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Starting Material For Products Formed Over An Iron Fischer-Tropsch Catalyst

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Iron catalysts are particularly useful for Fischer-Tropsch (FT) synthesis when the H_2 to CO ratio of the synthesis gas is low since iron exhibits water gas shift as well as FT activity. Iron catalysts are active for Fischer Tropsch synthesis only when in the carbide state. The active iron carbide catalyst has a 1-3 nm carbonaceous layer, which can only be found on the carbided iron catalyst (no carbonaceous material is found on iron oxide particles that may be present). This paper will address the nature of the carbonaceous material that is required for product formation. The carbonaceous material is amorphous, does not require hydrogen to form, and is the starting material for FT products.

Introduction

The morphological reactions of iron Fischer-Tropsch catalysts during reaction have been well studied (1-4). The motivation for learning about phase changes during reaction is twofold. 1) Activity and selectivity may be enhanced by understanding the property-structure relationship of iron phase versus activity, and 2) attrition of the iron catalyst during synthesis gas reaction is caused primarily by the morphological changes of the catalyst during reaction as well as the deposition of carbon on the catalyst. The changes occurring during reaction are shown schematically in Figure 1. Initially, an iron FT catalyst, which may have additives and promoters such as copper, silica, and/or potassium begins as an oxide. As the freshly calcined iron is reduced (in H_2, CO or H_2/CO) it initially transforms quickly from hematite (Fe_2O_3) to magnetite (Fe_3O_4). If the catalyst is reduced further in hydrogen, α-iron is formed. If the catalyst is reduced in either CO or synthesis gas, the result is iron carbide. No hydrocarbon products are formed unless iron carbide is present (1).

From transmission electron microscopy work, it was seen that during the iron carbiding process, the individual catalyst particles are either carbide or magnetite, there is no measurable intermediate stage where a particle appears to be a mixture of both (1-3). The smaller the particle, the easier it is to form iron carbide. When a small crystallite that is attached to a larger crystal converts from oxide to carbide, it will appear to "bud" out from the larger crystal. In addition, a carbonaceous layer forms on the iron carbide. During reaction, this carbonaceous material is only found on iron carbide and not on iron oxides or reduced iron metal.

Experimental

The catalysts used in the temperature programmed reduction experiments were all precipitated iron. The catalyst used in Figure 2 was obtained from the Department of Energy, United Catalysts Inc., #1185-78-3950; L-3950 type and was 88.95% Fe2O3, 11% CuO, and 0.05% K_2O. The other iron catalysts were made by starting with iron nitrate and precipitated with a base. Potassium was added by incipient wetness using K_2CO_3 solution. The catalysts were calcined in air at 300°C and were characterized using N_2 adsorption with BET analysis. The temperature programmed reduction apparatus had a ¼ inch stainless steel tube catalyst bed. The catalyst was placed in the TPR reactor, and before TPR, the FT reaction or a 2-hour pretreatment was carried out. For some experiments, the TPR was then performed in the same reactor eliminating the need for catalyst passivation in order to be safely transferred. When the reaction occurred in the same reactor as the TPR reactor, the reaction effluent was directed towards the vent with a cold trap in line to collect wax produced by the reaction. For the potassium catalysts, the catalyst was reacted in synthesis gas ($H_2/CO=0.7/1$) at 16 atm and 215°C for 24 h. Following reaction, the catalyst was cooled to 180-200°C and was flushed with He for anywhere from 4 h to 2 days until no more hydrocarbons could be detected in the helium stream by an FID detector. For all TPR experiments, the reduction gas, 10% H_2/90% He, was introduced after the catalysts had been cooled to 100°C. The temperature was raised at 5°C/min until it reached 270°C where it remained for 1 h. Next the temperature was raised at 2°C/min until it reached the maximum temperature for that experiment (either 550° or 700°C). The catalyst was held at the high temperature for 30 minutes or until baseline was reached. An FID detector was used to measure the methane produced from hydrogen reacting with the catalyst carbon. The use of an FID detector, versus a TCD, allowed us to differentiate between desorption of water and carbon species as well as to realize the high sensitivity for hydrocarbon detection of an FID versus a TCD.

To passivate samples for TPR testing, the samples in the TPR reactor were flushed with helium at reaction temperature, cooled to room temperature and a mixture of 1% O_2 in He was slowly pulsed over the gas to make sure that were no noticeable exotherms.

Results and Discussion

The carbonaceous layer of material found deposited on the surface of iron carbide particles of the active catalyst is difficult to study because of its extreme reactivity towards oxygen. Previous work has shown that three different types of carbon can be found on a used FT catalyst (5). Carbonaceous material, amorphous carbon found on the surface of all iron carbide particles, reduces at 270°C, the carbon from iron carbide reduces from 300°-500°C and graphitic carbon reduces at 650°C-700°C. Figure 2 shows the TPR of two identical catalysts, both treated with H_2/CO at 270°C for two hours. One sample was carefully passivated before TPR, one sample was not exposed to oxygen prior to TPR. As can be seen in Figure 2, passivation, even careful passivation with 1% O_2 with no noticeable exotherm, decreases the carbonaceous material present on the catalyst.

The carbonaceous material that forms on the iron carbide during exposure to syngas appears to be a necessary precursor to FT products. Earlier work showed that the when the carbonaceous material was carefully removed from the iron carbide surface in a reducing environment, there was a five minute induction period during which no FT products were formed despite the presence of syngas at reaction temperature (6). This implied that the carbonaceous material was necessary for product formation and was, most likely, the carbon source for the hydrocarbon product. This carbonaceous material also formed only in the presence of CO. Hydrogen was not required for the formation of this material on a carbided iron.

Using TPR, we can measure the amount of carbonaceous material present during the course of the reaction. Using a combination of TPR and carbon elemental analysis, we were able to quantify the amount of carbidic and carbonaceous carbon on the reaction up to 45 hours on stream at one atmosphere with a succession of several experiments. The activity for this catalyst leveled out at 15 hours, but the carbonaceous material and the amount of carbidic carbon continued to grow as seen in Figure 2. Since the deposition of carbon on the surface of the catalyst contributes to the attrition of the catalyst by prying the catalysts apart, the continued growth of surface carbon without a commensurate increase in activity is undesired.

Potassium, which in small quantities is known to improve the selectivity of FT catalysts (larger α), is also known to decrease the activity at higher quantities. Figure 4 is the TPR of three catalysts: Fe_2O_3 with no promoters; Fe_2O_3 with 0.2% K and Fe_2O_3 with 6% K. These catalysts were all reacted at 215°C in synthesis gas ($H_2/CO = 0.7$) for 24 h at 220 psi and a TPR was performed without exposing the reacted catalyst to oxygen. The unpromoted iron catalyst is the least active catalyst. As can be seen from the TPR the amorphous carbon peak is the smallest for the unpromoted catalyst. The amorphous peak for the 0.2% potassium increases significantly over that of the unpromoted catalyst. The 6% K iron catalyst is very selective towards longer chains, but is not as active as other catalysts promoted with less potassium. The 6% K catalyst does not show a large amount of easily-reduced carbonaceous material but does show a significant amount of graphitic carbon. This increase in graphitic carbon is seen as chain length increases and activity decreases, implying that graphite formation on the catalyst may have a deactivating effect, even though it may lead to the formation of longer chains.

Conclusions

The amorphous, carbonaceous material, which is found on the surface of iron carbide particles formed during Fischer-Tropsch synthesis with an iron-based catalyst, is essential for catalyst activity. This material is probably an unsaturated carbon with little or no hydrogen present. This amorphous material appears to also lead to graphitic carbon under certain circumstances (catalysis composition, time on stream). Although this material is required to have an active catalyst, the growth of the carbonaceous material should be minimized if possible to minimize attrition caused by large carbon deposits and to minimize the possibility of deactivating graphitic formation.

Acknowledgements

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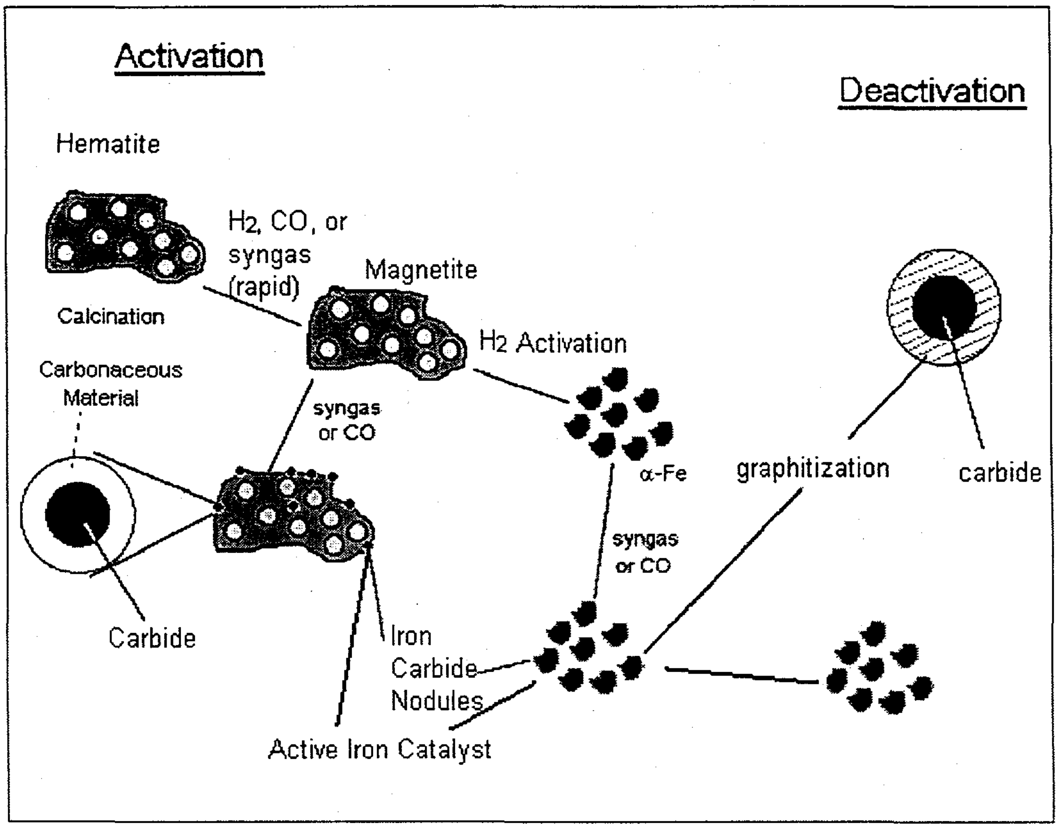

Figure 1. Schematic of morphology of iron Fischer-Tropsch catalyst during pretreatment and reaction.

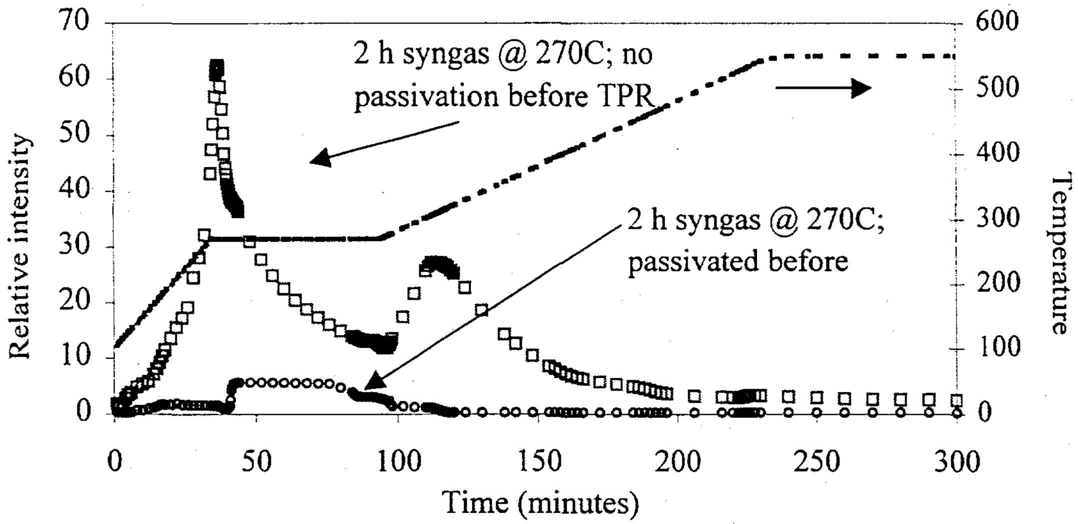

Figure 2. Temperature programmed desorption of a passivated and an unpassivated FT catalysts that had been exposed to H_2/CO ($H_2/CO=0.7$) for 2 h at 1 atm.

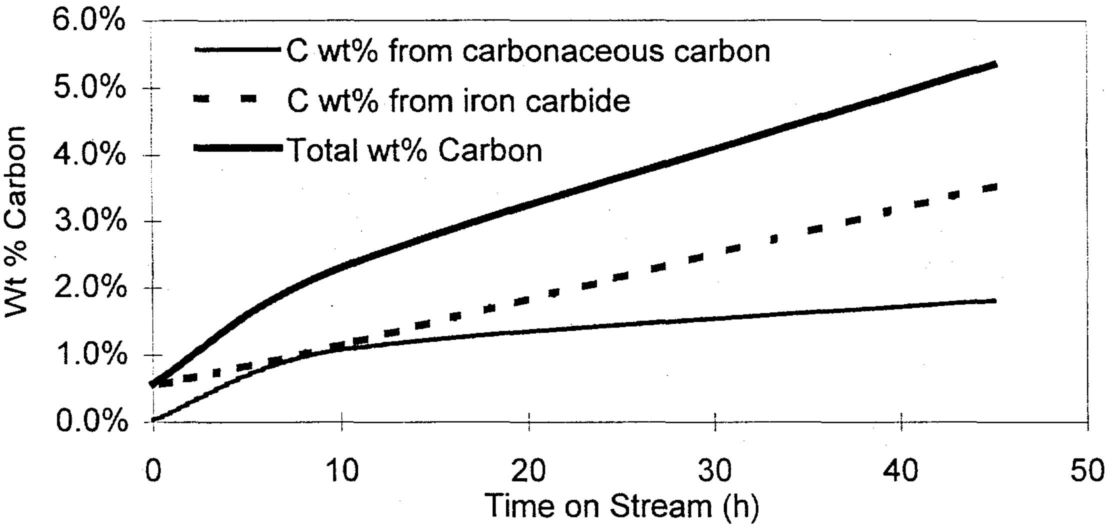

Figure 3. The weight percent carbide associated with carbidic and amorphous (carbonaceous) carbon versus time on stream (270°C, 1 atm, $H_2/CO=0.7$).

Figure 4. TPR of three iron catalysts following reaction in $H_2/CO = 0.7$ for 24 h at 220 psi. One catalysts is Fe_2O_3, the other catalysts are promoted with potassium at 0.2% and 6% K.