

ATTRITION AND CARBON FORMATION ON IRON CATALYSTS

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ABSTRACT

A serious engineering problem that needs to be addressed in the scale-up of slurry-phase, Fischer-Tropsch reactors is attrition of the precipitated iron catalyst. Attrition, which can break down the catalyst into particles too small to filter, results from both mechanical and chemical forces. This study examines the chemical causes of attrition in iron catalysts. A bench-scale, slurry-phase CSTR is used to simulate operating conditions that lead to attrition of the catalyst. The average particle size and size distribution of the catalyst samples are used to determine the effect of slurry temperature, reducing gas, gas flow rate and time upon attrition of the catalyst. Carbon deposition, a possible contributing factor to attrition, has been examined using gravimetric analysis and TEM. Conditions affecting the rate of carbon deposition have been compared to those leading to attrition of the precipitated iron catalyst.

INTRODUCTION

In the investigation of the use of slurry-phase bubble columns for exothermic synthesis gas reactions, including Fischer-Tropsch synthesis and methanol synthesis, one of the biggest challenges presented by the process is development of the catalyst. In the typical Fischer-Tropsch use of the bubble column, the catalyst is suspended in a wax and synthesis gas is bubbled up through the column. Since the Fischer-Tropsch process produces wax, the wax must be continuously extracted from the column and the catalyst must be separated from the wax for sake of purity and to keep the catalyst concentration constant within the reactor. Therefore, the catalyst must be large enough to be filtered easily from the wax, but as small as feasibly possible to enhance activity. Catalyst attrition is a major problem at low H_2/CO ratios with carbon deposition proposed as the contributing factor to chemical attrition of the catalyst.

EXPERIMENTAL

The catalyst used in this study was a precipitated and spray-dried, proprietary iron catalyst made by United Catalyst Inc. for the U.S. Department of Energy. The catalyst consisted of iron oxide and copper oxide in a ratio of about 9:1. Trace amounts of potassium oxide were also present. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) of the untreated catalyst particles showed that the samples were about 20-50 μm in diameter with a significant amount of micron and submicron fines. The larger particles were made up of angular, faceted, single-crystal grains (1-2 μm) with similar orientation that were agglomerated together. See Figure 1. The particle size of three similarly prepared Fischer-Tropsch catalysts were measured using a sedimentation-type particle size analyzer. Particle size analysis confirmed the existence of large amounts of micron and submicron fine particles. Particle size measurements are listed in Table 1.

The transmission electron microscopy was performed on a 200 kV JEOL JEM 2000FX microscope and the scanning electron microscopy utilized a Hitachi S800 microscope. Thermal gravimetric analysis (TGA) was performed using a Dupont 951 Thermalgravimetric Analyzer.

Carbon deposition was studied during pretreatment and during Fischer-Tropsch synthesis by TGA and TEM. The catalysts were pretreated in the TGA or in a microreactor for TEM work with H_2 or CO at 270°C and then reacted in H_2/CO (0.7:1) at 250°C, 275°C, and 300°C. The catalysts were pretreated for 10-14 hrs and reacted for 10-14 hrs in the TGA. In the microreactor for TEM studies, the catalysts were pretreated for 3 hrs and reacted for 3 hrs.

RESULTS

Analysis in TEM showed that activation in carbon monoxide before reaction in synthesis gas deposited more carbon on the surface of the catalyst than activation in hydrogen before reaction. The deposited carbon was amorphous in structure. All catalysts, regardless of pretreatment, appeared to have both carbide and oxide phases present after reaction. As the temperature of the synthesis gas reaction is increased, the thickness of the carbon deposited on the iron oxide

catalyst also increased. Pretreatment in CO followed by synthesis gas at 300°C showed the thickest layer of amorphous carbon. The individual grains showed signs of separation; the agglomerate was breaking up. The diffraction pattern showed a greatly diminished oxide phase while the pattern of the carbide phase suggested randomly oriented grains with loss of orientation relative to the original crystal. This breakup was also seen in catalysts pretreated in hydrogen and followed by synthesis gas at 300°C. It also appears from TEM that there is a breakdown of the parent agglomerate template at synthesis temperature greater than 275°C which causes separation of the catalyst into individual crystallites (1-2 μm in size) which leads to attrition over time. At synthesis temperatures below 275°C, oxidation of the iron catalyst showed a return of the original microstructure of the catalyst. Oxidation immediately following pretreatment of the catalyst in either H₂ or CO caused a return to the original microstructure.

TGA results confirm the increase in the amount of amorphous carbon during pretreatment in carbon monoxide and at higher synthesis reaction temperatures. In addition, TGA results indicate that the breakdown of the catalyst due to carbon deposition can occur at temperatures lower than 275°C, but at reaction times longer than those analyzed using TEM. TGA results show that regardless of the temperature of reaction or pretreatment gas, as the reaction in synthesis gas proceeds, the catalyst continues to gain weight at a rate proportional to the temperature. This continued weight gain implies continued carbon deposition leading to an eventual breakdown of the catalyst agglomerate into individual particles. The weight gain of the samples in the TGA due to synthesis reaction is shown in Table 2.

CONCLUSIONS

1. TEM analyses show that at reaction temperatures above 275°C there is significant carbon deposition and a breakdown of the parent iron catalyst agglomerate which causes the particles to disintegrate into individual crystallites (1-2 μm in size), a phenomena which would lead to attrition.
2. Pretreatment in CO followed by synthesis gas at 300°C showed the thickest layer of amorphous carbon in TEM.
3. The amount of carbon deposited increased with increasing temperature. The deposition rate was proportional to temperature.
4. TGA results show that weight gain continues at reaction temperatures below 275°C. The continued weight gain implies continued carbon deposition which could lead to eventual breakdown of the agglomerate into individual crystallites.
5. The diffraction pattern of the catalyst after reaction showed both a carbide and oxide phase. The diffraction pattern did not depend upon the pretreatment gas used.

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SAMPLE	NUMBER DISTRIBUTION MEDIAN DIAMETER	NUMBER DISTRIBUTION MODAL DIAMETER	MASS DISTRIBUTION MEDIAN DIAMETER	MASS DISTRIBUTION MODAL DIAMETER
CATALYST A	0.37 μm	0.31 μm	7.97 μm	28.85 μm
CATALYST B	0.32 μm	0.20 μm	22.22 μm	30.93 μm
CATALYST C	NOT AVAILABLE	10.0 μm	10.24 μm	21.94 μm

Table 1 - Particle size analysis of iron oxide catalysts

PRETREATMENT GAS	PRETREATMENT TEMPERATURE 250°C	PRETREATMENT TEMPERATURE 275°C	PRETREATMENT TEMPERATURE 300°C
HYDROGEN	0.045 mg/hr	0.083 mg/hr	0.11 mg/hr
CARBON MONOXIDE	0.22 mg/hr	0.68 mg/hr	1.84 mg/hr

Table 2 - Rate of catalyst weight gain during reaction in synthesis gas at 270°C. Weight gain was measured by thermal gravimetric analysis after pretreatment in either hydrogen or carbon monoxide at 250°C, 275°C, or 300°C.



Figure 1 - SEM shows that the surface of the iron catalyst consists of agglomerated smaller, angular crystallites, which are particularly susceptible to attrition.

FIGURE 1

PROPERTIES: SUPPORTED OXIDES ON STEAMED Y ZEOLITE

CAT NO/RUN NO	SUPPORT SA/PV ²	METALS, WT%, AAS			
		Co	Mn	Zr	Ru
UNION CARBIDE/65	—	8.3	1.3	1.0	—
6827-81/97	582/0.56	17.6	2.0	1.6	1.0
6827-160/110	561/0.54	26.8	2.3	1.0	0.4
6827-161/123	588/0.55	28.7	1.8	1.1	—

1. m²/g
2. cc/g

FIGURE 2

PERFORMANCE OF THE REFERENCE TO A HIGH COBALT CATALYST

RUN NO.	LOADING CAT/QUARTZ, g	MAX T °C	CO CONV, %	SELEC, MOL %		
				C ₁	C ₂	C ₂ ⁺
65	13/160	213	40	7	0.6	0
97	13/160	222	72	13	1.8	0.1

FIGURE 3

CATALYST BED TEMPERATURE PROFILES DURING RUN 97

