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CO and CO_2 hydrogenation study on supported cobalt Fischer–Tropsch synthesis catalysts

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Abstract

The conversion of CO/H_2, CO_2/H_2 and $(CO + CO_2)/H_2$ mixtures using cobalt catalysts under typical Fischer–Tropsch synthesis conditions has been carried out. The results show that in the presence of CO, CO_2 hydrogenation is slow. For the cases of only CO or only CO_2 hydrogenation, similar catalytic activities were obtained but the selectivities were very different. For CO hydrogenation, normal Fischer–Tropsch synthesis product distributions were observed with an α of about 0.80; in contrast, the CO_2 hydrogenation products contained about 70% or more of methane. Thus, CO_2 and CO hydrogenation appears to follow different reaction pathways. The catalyst deactivates more rapidly for the conversion of CO than for CO_2 even though the H_2O/H_2 ratio is at least two times larger for the conversion of CO_2. Since the catalyst ages more slowly in the presence of the higher H_2O/H_2 conditions, it is concluded that water alone does not account for the deactivation and that there is a deactivation pathway that involves the assistance of CO.

Keywords: Hydrogenation; Fischer–Tropsch synthesis; Catalysts; Cobalt catalyst; Carbon monoxide; Carbon dioxide

1. Introduction

From a mechanistic point of view, the hydrogenation of carbon dioxide is of interest. For the production of methanol from synthesis gas, it appears that the pathway to methanol formation is through CO_2 as an intermediate; i.e., carbon monoxide is first converted to carbon dioxide which is then converted to methanol (e.g., [1–4]). It is therefore of interest to learn whether a similar situation applies for the Fischer–Tropsch synthesis (FTS).

Fixation of carbon dioxide has become of greater interest in recent years, primarily because of its impact on the environment through the greenhouse effect. One approach that has attracted attention is to produce synthesis gas through its reaction with methane even though the syngas produced only has a H_2/CO ratio of 1 for the idealized reaction. Another option is to recycle carbon dioxide to a gasification unit; however, there is a limit to the amount of carbon dioxide that can be utilized in this manner. Another approach is to hydrogenate carbon dioxide in FTS plants; this has become an attractive approach to some even though one must find a source of hydrogen to accomplish this (e.g., [5–12]).

For high temperature (330–350 °C) FTS the water-gas shift (WGS) reaction is sufficiently rapid so that it is nearly at the equilibrium composition. The direct or indirect hydrogenation of CO_2 at high temperatures is possible and occurs in the fluid bed

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reactors operated by Sasol and Mossgas. However, today the use of a slurry phase bubble column reactor is very attractive since its use allows the FTS reaction to be carried out isothermally. In the liquid phase synthesis, lower temperatures are utilized (220–240 °C) with either a cobalt or iron catalyst and the WGS may be far from the equilibrium value.

It was of interest to compare the FTS reactions of CO and CO_2 with a cobalt catalyst. In this initial work simple catalyst formulations have been utilized: cobalt supported on a silica without promoters and Co–Pt–Al_2O_3. Another purpose of this investigation is to determine the deactivation rate for CO_2 hydrogenation at different H_2:CO_2 ratios and for different conversion levels, and to compare these to the deactivation rate for CO hydrogenation.

2. Experimental

2.1. Catalysts

Co/SiO_2. The Co/SiO_2 catalyst was prepared by three incipient wetness impregnations of silica (Davisil 644, 100–200 mesh, 300 m^2/g, and pore volume of 1.15 cm^3/g) with aqueous cobalt nitrate to produce a final loading of 15 wt.% CO. The material was dried in a fluidized bed and then calcined for 4 h in an air flow at 400 °C.

Co–Pt/Al_2O_3. Condea Vista B alumina with a surface area of 300 m^2/g and pore volume of 1.15 m^3/g was used as support material. The cobalt loading was 15%. A multi-step incipient wetness impregnation method was used to add cobalt nitrate solution to alumina with a drying procedure after each impregnation at 80 °C in a rotary evaporator. Following cobalt addition, tetramineplatinum nitrate solution was added by an incipient wetness impregnation method to give a platinum loading of 0.5%. The catalyst was then dried in a rotary evaporator at 80 °C and calcined at 400 °C for 4 h.

2.2. Fixed-bed synthesis

The Co–Pt/Al_2O_3 catalyst (3 g) was diluted by 15 g of glass bead and then loaded in a 2 in. (5.1 cm) i.d. reactor located in a three zone furnace that was used for temperature control. The catalyst was reduced in situ using a H_2(33%)/Ar flow for 10 h at 350 °C. Four Brooks mass flow controllers were used to control the flow rate of CO, CO_2, H_2 and He. FTS was conducted at 210 °C, 350 psig with H_2:CO = 2:1 and GHSV = 5.0 SL/h g catalyst (H_2:CO:He = 2:1:2). CO_2 hydrogenation was conducted at the same temperature and pressure but H_2:CO ratios of both 2:1(H_2:CO:He = 2:1:2) and 4:1(H_2:CO_2:He = 4:1:4) were used. The space velocity was varied from 5.0 SL/h/g catalyst to 9.0 SL/h/g catalyst. For the Co–SiO_2 catalyst, the FTS was conducted in the same equipment and conditions except the run was conducted at 220 °C, 24 atm (2.4 MPa), $H_2/CO = 2/1$, and 1 or 3 NL/g catalyst/h. Gaseous and liquid products were analyzed using gas chromatography.

3. Results

Data for the conversion of CO and CO_2 during 10 days on-stream with the Co–silica catalyst are given in Fig. 1. Compared to the CO conversions of the same and another similar Co–silica catalyst, it appears that the initial CO conversion is about the same in a CSTR and in the fixed bed reactor; however, the activity decline is more rapid in the fixed bed reactor. The run data and conversions for the fixed bed reactor are compiled in Table 1.

There was a decline in activity during the period between collecting the first two samples. The exit gas from the CO_2 conversions contained more CO_2 than the calibration gas so that CO_2 conversions were calculated from the mass balance for the other gaseous and liquid products; thus, there is some uncertainty in the absolute CO_2 conversion data but the trend shown in Table 1 and Fig. 1 is certainly valid. Thus, with the cobalt–silica catalyst the conversion of CO and CO_2 occur at about the same rate. This is in contrast to the observations with an iron catalyst under low temperature FTS conditions where the rate of conversion of CO_2 is considerably lower than for CO [13–18].

A striking difference for the cobalt catalyst, compared to the iron catalyst, is the formation of methane. Under the same reaction conditions, the amount of methane produced is much higher for the CO_2 reactant (Fig. 2). Whenever CO_2 was the reactant, methane accounted for greater than 70% (based on carbon)

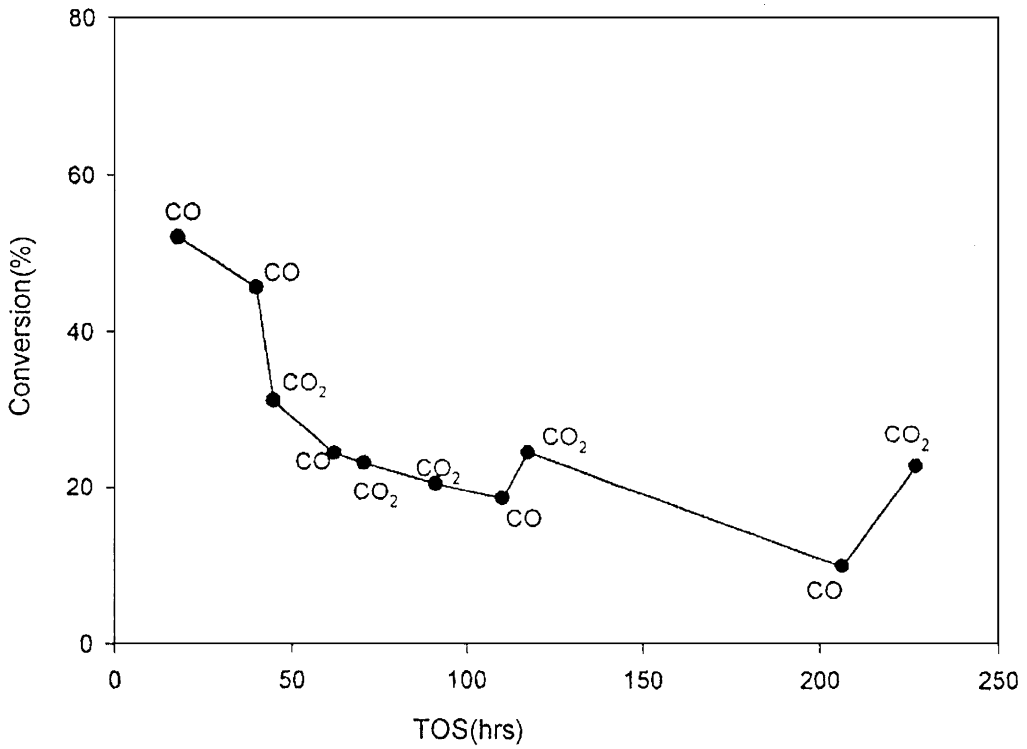


Fig. 1. CO and CO_2 conversion as a function of time on stream for the CO–SiO_2 catalyst.

of the products. However, under the same reaction conditions and with the same catalyst, methane accounted for less than 10% of the products with CO as reactant. Similar results are reported by Riedel et al. [18]. This requires that methane be formed by two pathways or that a common reaction intermediate does not occur with CO and CO_2 conversion.

During period 9, the feed was changed so that equal amounts of CO and CO_2 were present in the feed and the flows of Ar, H_2 and ($CO + CO_2$) were the same

Table 1
Run conditions and results from the conversion of CO and CO_2 with a cobalt–silica catalyst

Sample number	Time on stream (h)	Feed gas	Conversion (%)
1	17.3	CO	52.2
2	39.5	CO	45.8
3	44.5	CO_2	31.2
4	62.0	CO	24.4
5	70.5	CO_2	23.1
6	91.0	CO_2	20.5
7	109	CO	18.6
8	117	CO_2	24.5
9	134	$CO + CO_2$	CO: 53.5%, CO_2: 3.98%
10		Methanol	
11	206	$CO + CO_2$ (different flow rate)	CO: 9.86%, CO_2: 6.1%
12	226	CO_2	22.8

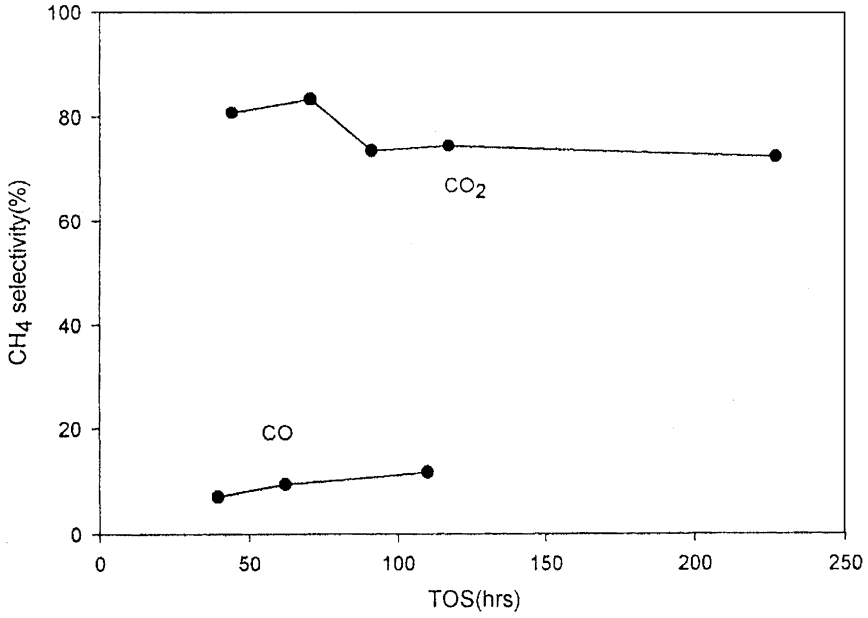


Fig. 2. Methane selectivity as a function of time on stream for the CO–SiO_2 catalyst.

as when either pure CO or CO_2 was converted. Under competitive conversions, CO was converted more rapidly than CO_2, clearly showing that CO is adsorbed on the Co catalyst to a greater extent than CO_2. Whereas the total carbon oxide conversion is about the same as would be expected from the trend of the previous runs, the conversion of CO accounted for more than 90% of the total conversion of the carbon oxides. Thus, CO conversion exceeds that of CO_2 by a factor of 4–10 under competitive adsorption conditions. A similar result was obtained following the conversion of methanol except that there was not as dramatic a difference as would be expected from the trend of the previous conversions. The CO conversion following the period of methanol feed was lower than expected from the trend of the prior periods. Since the water partial pressure was much higher during the conversion of methanol, it is anticipated that irreversible, or slowly reversible, damage of the catalyst occurred during the exposure to the high water partial pressure conditions.

Following the first conversion of the mixture of CO and CO_2, methanol was substituted for the carbon oxides feed. Because of the limitations of the liquid pump, the feed during this period was only H_2 and methanol. The total flow was 4 NL/h/g catalyst and the H_2/methanol molar ratio was 2/1. Thus, the H_2/carbon ratio in the feed was the same as when CO and/or CO_2 was the feed but the flow rate of methanol was four times that of the carbon oxide. Under the reaction conditions used, the conversion of methanol was about 50%, whereas the conversion of CO or CO_2 was slightly less than 25%. Thus, considering the higher flow rate (four times higher) and higher conversion (two times higher) of methanol, the total carbon converted with the methanol feed was about eight times greater than for the carbon oxides. Thus, the relative rate is rapid enough that any methanol intermediate could be converted to methane so that methanol would not be detected in the liquid sample. During another run, an analysis of the gas sample showed that the amount of methanol in the gas phase was at least below 0.1% of the amount of CO. The only significant products from the conversion of methanol under the FTS conditions were methane and water; thus, any methanol formed during the reaction could have been converted to methane.

Since, for the initial work with the Co–Pt/Al_2O_3 catalyst, we used a H_2:CO ratio of 2:1 as the feed

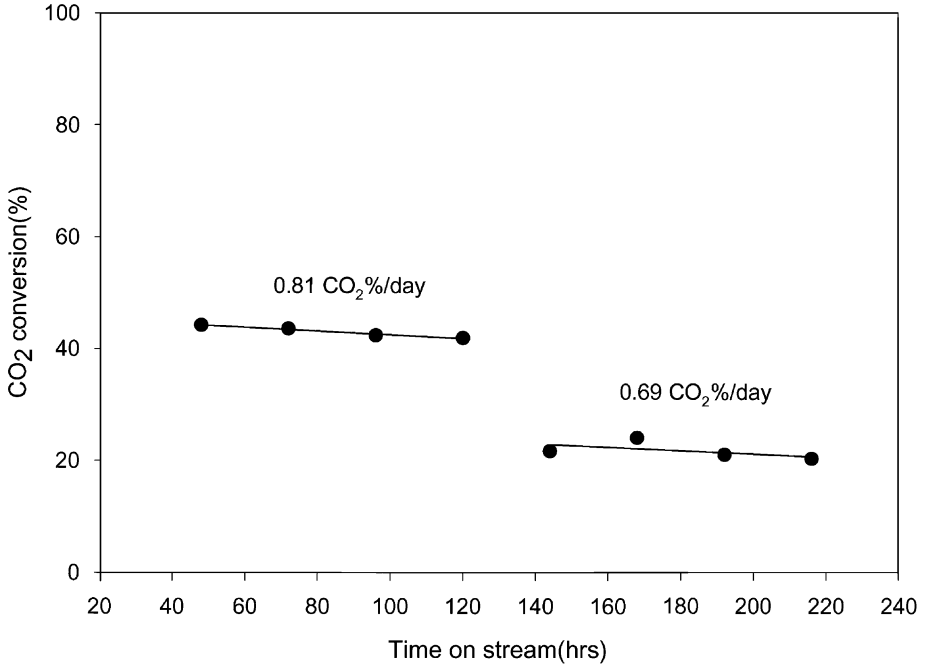


Fig. 3. CO_2 hydrogenation over Co–Pt/Al_2O_3, 210 °C, 350 psig (2.4 MPa), H_2:CO = 2:1, GHSV = 5.0 SL/h/g catalyst.

gas, the highest possible CO_2 conversion is 50%. At a time-on-stream of 48 h, the observed CO_2 conversion was 45%, which is close to the equilibrium value. The conversion decreased at 0.81% CO_2 conversion per day, indicating that the catalyst is reasonably stable for CO_2 hydrogenation (Fig. 3). To investigate the stability of the catalyst far from equilibrium, the flow rate was increased from 5.0 SL/h/g catalyst to 9.0 SL/h/g catalyst. The deactivation rate was even lower (from 0.81 to 0.69% CO_2 conversion per day) for the 20% CO_2 conversion range.

Since the methanation of CO_2 requires H_2:CO ratio of 4:1, the feed gas was adjusted to this ratio to further study the stability of the catalyst and the results are shown in Fig. 4 for the Co–Pt/Al_2O_3 catalyst. When the conversion level is 42%, the catalyst did not deactivate after 24 h. The flow rate was then decreased to achieve a conversion of about 55%, the catalyst started to deactivate slowly but leveled off at about 40% CO_2 conversion. It can been concluded that during CO_2 hydrogenation, deactivation is slower for CO_2 than for CO hydrogenation even at high conversion levels.

After 504 h of using CO_2 as a feed gas, CO hydrogenation was accomplished with a H_2:CO ratio of 2:1 and space velocity of 5 SL/h/g catalyst. Fig. 5 shows the results of CO conversion as a function of time on stream, and Fig. 6 is CO and CO_2 conversion as a function of time-on-stream when CO was used as the feed gas first and then switching for CO and CO_2 and back again to CO_2. It can been concluded that CO_2 hydrogenation did cause deactivation of the catalyst for subsequent CO hydrogenation since, after 504 h of time on stream, CO conversion decreased from 52.5 to 28.7%. However, it can been seen from Fig. 5 that the deactivation rate of CO hydrogenation is much faster than for CO_2 hydrogenation at the 30% CO conversion level. If the feed gas is CO and the conversion is 60%, the deactivation rate could have been much higher and after 504 h of time on stream, CO conversion rate would have been much lower than 28.7%. From Fig. 5, it seems that the CO conversion stayed at about 20% and it agrees with our CSTR data that the deactivation rate is a function of CO conversion level; the lower the CO conversion, the lower the deactivation rate.

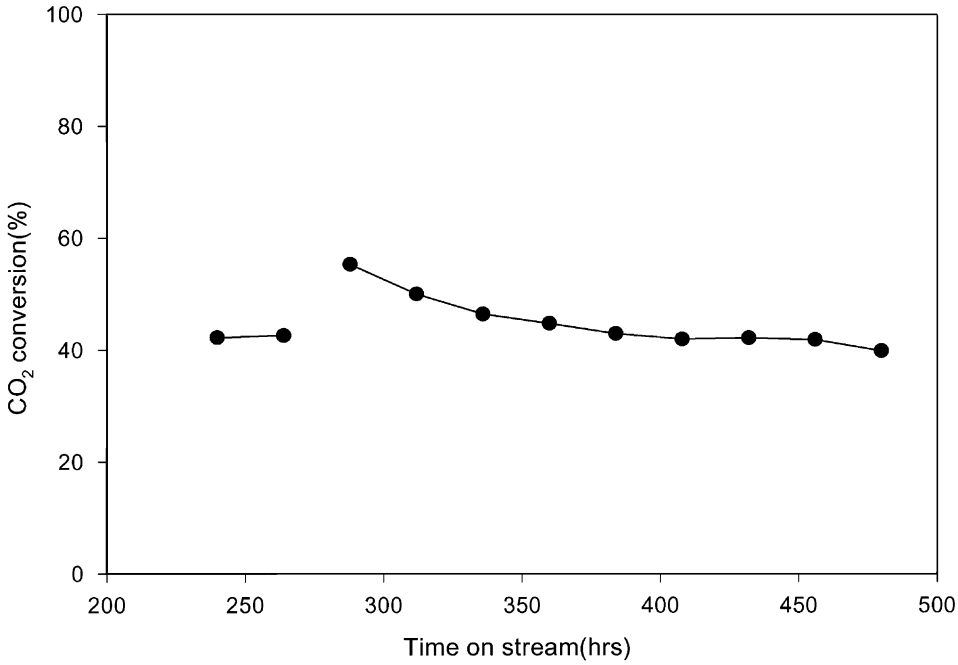


Fig. 4. CO_2 hydrogenation over a Co–Pt/Al_2O_3 catalyst at 210 °C, 350 psig (2.4 MPa), H_2:CO = 4:1, GHSV = 9.0 and 5.0 SL/h/g catalyst.

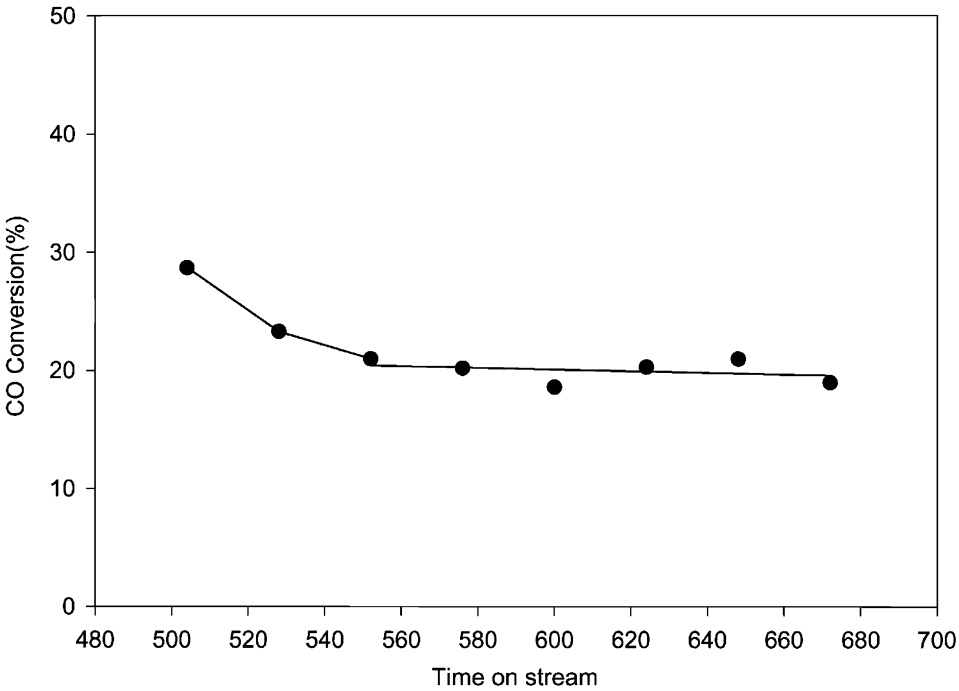


Fig. 5. CO hydrogenation over Co–Pt/Al_2O_3 at 210 °C, 350 psig (2.4 MPa), H_2:CO = 2:1, GHSV = 5.0 SL/h/g catalyst.

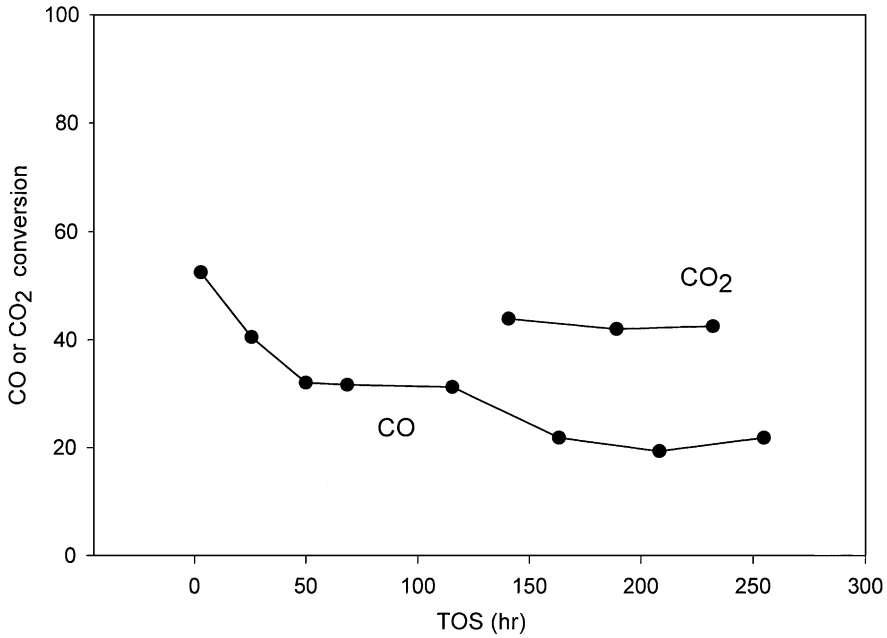


Fig. 6. CO or CO_2 conversion as a function of time on stream for conversions with the Pt–Co/Al_2O_3 catalyst.

4. Discussion

One of the assumptions for the deactivation mechanism of cobalt FTS catalyst is the oxidation of surface cobalt to oxide or cobalt aluminate by water. One view for the oxidation mechanism is that when H_2O/H_2 partial pressure ratio attains a certain level, oxidation of the cobalt cluster starts to occur. For CO_2 hydrogenation, when the conversion level is at 40%, the H_2O/H_2 partial pressure ratio is about 2.0 and this is much higher than CO hydrogenation (0.3 at 40% CO conversion). But for CO_2 hydrogenation, the deactivation is not as rapid (Fig. 3). One explanation is that oxidation only occurs for the smaller clusters and the methanation of CO_2 is catalyzed by the larger cobalt clusters. Another explanation is that the surface oxidation does not occur as fast for CO hydrogenation. Since the H_2O/H_2 ratio is two times greater for CO_2 conversion than for an equivalent CO conversion, the assumption that the H_2O/H_2 partial pressure ratio is the decisive factor for the oxidation is invalid. Another explanation of the deactivation for CO hydrogenation is that the H_2O/CO ratio is a more important factor. One possibility to account for this is that the adsorption of H_2O and CO is competitive and since more H_2O has been formed, less CO can been adsorbed. But the results of CO_2 hydrogenation eliminate that possibility since the H_2O/CO ratio is much larger for CO_2 conversion. Therefore, it is concluded that H_2O and CO forms some intermediate which caused the oxidation or crystal growth of cobalt clusters.

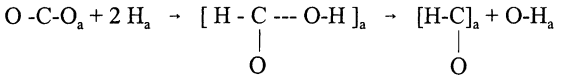
The difference in the product distributions obtained from the hydrogenation of CO and CO_2 preclude a common reaction pathway for FTS unless there is a second reaction pathway for the conversion of CO_2, but not CO, to methane. Furthermore, if there is a second pathway, then the FTS with CO_2 occurs at about only 20% of the rate for CO.

Based on the preliminary data, it is proposed that the conversion of CO and CO_2 occurs by different reaction pathways. It is assumed that the hydrogenation and breaking of the two C–O bonds of the CO_2 provide the source of the different pathways. In this proposal, the breaking of the C–O bond, presumably by the addition of adsorbed H to form C–O–H, competes with, and probably leads, the addition of adsorbed H to form the C–H bond. Thus, for CO the following reaction

pathway could apply:

$$C\text{–}O_a + 2H_a \rightarrow [H\text{–}C\cdots O\text{–}H]_a \rightarrow H\text{–}C_a + O\text{–}H_a \quad (1)$$

In the case of CO_2 the reaction is more complex since there are two C–O bonds that must be broken prior to, or simultaneous with, the formation of the C–H bond. If it is assumed that similar rates apply for the formation of the first O–H and C–H bonds as in the case of CO we would have a different situation, idealized in reaction (2)



(2)

If reaction (2) is valid, it is then a matter of the hydrogenation of the adsorbed oxygen species to produce the adsorbed intermediate (methanol) and its subsequent hydrogenation

$$[H\text{–}C\text{–}O]_a + 3H_a \rightarrow [H_3C\text{–}O\text{–}H]_a + 2H_a \rightarrow CH_4 + H_2O \quad (3)$$

Based on the carbon mass balance, about 75% of the hydrogenation of CO_2 would proceed by reaction (3) and the remainder would involve the breaking of the second C–O bond to continue along the normal FTS reaction pathway that is followed by CO hydrogenation. At this time, while the above mechanism accounts for the products that are produced from the hydrogenation of CO_2, it is very speculative. ^{14}C-tracer studies are planned that should provide some evidence to establish whether the speculation has merit.

Another possibility is that the conversion follows the same mechanism as has been observed by Fischer and Bell [19] for a Rh/SiO_2 catalyst. They conclude that at constant hydrogen partial pressure and temperature, the kinetic expression they derived predicts that a maximum in the methane formation rate should be observed at intermediate CO coverages and that the rate should fall to zero as the CO surface concentration approaches either 0 or θ_{max}. In the present study, this would mean that CO_2 would have to hydrogenate to provide a surface concentration of CO that is closer to the intermediate CO coverage than is obtained for the CO reactant or that the fraction of the surface that is covered by hydrogen is much higher when CO_2 is the reactant than when it is CO.

The results to date for the hydrogenation of CO_2 indicate that it will not be commercially attractive using typical FTS catalysts based on iron or cobalt.

Acknowledgements

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