MÖSSBAUER STUDY OF IRON-CARBIDE GROWTH AND FISCHER-TROPSCH ACTIVITY

K.R.P.M. Rao, F.E. Huggins, G.P. Huffman, R.J. O'Brien[#], R.J. Gormley[1], and B.H. Davis[#],

341, Bowman Hall, University of Kentucky, Lexington, KY 40506-0059
[#]Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511,
[1]Pittsburgh Energy Technology Center, Department of Energy, Pittsburgh, PA 15236

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ABSTRACT: There is a need to establish a correlation between the Fischer-Tropsch (FT) activity of an iron-based catalyst and the catalyst phase during FT synthesis. The nature of iron phases formed during activation and FT synthesis is influenced by the gas used for activation. Mössbauer investigations of iron-based catalysts subjected to pretreatment in gas atmospheres containing mixtures of CO, H_2, and He have been carried out. Studies on UCI 1185-57 catalyst indicate that activation of the catalyst in CO leads to the formation of 100% magnetite and the magnetite formed gets rapidly converted to at least 90% of χ-Fe_5C_2 during activation. The χ-Fe_5C_2 formed during activation gets partly (≈ 25%) converted back to Fe_3O_4 during FT synthesis and both χ-Fe_5C_2 and Fe_3O_4 reach constant values. On the other hand, activation of the catalyst in synthesis gas leads to formation of Fe_3O_4 and which is slowly converted to χ-Fe_5C_2 and é-$Fe_{22}C$ during activation, and both carbide phases increase slowly during FT synthesis. FT synthesis activity is found to give rise to ≈ 70% (H2+CO) conversion in the case of CO activated catalyst as compared to ≈ 20% (H2+CO) conversion in the case of synthesis gas-activated catalyst.

INTRODUCTION: Pretreatment is an important step in the development of an efficient catalyst. It affects the distribution of iron phases that are formed during the pretreatment and changes that take place during synthesis. It is controlled by the type of gas, temperature (T), pressure (P) and gas space velocity (S.V.) used. The FT activity and possibly selectivity may be related to the iron phases present in the catalyst; however the role of any specific phase on the FT synthesis is not yet clearly understood.

Mössbauer characterization of two iron based catalysts,viz., UCI 1185-57 and UCI 1185-149 has been carried out with a view to identify and quantify the iron phases that are present in the activated and spent catalysts and define their influence on Fischer-Tropsch (FT) synthesis. The catalysts were activated in (i) CO or (ii) H_2/CO (syngas) and then subjected to FT synthesis.

EXPERIMENTAL:

CO-ACTIVATED UCI 1185-57 CATALYST: The UCI 1185-57 catalyst (64%Fe_2O_3/5%CuO/1%K_2O/30% Kaolin) was pretreated under CO at 270°C and then subjected to FT run conditions with a syngas of H_2/CO=0.7. Catalyst samples were withdrawn at various times during the pretreatment and FT synthesis. The phase distributions are given in Table I. The χ-Fe_5C_2 is formed rapidly during activation in CO.

SYNGAS-ACTIVATED UCI-1185-57 CATALYST: The UCI 1185-57 catalyst was preheated in He up to 200°C, then heated in H_2+CO at 280°C during the remainer of a 24 hour period and then subjected to a FT run with a syngas of H_2/CO=0.7. The catalyst samples were withdrawn at various times during pretreatment and FT synthesis. The phase distribution determined is given in Table II. As compared to the CO pretreatment, activation in synthesis gas leads to the formation and a slow increase of χ-carbide and é-carbide at the expense of Fe_3O_4. The carbides are formed in proportion to the pretreatment and synthesis duration; in addition to magnetite, some substituted magnetite and a small fraction of superparamagnetic iron oxide.

RESULTS AND DISCUSSION: As can be seen from the data in Table I, the hematite is converted into magnetite (Fe_3O_4) during heating the catalyst in CO up to 270°C in 2 hrs 43 min. The magnetite is converted into χ-Fe_5C_2 during further pretreatment under CO at 270°C; this phase represents is 90% at the end of 24hrs of pretreatment. The remaining 10% of magnetite is converted into superparamagnetic (spm) phase. Low temperature (12°C) measurement on RJO-139J has revealed that the spm phase is magnetite. During FT synthesis part of the χ-Fe_5C_2 (~25%) converted again to Fe_3O_4 and spm phase. However, after about 20 hrs of FT synthesis, the amounts of χ-Fe_5C_2 , Fe_3O_4 and the spm phases do not change further. The FT activity remains essentially constant at ≈70% H_2+CO during these changes.

The activity of the catalyst is higher when activated in CO than in synthesis gas. As compared to the CO pretreatment, the synthesis gas pretreatment leads to a slow increase in the χ-Fe_5C_2 and

é-$Fe_{2.2}C$ phases at the expense of Fe_3O_4 and the conversion ≈ 30% (H_2+CO) at the end of 24 hrs of activation. The χ-Fe_5C_2 and é-$Fe_{2.2}C$ continue to grow during FT synthesis while Fe_3O_4 continues to decrease indicating that magnetite converts into carbides, a trend which is opposite to that seen in the case of CO-activated catalyst (Fig.1a). It may be noted that there is no é-$Fe_{2.2}C$ detected in samples withdrawn during either pretreatment or FT synthesis in the case of the CO pretreated catalyst.

The (CO+H_2) conversion for the two types of pretreatment is shown in Fig. 1b. The (CO+H_2) conversion is maintained at ≈70% in the case of CO pretreated catalyst. On the other hand, in the case of synthesis gas pretreated catalyst, the conversion reaches ≈ 60% during activation but drops to ≈ 30% at the start of FT run when process conditions are changed. Some carbides were formed during activation and they continue to increase during the FT run.

We have also carried out Mössbauer investigations on the low α catalyst, UCI 1185-149 (2nd preparation) (57.2Fe/9.3Cu/0.05K) that had been subjected to pretreatment in (i) CO and (ii) H_2/CO. The pretreatment and FT synthesis conditions are given below and the results of are given in Tables III and IV.

CO-ACTIVATED UCI 1185-149 (2ND): This catalyst was pretreated in CO at 270°C, 175 psig, for 22hrs in 1.4 nL CO/g-Fe hr. FT synthesis was carried out with 10% catalyst loading in distilled Allied-Signal heavy wax at 270°C, 175psig, 2.4 nL syngas/g-Fe hr, at 1000rpm.

The activation is not complete during pretreatment. As can be observed from the Table III, the amount of χ-carbide continues to increase during FT synthesis and the FT activity decreases with increasing time on stream.

SYNGAS-ACTIVATED UCI 1185-149 (2ND): This catalyst was pretreated in H_2/CO at 280°C, 175 psig, for 14hrs in 1.4 nL CO/g-Fe hr. FT synthesis was carried out in C28 wax with 10% catalyst loading at 270°C, 175psig, 2.4 nL syngas/g-Fe hr, at 1000rpm. For this catalyst also the carbiding is not complete during pretreatment. As can be observed from the data in Table IV, the χ-carbide continues to increase during FT synthesis and the FT activity decreases with increasing time on stream, similar to the other catalyst used in this study. It may be noted that the FT activity is low even when the χ-Fe_5C_2 present in the spent catalyst is as much as 91%. This indicates that the absolute amount of χ-Fe_5C_2 present in the catalyst is not significant for FT activity.

Zarochak and McDonald [1] have carried out studies on the effects of pretreatment on the slurry phase FT synthesis activity and selectivity of a potassium-promoted precipitated iron catalyst and characterized the catalyst by Mössbauer spectroscopy measurements. They carried out two kinds of activation for the potassium promoted catalyst ((i) in CO and (ii) in syngas) were used and then the materials were subjected to FT synthesis. The catalyst activated in CO for 24 hrs gets completely converted into χ-Fe_5C_2 while the catalyst activated in syngas was converted partly to é-$Fe_{2.2}C$ during 24hrs of activation, and was completely converted to this phase only after 503 hrs of synthesis. The FT activity of the catalyst subjected to CO pretreatment was found to be higher than that found for the catalyst activated in syngas and the decrease in the FT activity with time on stream was slower for the CO pretreated sample.

References: [1] M.F.Zarochak and M.A. McDonald
Slurry-Phase Fischer-Tropsch Synthesis
6th DOE Indirect Liquefaction Contractor's Meeting
Dec 1-9, 1987, Pittsburgh Energy Technology Center, Pittsburgh

Table I†

CO-activated UCI 1185-57 catalyst:

Sample		%Fe_3O_4	%χ-carbide	Spm Phase
Preheat conditions:				
RJO139A	Heating up to 270°C under CO in 2hr 43min	100	---	--
RJO139B	2.5hr under CO@270°C	95	---	5
RJO139C	6.5hr under CO@270°C	62	26	12
RJO139D	10.5hr under CO@270°C	33	56	11
RJO139E	18.5hr under CO@270°C	12	78	10
RJO139F	24hr under CO@270°C	--	90	10

Synthesis conditions

RJO139G	6hr of synthesis	--	87	13
RJO139H	19.75hr synthesis	8	69	23
RJO139I	27.75hr synthesis	10	67	23
RJO139J	48.75hr synthesis	13	62	25
RJO139K	140 hr synthesis	16	66	18

Spm= Superparamagnetic

Pretreatment conditions: Ramped up to 270°C @ 1.5°C/min. under CO @ 175 psig. Maintained at 270°C and 175psig with CO flow for 24 hr.

Synthesis conditions: H_2/CO=0.7, space velocity=3.4nL/hr/g(Fe) T=270°C and pressure 175psig.

Table II†

(H_2+CO) activated UCI 1185-57 catalyst:

Sample	α-Fe_2O_3	Fe_3O_4	S-Fe_3O_4	χ-Carbide	é-carbide	Spm
RJO-140A taken after heating to 200°C in He in 2hr 43 min	94	--	--	2	--	4
RJO-140C 7hr in (CO+H2) Taken at 250C during heat upto 280 C 150psig,TOS*=7hr, S.V.=2.	--	93	7	--	--	--
RJO-140E Taken after reaching 280°C,TOS=11.2hr	--	85	5	--	5	5
RJO-140F taken 3.75h after reaching 280°C, TOS=15hr	--	69	5	6	13	7
RJO-140G Taken 12.5hr after reaching 280°C TOS=23.75hr	--	44	5	12	23	17
FT synthesis conditions:						
RJO-140H Taken 3.25hr after switching to synthesis conditions,S.V=2.5, 200psig, TOS=27hr	--	25	4	27	33	11
RJO-140I Taken after 26.5hr under synthesis conditions, TOS=50.25hr	--	17	--	35	42	6

TOS= time on stream

S-Fe_3O_4 = substituted magnetite

† Catalyst preparation and FT synthesis runs were carried out CAER

Table III

UCI 1185-149 2nd catalyst activated in CO:

SAMPLE	χ-Fe_5C_2	Fe_3O_4	Spm	(H 2+CO) Conv%*
CW-S3-11-D TOS=84HRS	40	37	23	84.0
CW-S3-11-J TOS=235HRS	60	30	10	67.7
CW-S3-11-M TOS=305	68	27	5	51.2

* Catalyst preparation and FT synthesis runs were carried out at PETC, Pittsburgh

Table IV

UCI 1185-149 2nd catalyst activated in syngas:

Sample	χ-Fe_5C_2	Fe_3O_4	Spm phase	(H2+CO)* conversion
CW-S3-10-ACT Activated for 14hrs	36	48	16	--
CW-S3-10-A FT run for 26hrs	84	14	2	16
CW-S3-10-B FT run for 49hrs	91	7	2	6

* Catalyst preparation and FT runs were carried out at PETC, Pittsburgh

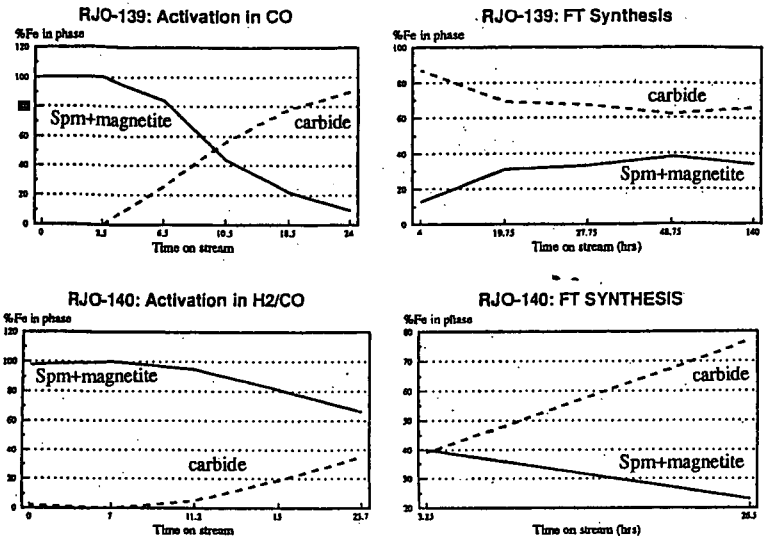

Fig.1a Variation of iron phases with time on stream

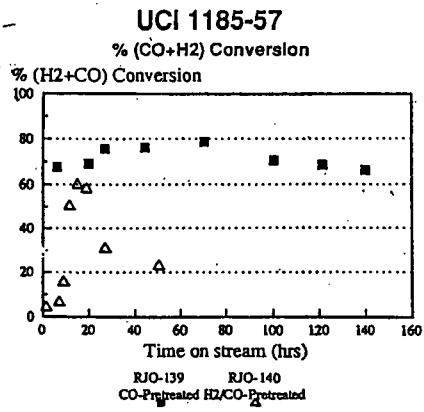

Fig.1b (H2+CO) conversion dependence on pretreatment