

CO and CO₂ Hydrogenation Over Co/SiO₂ Catalyst

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Summary

CO and CO₂ hydrogenation was studied in a fixed bed reactor on a Co/SiO₂ catalyst. Reaction was carried out at 220°C, 350psig, H₂:CO=2:1, H₂:CO₂ = 2:1, with a total flow rate of 150 mL/min (3NL/hr/g catalyst) and a H₂+CO, H₂+CO₂ or H₂+CO+CO₂ flow rate of 50 mL/min(1NL/hr/g catalyst). CO, CO₂ and CO,CO₂ mixture feed gas were used respectively for comparison. The results indicated that in the presence of CO, CO₂ hydrogenation hardly occurred. For the cases of only CO or only CO₂ hydrogenation, the activity of the two were similar but the selectivity was very different. For CO hydrogenation, normal Fischer-Tropsch synthesis product distribution were observed with an α of about 0.80; in contrast, the CO₂ hydrogenation product contained about 70% methane. Thus, CO₂ and CO hydrogenation appears to follow different reaction pathways.

Introduction

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 H₂/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 Fischer-Tropsch synthesis (FTS) plants; this has become an attractive approach even though one must find a source of hydrogen to accomplish this.

For high temperature (330-350°C) FTS the water-gas-shift (WGS) reaction is sufficiently rapid that it is nearly at the equilibrium composition. The hydrogenation of CO₂ at high temperatures is possible and occurs in the fluid bed reactors operated by Sasol and Mossgas. However, 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 must be utilized (220-240°C) with either a cobalt or iron catalyst. It was of interest to compare the FTS reactions of CO and CO₂ with a cobalt catalyst. In this initial work a simple catalyst formulation has been utilized: cobalt supported on a silica without any promoters.

Experimental

The catalyst was prepared by three incipient wetness impregnations of silica (Davisil 644, 100-200 mesh, 300 m²/g, and pore volume of 1.15 cm³/g) with aqueous cobalt nitrate to produce a final loading of 15 wt.%. The material was dried in a fluidized bed and then calcined for 4 hrs. in an air flow at 400°C. Three grams of the calcined catalyst was diluted with 15 g of glass beads and placed in a fixed bed reactor where it was reduced in a H₂(33%)/Ar flow for 10 hours at 350°C. The reaction conditions were: 220°C, 24 atm (2.4MPa), H₂/CO = 2/1, 3 NL/hr/g catalyst total gas flow, 1 NL/hr/g catalyst synthesis gas flow. Analysis of the gaseous products was accomplished using gas chromatography.

Results.

The conversion of CO and CO₂ during 10 days on-stream are given in figure 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 the 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 CO₂ conversions contained more CO₂ than the calibration gas so that CO₂

conversions were calculated from the mass balance for the other gaseous and liquid products; thus, there is some uncertainty in the absolute CO₂ conversion data but the trend shown in Table

Table 1 Run conditions and results from the conversion of CO and CO₂ with a cobalt-silica catalyst.

sample No.	time on stream(hrs)	feed gas	conversion(%)
1	17.3	CO	52.2
2	39.47	CO	45.8
3	44.47	CO ₂	31.2.
4	61.97	CO	24.4
5	70.47	CO ₂	23.1
6	90.97	CO ₂	20.5
7	109.97	CO	18.6
8	117.22	CO ₂	24.5
9	134.47	CO+CO ₂	CO, 53.5% CO ₂ , 3.98%
10		methanol	
11	206.22	CO+CO ₂ (different flow rate)	CO: 9.86% CO ₂ : 6.1%
12	226.89	CO ₂	22.8

1 and figure 1 are certainly valid. Thus, with the cobalt catalyst the conversion of CO and CO₂ 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 CO₂ is considerably lower than for CO (1-6).

A striking difference for the cobalt catalyst is the formation of methane. Under the same reaction conditions, the amount of methane produced is much higher for the CO₂ reactant (figure 2). Whenever CO₂ was the reactant, methane accounted for greater than 70% (based on carbon). However, under the same reaction conditions and with the same catalyst, methane accounted for less than 10% of the products. Similar results are reported by Riedel et al. (6). This requires that methane be formed by two pathways or that a common reaction intermediate and reaction pathway does not occur with CO and CO₂.

During period 9, the feed was changes so that equal amounts of CO and CO₂ were present in the feed and the flows of Ar, H₂ and (CO + CO₂) were the same as when either pure CO or CO₂ was converted. Under competitive conversions, CO was converted much more rapidly than CO₂, clearly showing that CO is adsorbed on the Co catalyst to a much greater extent than the CO₂. Whereas the total carbon oxide conversion is about the same 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. 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.

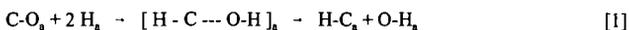
Following the first conversion of the mixture of CO and CO₂, methanol was substituted for the carbon oxides feed. Because of the limitations of the liquid pump, the feed during this period was only H₂ and methanol. The total flow was 4 NL/hr/g catalyst and the H₂/methanol molar ratio

was 2/1. Thus, the H₂/carbon ratio in the feed was the same as when CO and/or CO₂ 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 CO₂ was slightly less than 25%. Thus, considering the higher flow rate (4 times higher) and higher conversion (2 times higher) of methanol, the total carbon converted with the methanol feed was about 8 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; unfortunately, in this preliminary run the analysis of the gas sample did not provide a measure of the amount of methanol in the gas phase. 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.

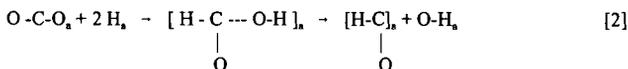
Discussion.

The difference in the product distributions obtained from the hydrogenation of CO and CO₂ preclude a common reaction pathway for FTS unless there is a second reaction pathway for the conversion of CO₂, but not CO, to methane. Furthermore, if there is a second pathway, then the FTS with CO₂ occurs at about only 20% of the rate with CO.

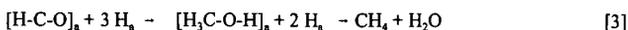
Based on the preliminary data, it is proposed that the conversion of CO and CO₂ occurs by different reaction pathways. It is assumed that the hydrogenation and breaking of the two C-O bonds of the CO₂ provide the source of the different pathways. In this proposal, the breaking of the C-O bond, presumably 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:



In the case of CO₂ 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]:



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:



Based on the carbon mass balance, about 75% of the hydrogenation of CO₂ 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 CO₂, it is very speculative. ¹⁴C-tracer studies are planned that should provide some evidence to establish whether the speculation has merit.

The results to date for the hydrogenation of CO₂ indicate that it will not be commercially attractive using typical FTS catalysts based on iron or cobalt.

Acknowledgment

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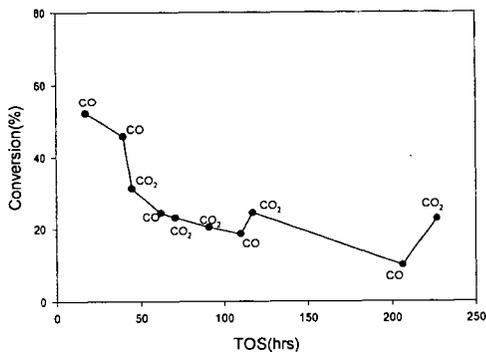


Fig. 1 CO and CO₂ conversion as a function of time on stream

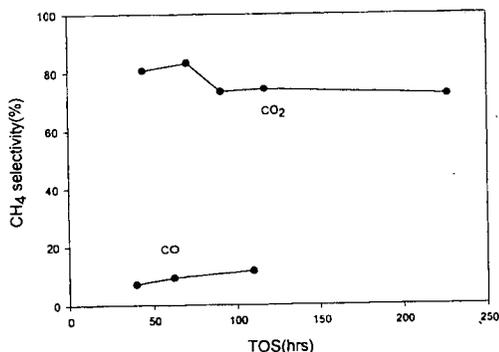


Fig. 2 Methane selectivity as a function of time on stream

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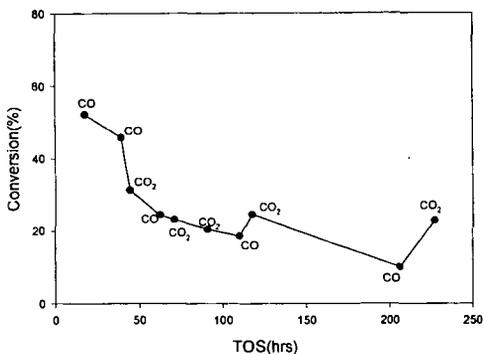


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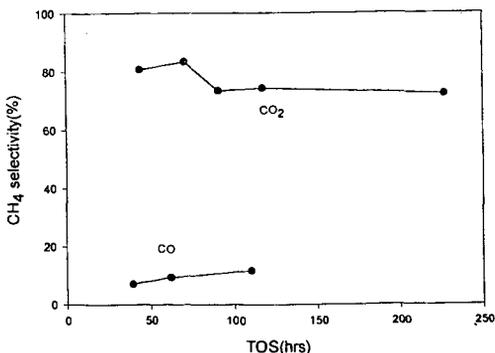


Fig. 2 Methane selectivity as a function of time on stream