

EFFECTS OF H₂O AND CO₂ ON THE ACTIVITY AND COMPOSITION OF IRON FISCHER-TROPSCH CATALYSTS

Mark A. McDonald

U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, Pennsylvania 15236

INTRODUCTION

The composition of an iron Fischer-Tropsch (F-T) catalyst is strongly affected by the % conversion of H₂-CO syngas (1,2). At low % conversion, the strongly reducing syngas mixture tends to convert metallic or oxidic iron species to a bulk iron carbide phase or phases. As % syngas conversion increases, H₂ and CO are converted to organic products, and to H₂O and CO₂. The gas mixture can therefore oxidize an iron catalyst (3). However, the catalyst's synthesis behavior (activity, selectivity, activity and selectivity maintenance) also depends strongly on % syngas conversion (4). Thus, an iron catalyst's composition and synthesis behavior are not easily correlated under typical F-T reaction conditions.

This study was designed to determine how the build-up of H₂O and CO₂ during reaction affect F-T catalyst composition and synthesis behavior. Reaction rate measurements were conducted at differential % syngas conversion using catalyst wafers mounted in an *in-situ* cell. This cell allowed Mössbauer effect spectroscopy of the used catalyst for determination of the catalyst composition. Additional H₂O and CO₂ were added to syngas to determine the effects on catalyst composition, activity, and selectivity. Furthermore, these experiments were carried out at pressures well above atmospheric, the pressure range required for good iron F-T catalyst behavior (5). Thus, results presented here are more closely related to the state of working F-T catalysts than are previous *in-situ* Mössbauer studies of iron catalysts, which were done almost exclusively at atmospheric pressure. This paper focuses on initial experiments involving the addition of only H₂O, not CO₂, to a syngas stream.

EXPERIMENTAL METHODS

Flows of 1/1 H₂/CO, H₂, CO₂, CO and He were obtained from cylinders, with purification traps located downstream from each cylinder. Two Brooks 5850 mass flow controllers regulated flows from one or two cylinders at a time. Water was added to the gas streams with an ISCO 314 syringe pump. The water flowing from the pump was vaporized and combined with the gas stream. Gas lines were heated downstream to prevent water condensation. The syringe pump was filled from a distilled water reservoir. The water in this reservoir was sparged 4-10 h with He to remove dissolved gases.

The spectroscopy cell used for reaction experiments was constructed at West Virginia University under the supervision of Dr. Pedro Montano. The cell pressure was regulated with a Tescom back-pressure regulator located downstream. Reaction products were analyzed using a Hewlett-Packard 5730 gas chromatograph. A flame ionization detector analyzed organic products eluted from a capillary column, while a thermal conductivity detector analyzed other gases (CO₂, CO) eluting from a Porapak R column. The Mössbauer spectrometer is an MS-900 manufactured by RANGER Scientific. The source was 100 millicuries of ⁵⁷Co in Rh, obtained from New England Nuclear.

The iron catalyst was prepared by incipient wetness impregnation of Davison 952 silica with aqueous Fe(NO₃)₃ solution, yielding a catalyst precursor of

approximately 12 wt% Fe following drying and calcination. Approximately 0.15 g of this precursor was pressed into a wafer and mounted in the reaction cell for each experiment. The cell was then pressure tested by heating in a He flow to 383 K for 2 h, then given a standard reduction in flowing H₂ at 523 K for 14 h, 623 K for 8 h, and finally 698 K for 14 h. Before exposure to syngas, the catalyst was cooled in H₂ flow to 523 K. All gas treatments reported here were carried out at 2.06 MPa (20.3 atm).

RESULTS

Rates of synthesis of CH₄ and CO₂ obtained after 2 h exposure to 1/1 H₂/CO are shown in Table 1, reported as (moles product)/(mole total Fe · s). Product selectivities to light hydrocarbons are also listed, shown as mole/mole CH₄. The catalyst reached maximum conversion after two hours on stream, and maintained essentially constant activity and selectivity during the entire 24 h of synthesis.

In a separate experiment, a catalyst sample given the same reduction pre-treatment and 24 h exposure to syngas was then exposed to syngas containing 12% H₂O. Catalyst activity declined fifty-fold during the first four hours on stream, to a level of activity approaching the accuracy of chromatographic analysis. (Thus, no data are given.) Production of CO₂ declined rapidly over the same period of time.

Mössbauer effect spectra of catalyst samples are shown in the Figure 1. Figure 1a shows the spectrum of the initially reduced catalyst. This spectrum displays the characteristic six-peak spectrum of α -Fe, demonstrating thorough reduction occurred before exposure to syngas. The spectrum may also contain an Fe⁺² component overlapping with the fourth peak, although no computer fitting of the spectrum has been yet made. Figure 1b shows that during 24 h of syngas exposure, the catalyst was completely converted to iron carbide. The six-peak spectrum is that of ϵ' -carbide (6,7), although a small amount of χ -carbide may also be present. The sample exposed to an additional 24 h of syngas containing 12% H₂O gave essentially the same spectrum (Figure 1c), even though catalyst activity declined dramatically during this treatment. Thus, the decline in activity upon exposure to syngas + 12% H₂O was not accompanied by any measurable bulk oxidation of iron carbide.

DISCUSSION

At least two processes need to be considered in discussing the effects of adding the oxidant H₂O to syngas: (a) bulk oxidation of the iron catalyst by H₂O, and (b) oxidation of CO by H₂O to form H₂ + CO₂, the water-gas shift reaction. The latter reaction is clearly favored thermodynamically under these conditions (8), and is typically equilibrated for K-promoted F-T catalysts operating at non-differential conversions and slightly higher temperatures than used here (9). However, for the experimental conditions reported here, there is little reason to expect the reaction to approach equilibrium. Thus, it is sufficient to consider only the first process and to neglect the water-gas shift reaction. (This statement is equivalent to saying that one need only consider the oxidation of iron by H₂O and need not consider the reverse process, the reduction of iron oxide by CO.)

For the run in which H₂O was added to syngas, the (H₂O)/(H₂) ratio was clearly above that required to oxidize α -Fe to Fe₃O₄ (8). However, ϵ' -carbide, not α -Fe, was present before exposure to H₂O-containing syngas, and the thermodynamics of the iron carbides are not well-defined (3). The absence of any detectable bulk carbide oxidation during H₂O exposure thus may be due to either the unfavorable thermodynamics or kinetics of bulk oxidation.

Nevertheless, the addition of H₂O to syngas certainly made the gas much more oxidizing. The loss of catalyst activity upon exposure to H₂O-containing syngas suggests that surface oxidation of the catalyst took place. This would be consistent with the idea that reduced iron species are required for hydrocarbon synthesis from syngas (10,11).

The severe loss of catalyst activity upon exposure to H₂O/H₂/CO was larger than the magnitude of effects reported by other workers (9,11,12). In fixed-bed experiments, Karn *et al.* reported that 10-30% H₂O added to 1/1 H₂/CO had relatively little effect on % CO conversion (12). The main effect was to decrease the % CH₄ in the outlet stream while increasing % CO₂. Thus, the extent of water-gas shift reaction was increased while hydrocarbon synthesis was inhibited. The increase in water-gas shift and inhibition in methane synthesis was most noticeable at low % conversions (high space velocities). At higher % conversions, less inhibition of methane production was observed, attributed to the enhanced H₂/CO ratio resulting from water-gas shift.

In slurry-phase F-T synthesis experiments, Satterfield *et al.* (9) reported trends similar to those of Karn *et al.* but of smaller magnitude. Addition of 12% H₂O slightly increased the rate of CO consumption, due to an increase in CO₂ production from water-gas shift. The rate of CO conversion to organic products appears to have declined very slightly. The magnitude of these trends was not much larger even for addition of up to 42% H₂O; the increase in CO₂ production and decrease in CO conversion to organic products still were each only about a factor of two. It should be noted that these runs had H₂ + CO conversions over 50%. Since these authors used a mixed reactor, it is probably most reasonable to compare results presented here with their experiments containing 42% H₂O in the feed, since in each case the reactor concentrations of H₂O were in the same range.

Reymond *et al.* (13) reported trends somewhat closer to those reported here. In studies at atmospheric pressure and differential % conversion, addition of only 0.6% H₂O to 9/1 H₂/CO produced about a three-fold drop in rates of both CH₄ and CO₂ synthesis.

The difference among these studies are attributable to differences in reactor type and catalyst used. Studies of H₂O addition carried out at high % conversion showed relatively small changes in reaction rates (9,12). Additional CO₂ was produced, synthesis of F-T products was inhibited, but these trends became less pronounced as % conversion increased. In contrast, reactions carried out under differential % conversion (13) showed much larger effects of H₂O addition on catalyst activity but no clear effect on selectivity.

These trends can be rationalized from the following observations. The studies carried out at high % conversion (9,12) had substantial concentrations of H₂O, CO₂, and organic products in the outlet stream, while concentrations of H₂ and CO were well below concentrations in the inlet stream. In addition, K-promoted catalysts were used in both studies. High % conversions and K-promotion both favor equilibration of the water-gas shift reaction (9,14), so this reaction is likely to approach equilibrium under these conditions. Addition of H₂O to the feed perturbs the water-gas shift reaction away from equilibrium and makes the gas mixture more oxidizing. Therefore, the % CO conversion to CO₂ (water-gas shift) increases while F-T activity drops. As % conversion is increased (space velocity is lowered), the water-gas shift reaction approaches equilibrium and the oxidizing effect of H₂O addition is minimized. F-T synthesis is not as strongly inhibited under these conditions.

In contrast, at differential % conversions, the H₂O concentration in the feed is essentially the same as in the outlet. The water-gas shift reaction is not equilibrated, so the increase in H₂O concentration is accompanied by a much larger drop in activity.

DISCLAIMER

Reference in this paper to any specific commercial product, process, or service is to facilitate understanding, and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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TABLE 1. Rates and Selectivities of F-T Synthesis
(523 K, 2.06 MPa, 1/1 H₂/CO, 2 h on stream)

Product	Rate/10 ⁻⁴ mol (mol Fe · s) ⁻¹	
CH ₄	3.2	
CO ₂	0.75	
Product	Selectivity/mol (mol CH ₄) ⁻¹	
CH ₄	1.00	
ΣC ₂	0.31	
	C ₂ H ₄	.077
	C ₂ H ₆	.235
ΣC ₃	0.18	
	C ₃ H ₆	.118
	C ₃ H ₈	.064
ΣC ₄	0.095	
ΣC ₅	0.050	

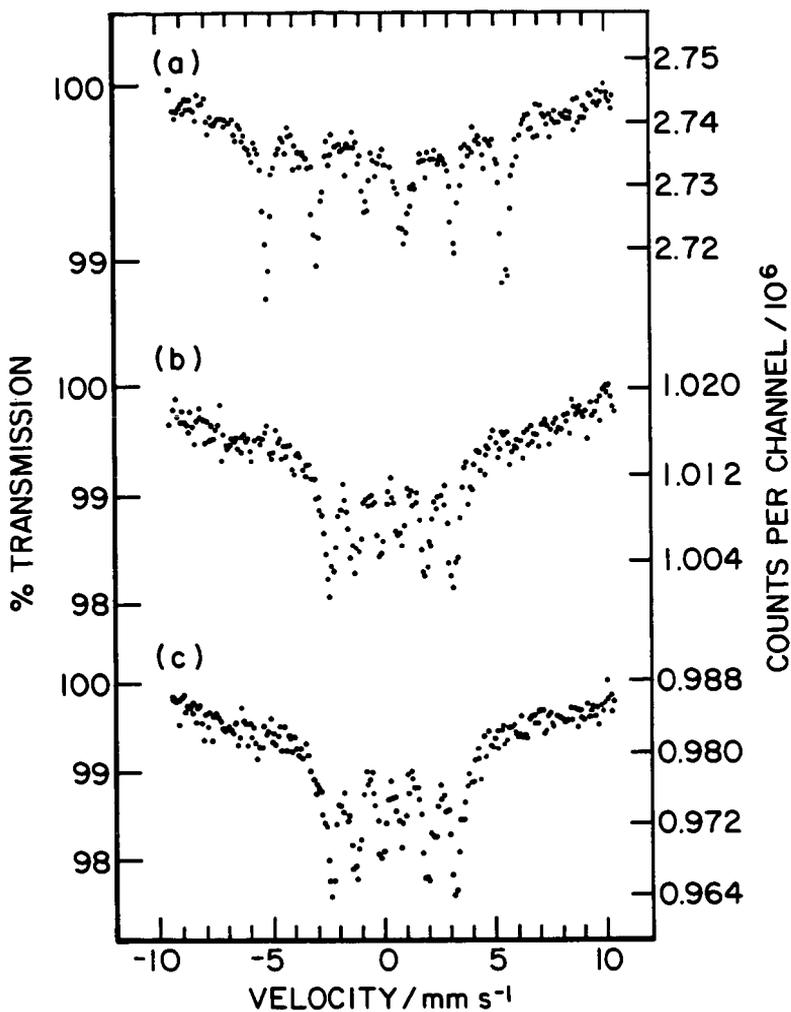


FIGURE 1. Mössbauer Effect Spectra of Fe/SiO₂

- (a) Reduced catalyst
- (b) Reduced catalyst, reacted 24 h in 1/1 H₂/CO
- (c) Reduced catalyst, reacted 24 h in 1/1 H₂/CO,
24 h in 1/1 H₂/CO + 12% H₂O