcined-only sample such as the Co_C was actually formed during reduction as the TPR data was collected.

3.4. *Effect of hydrothermal treatment*

The effect of water vapor on the FTS activity of cobalt catalysts has been widely investigated [6–9,15]. Water has been claimed to enhance the formation of nonreducible cobalt aluminate and to cause partial oxidation of the metal, depending on the pretreatment conditions and the metal dispersion [7]. From a thermodynamic point of view, during FTS, the oxidation of the bulk cobalt metal phase to CoO or Co_3O_4 is unlikely at low conversions, while the formation of $CoAl_2O_4$ is kinetically restricted [9]. However, at high conversions where the H_2O/H_2 ratio is high, significant oxidation of the cobalt is possible. When water treatment was carried out in the absence of hydrogen, the formation of reducible and less-reducible cobalt oxide species was detected, but the metal was not completely oxidized to Co_3O_4 [7,9].

TPR curves in figure 2 show the effect of water treatment on the dried, calcined, or reduced catalysts. In table 1, the reducibilities obtained after hydrothermal treatments are given (entries 7–14). Before discussing the TPR results further, the importance of water contact should be emphasized. On the one hand, water vapor is able to hydrate the alumina support, so the number of OH groups on the surface is able to increase. On the other hand, the prolonged heat treatment in the presence of water (10 h compared to the standard 2 h calcination) removes the residual nitrate (see figure 2).

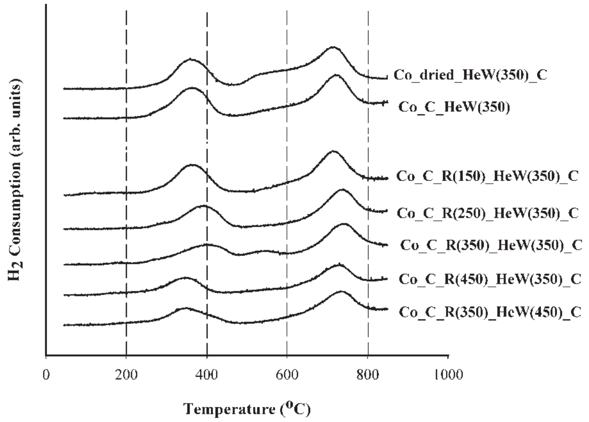

Figure 2. TPR profiles of catalyst samples after hydrothermal treatments.

Co_C_R(350){}_C can serve as a reference sample, since its residual nitrate has been removed, and it has not undergone any significant hydrothermal treatment except for a slight exposure to water vapor resulting from reduction of the catalyst in a differential bed. However, the catalyst sample that was hydrothermally treated after the drying step during catalyst preparation (entry 7, table 1) resulted in a catalyst with no residual nitrate but more reducible than the reference. It is important to note that the sample was calcined after the hydrothermal treatment. For the sample hydrothermally treated after calcination (entry 8, table 1), there was a decrease in reducibility, mainly above 400 °C, i.e., the amount of those cobalt oxide species strongly interacting with the support but still able to be reduced during TPR decreased relative to entry 7, although the reducibility was still better than that of the reference (see figure 3). The hydrothermally treated dried catalyst

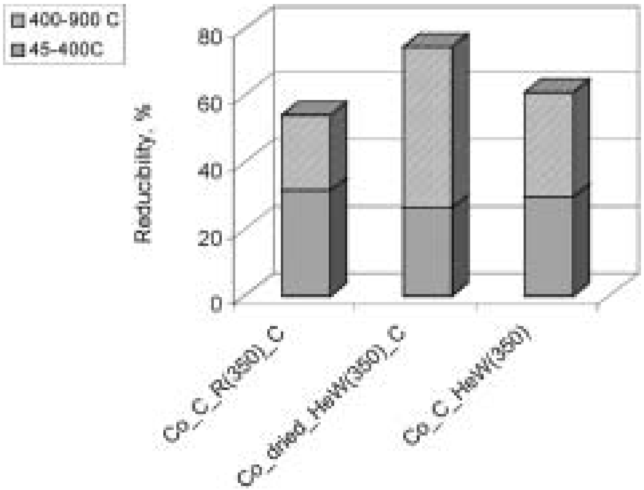

Figure 3. Effect of hydrothermal treatment at 350 °C on different catalyst precursors.

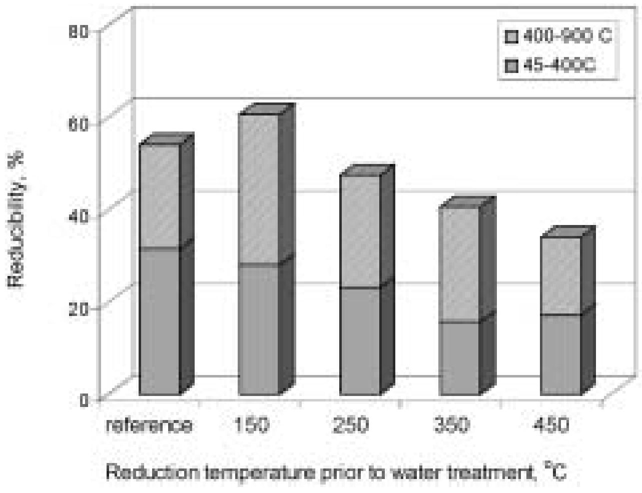

Figure 4. Effect of increasing degree of reduction prior to the hydrothermal treatment at 350 °C (reference: Co_C_R(350)_C).

had a better reducibility probably because the subsequent calcination dehydrated the alumina, making cobalt aluminate harder to form during TPR. Hydrothermal treatment of the dried and calcined catalyst was apparently not as detrimental as the standard reduction, because the catalyst sample had higher reducibility than Co_C_R(350){}_C. Haddad *et al.* [16] investigating the effect of water impregnation and drying on Co/SiO_2 observed that the reduced/passivated/recalcined catalyst exhibited very similar reduction properties before and after water contact.

As can be seen in figure 1, H_2 treatment at 150 °C was sufficient to remove all the residual nitrate from the Co_C_R(150) sample. Thus, the results for entries 8 and 9 indicate that the presence/absence of residual nitrate was not a factor in cobalt aluminate formation during hydrothermal treatment of the catalyst in a highly oxidized state.

Hydrothermal treatment was also carried out immediately after reduction at different temperatures (entries 9–13 in table 1). The ultimate reducibility decreased parallel with the increase in reduction temperature prior to the hydrothermal treatment (see figure 4). However, a 100 °C increase in the helium hydrothermal treatment temperature had no significant effect on the reducibility (entry 13 in table 1). In this case, one should consider the effect of hydrogen treatment and the presence of hydrated alumina simultaneously, so that the following explanation may be relevant. When a reduction temperature of 150 °C was applied before water vapor treatment (entry 10), the reducibilities were the same as in the case of Co_C_HeW (350) (entry 8). H_2 treatment at 150 °C is able to decompose the residual cobalt nitrate, but the CoO formed is probably not reduced to the metal, so the composition of the active phase must have been similar to Co_C_HeW(350) resulting in similar reducibility. This fact suggests that a significant degree of reduction is required before hydrothermal treatment is able to affect reducibility. Reduction prior to the hydrothermal treatment causes the disappearance of the Co_3O_4 spinel and produces CoO and Co^0, but leaves some Co_xO_y-Al_2O_3 strongly interacting oxide species untouched. The water vapor introduced subsequently can oxidize the metal to some extent (surface oxidation or the oxidation of highly dispersed cobalt particles has been reported in [9]). In addition, water vapor can enhance the interaction between the support and the partially reduced cobalt, so that after the recalcination step, less Co_3O_4 particles but more cobalt ions in the surface/subsurface regions are formed. This latter cobalt behaves like cobalt aluminate during TPR and is not reducible to 900 °C. This assumption is in agreement with the opinion of van Berge *et al.* [9] who postulated that the formation of cobalt aluminate in the presence of water should proceed via CoO as an intermediate.

It is interesting to observe that increasing the reduction temperature to 450 °C followed by water vapor treatment and recalcination (entry 12) produced more nonreducible cobalt than the reduction at 350 °C in such a way that the low-temperature peak area remained practically the same, but the higher-temperature peak area decreased. Thus, it is possible that a 100 °C increase in the reduction temperature and the subsequent contact with water vapor forces more Co^{2+} species to diffuse into the alumina structure. However, the large Co_3O_4 crystallites are resistant to reaction, so that after reduction/calcinations, they are still reducible below 400 °C (the first peak did not change significantly).

4. Conclusions

This study was undertaken to determine more details about the mechanism of formation of nonreducible cobalt species in alumina-supported cobalt catalysts at the relatively mild conditions of reduction and FTS. In particular, it was desired to determine what role the oxidation state of cobalt plays in this conversion. Our previous study of Co/SiO_2 showed that nonreducible silicates formed only when hydrothermal treatment was carried out on the reduced catalyst [4].

The results shown in this paper reveal that water vapor present during or after reduction, when partially reduced cobalt is present, can increase the formation of nonreducible cobalt compounds, probably a nonstochiometric form of cobalt aluminate. The suggested pathway for "cobalt aluminate" formation in Co/Al_2O_3 catalysts is as follows. Nonreducible, surface, or subsurface cobalt aluminate-like compounds are likely to form when Co^0 or surface Co^{2+} ions are well dispersed on the alumina surface. Increasing reduction temperature produces more partially/completely reduced species, while subsequent water vapor treatment may partly oxidize the metallic cobalt. The hydrated alumina appears to stabilize the cobalt oxidic species in strong interaction with the support and during prolonged treatment at temperature, they may diffuse into subsurface regions resulting in nonreducible cobalt aluminate formation. The presence of hydrated alumina seems to be important since the hydrothermally treated dried sample that was subsequently calcined (cobalt-dried_HeW(350){}_C) did not form as much nonreducible cobalt aluminate as the sample hydrothermally treated after calcination. In both cases, the majority of nonreducible cobalt aluminate was probably only formed during TPR as the cobalt started to reduce. In the latter case, the alumina was hydrated just before the start of TPR.

It would appear that, in order to have the maximally reducible cobalt (necessary for FTS activity), it is especially critical to control the water partial pressure for temperatures above 150 °C . This suggests that water vapor produced during catalyst reduction or reaction (when the cobalt is in a highly reduced state) may need to be controlled as much as possible if significant cobalt catalyst deactivation as a result of Co-support compound formation is to be prevented with time onstream.

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