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Catalysis Today 106 (2005) 275–281
CATALYSIS TODAY
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Attrition studies with catalysts and supports for slurry phase Fischer–Tropsch synthesis

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Abstract

Attrition properties of several oxide supports and precipitated iron-based F–T catalyst (100Fe/3Cu/4K/16SiO_2 in parts by weight) were evaluated using ultrasound irradiation test and stirred tank slurry reactor (STSR) test under non-reactive conditions. Attrition by fracture and erosion of the iron-based catalyst was small in both types of tests and its overall attrition strength was better than that of the alumina and silica supports, which were evaluated under the same conditions. Also, attrition studies with four iron-based F–T catalysts were conducted under reaction conditions in the STSR. Catalyst of similar composition, as that used in non-reactive studies, prepared by spray drying technique had the highest attrition strength among all catalysts tested.

Keywords: Catalyst; Fischer–Tropsch synthesis; Spray drying technique

1. Introduction

Recent developments in Fischer–Tropsch (F–T) technology have been directed towards the use of slurry bubble column reactors (SBCRs) and maximization of production of high molecular weight hydrocarbons (wax). The choice of catalyst is largely dictated by nature of the carbon source material used to generate the synthesis gas. Due to its high water–gas-shift (WGS) activity, iron (Fe) is the preferred choice for F–T synthesis with synthesis gas generated by coal gasification or natural gas CO_2 reforming (H_2/CO = 0.5–1). For natural gas-derived synthesis, gas produced by partial oxidation or steam reforming (H_2/CO = 2–3), cobalt (Co)-based catalysts are the preferred choice. Cobalt-based F–T catalysts are normally prepared by impregnation of oxide supports (alumina, silica or titania) whereas Fe catalysts are not supported, but may contain small amounts of silica binder.

A critical issue in commercialization of SBCRs for F–T synthesis is the ability to separate catalyst particles from the wax, which accumulates in the reactor [1,2]. Generation of fine particles, due to particle breakup, during F–T synthesis can result in downstream filter plugging, product contamination or increased slurry viscosity leading to mass transfer limitations and eventual reactor shutdown. Catalysts for use in SBCRs need to be resistant to both fracture (breakup into smaller fragments) and abrasion/erosion (the process during which particle surface layers or corners are removed). Particle erosion is particularly serious as it generates fine particles (micron size range).

In recent years, several research groups have studied attrition properties of iron- and cobalt-based F–T catalysts [3–9]. Most of attrition studies were conducted with catalysts in an oxide form and under hydrodynamic conditions that were not representative of those encountered in a SBCR or in a stirred tank slurry reactor (STSR). Attrition tests under these conditions provide information on relative physical attrition resistance (strength) of different materials. There have been only a few studies of attrition properties in a SBCR and/or STSR under reactive conditions. Zhao et al. [4] and Wei et al. [6] studied attrition properties of supported cobalt-based F–T catalysts in a SBCR, whereas O'Brien et al. [9] conducted a similar study with supported Fe catalysts in a STSR.

Recently, we evaluated a variety of commercially available oxide supports (alumina and silica) and Fe-based

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0920-5861/$ – see front matter
doi:10.1016/j.cattod.2005.07.170

F–T catalysts (prepared by either conventional precipitation or spray drying) under non-reactive and reactive conditions in a STSR [10–13]. Here, we summarize results from these studies and present new data on attrition properties of a spray-dried Fe-based catalyst synthesized at Texas A&M University (TAMU).

2. Experimental

Catalyst preparation involved three steps: preparation of the iron–copper precursor, incorporation of binder (silicon oxide) and finally potassium impregnation. The preparation procedure was described in detail previously [14,15]. Spray drying was conducted in laboratory spray dryer manufactured by APV (APV Anhydro Lab S1), 1 m in diameter and 2.4 m in height.

Two types of tests were conducted to assess the attrition resistance of F–T catalysts: ultrasonic fragmentation test and testing in a STSR. In the ultrasonic fragmentation test, approximately, 1 g of catalyst was added to 50 ml of a 0.05 wt.% sodium hexametaphosphate solution, which was used as a dispersant. The suspension was then subjected to ultrasonic energy at an amplitude setting of 20 (100 W) at 5 min intervals using a Tekmar 501 ultrasonic disrupter (20 kHz $\pm$ 50 Hz) equipped with a V1A horn and a 0.5 in. probe tip. After different periods of exposure to ultrasonic irradiation, the particle size distribution was determined to detect the mode of particle fragmentation (fracture and/or erosion).

Attrition properties were also studied under reactive and non-reactive conditions in a STSR. Experiments were conducted in a 1 dm^3 stirred tank reactor (Autoclave Engineers). A standard six-blade turbine impeller of 3.2 cm in diameter and a stirrer speed of 1200 rpm were used in all experiments. In a typical experiment, the reactor was charged with 15–25 g of catalyst dispersed in 350–400 g of Durasyn-164 oil (hydrogenated 1-decene homopolymer). Under non-reacting conditions, nitrogen was used as the feed gas. Slurry samples were withdrawn from the STSR at different times on stream, and Durasyn-164 oil (or hydrocarbon wax produced during F–T synthesis) was removed by filtration aided by addition of a commercial solvent Varsol 18 (a mixture of liquid aliphatic and aromatic hydrocarbons).

The particle size distributions (PSDs) of catalyst samples, separated from the slurry liquid medium, were determined using either SediGraph 5100 analyzer (Micromeritics) or a Coulter counter multisizer. The PSDs obtained by both instruments provide information on two attrition mechanisms: fracture (characterized by decrease in median particle size) and erosion (appearance of fine particles).

Particle morphology was obtained using a JEOL JSM-6400 scanning electron microscope (SEM). The samples were coated with Au/Pd layer to avoid charging problems and measurements were made at an acceleration voltage of 15 kV and a working distance of 39 mm.

3. Results and discussion

3.1. Attrition properties of supports and precipitated Fe catalyst during non-reactive attrition tests

Four silica and three alumina supports were evaluated in ultrasound fragmentation tests: Grace Division 644, 654, 948 and 952 silicas and Condea/Vista aluminas (Vista B 965, HP 14 and HP 14-150). Attrition properties of four of these supports (HP 14, Vista B 965, Davison 948 and 952) were also evaluated in the STSR under simulated F–T process conditions (nitrogen at 260 °C, 1.5 MPa and gas space velocity of 3 NL/(g of catalyst h); NL: normal liter at standard temperature, 0 °C and pressure, 1 bar). Selected results are shown in Figs. 1–3. These plots provide cumulative mass distribution (i.e. mass percent of the sample that is finer than a given size) as a function of

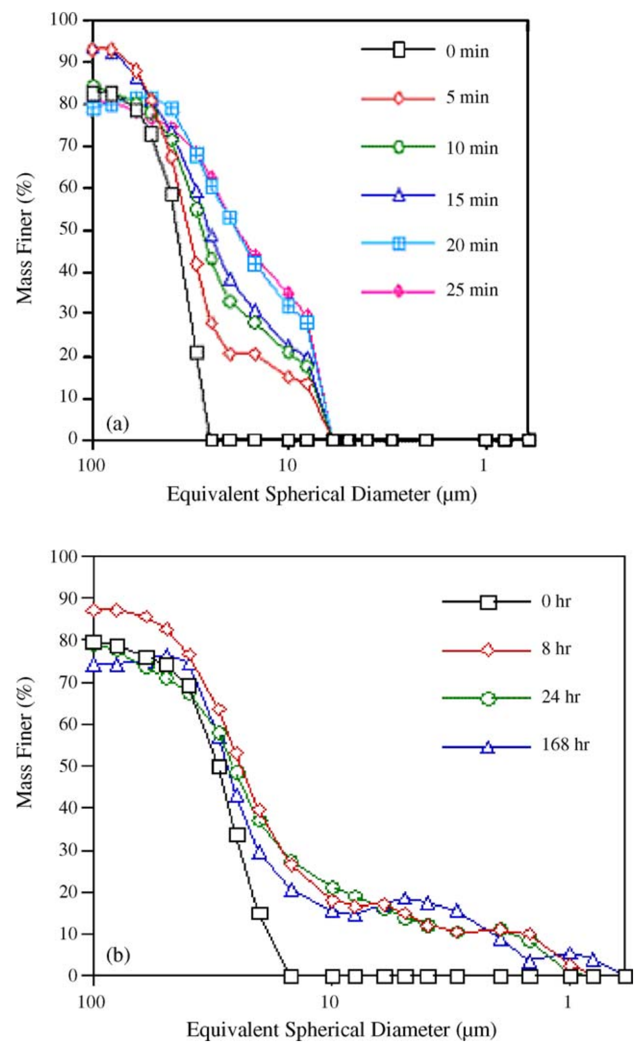

Fig. 1. PSD of Vista HP 14 alumina during: (a) ultrasound irradiation test and (b) STSR test. Reprinted with permission from Ind. Eng. Chem. Res., vol. 42, pp. 4001–4008, Attrition resistance of supports for iron Fischer–Tropsch catalysts, H.N. Pham, L. Nowicki, J. Xu, A.K. Datye, D.B. Bukur, C. Bartholomew, Copyright 2003 American Chemical Society.

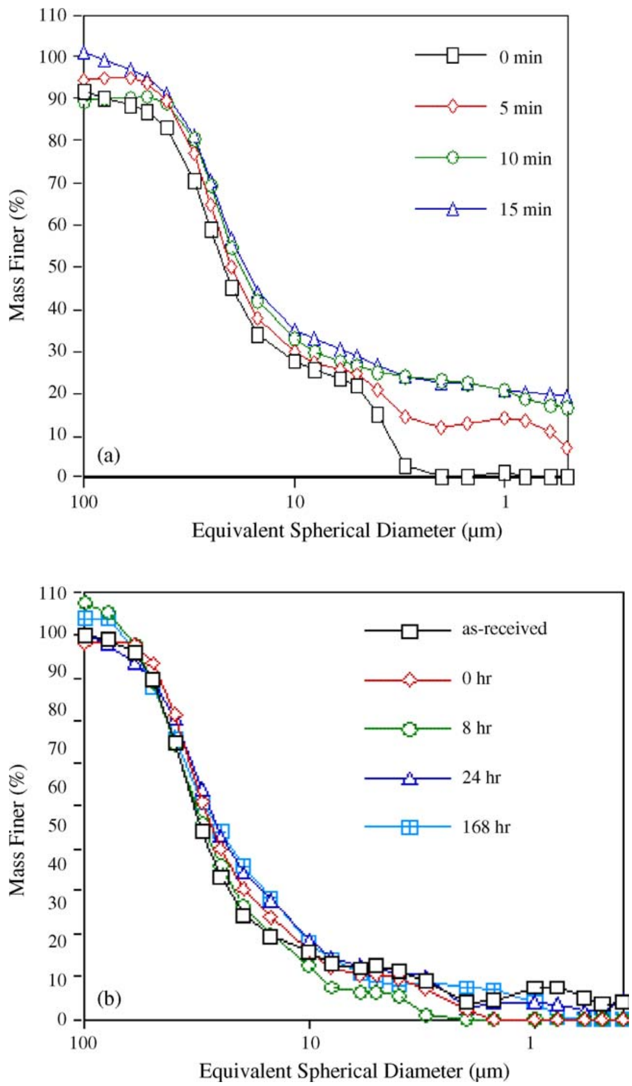

Fig. 2. PSD of Vista B 965 alumina during: (a) ultrasound irradiation test and (b) STSR test. Reprinted with permission from Ind. Eng. Chem. Res., vol. 42, pp. 4001–4008, Attrition resistance of supports for iron Fischer–Tropsch catalysts, H.N. Pham, L. Nowicki, J. Xu, A.K. Datye, D.B. Bukur, C. Bartholomew, Copyright 2003 American Chemical Society.

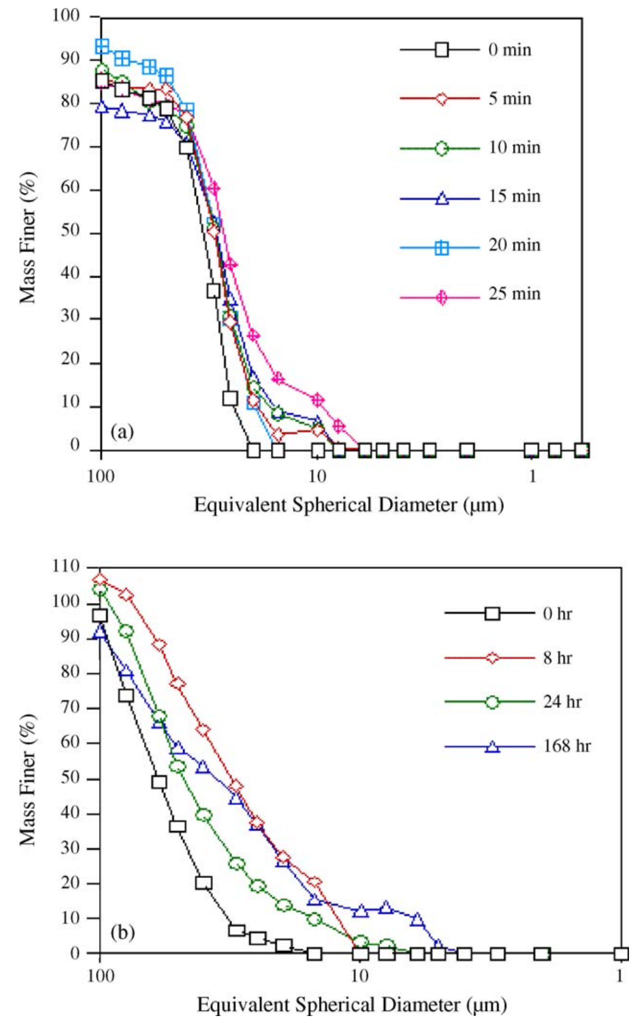

Fig. 3. PSD of Davison 948 silica during: (a) ultrasound irradiation test and (b) STSR test. Reprinted with permission from Ind. Eng. Chem. Res., vol. 42, pp. 4001–4008, Attrition resistance of supports for iron Fischer–Tropsch catalysts, H.N. Pham, L. Nowicki, J. Xu, A.K. Datye, D.B. Bukur, C. Bartholomew, Copyright 2003 American Chemical Society.

exposure to ultrasonic irradiation or mechanical agitation in the STSR. The shift in the median particle size to smaller particles with increasing time is indicative of the fracture of larger particles into smaller fragments.

Primary mechanism of particle breakup of Vista HP 14 (boehmite alumina, nearly spherical particles) is fracture, with no generation of fine particles by erosion (Fig. 1a, ultrasound irradiation). However, particle erosion was significant during agitation in the STSR (Fig. 1b). Vista B 965 alumina (boehmite, irregularly shaped particles) was more resistant to fracture than the HP 14 alumina, but the particle erosion was observed during the ultrasound irradiation test (Fig. 2a). The latter mechanism of particle breakup was also observed during the STSR test (Fig. 2b). However, the erosion was less severe relative to that in the ultrasound irradiation test. HP 14-150 (nearly spherical particles of γ-alumina) was less attrition resistant than the HP 14 alumina [10].

Davison 948 silica (nearly spherical particles) exhibited fracture during ultrasound irradiation test, but no significant erosion (Fig. 3a). However, the particle erosion was observed in the STSR test (Fig. 3b). Attrition strength of the other silica supports (Davison 952, 644 and 654) was inferior in comparison to that of Davison 948 [10].

Attrition properties of a precipitated Fe F–T catalyst with nominal composition $100Fe/3Cu/4K/16SiO_2$ (in parts by weight) were studied by ultrasound irradiation method and STSR test under simulated F–T conditions for comparison with alumina and silica supports. Results from these two tests are shown in Fig. 4. As can be seen from this figure, the extents of fracture and generation of fine particles (particles less than 5 μm in diameter) were relatively small. The

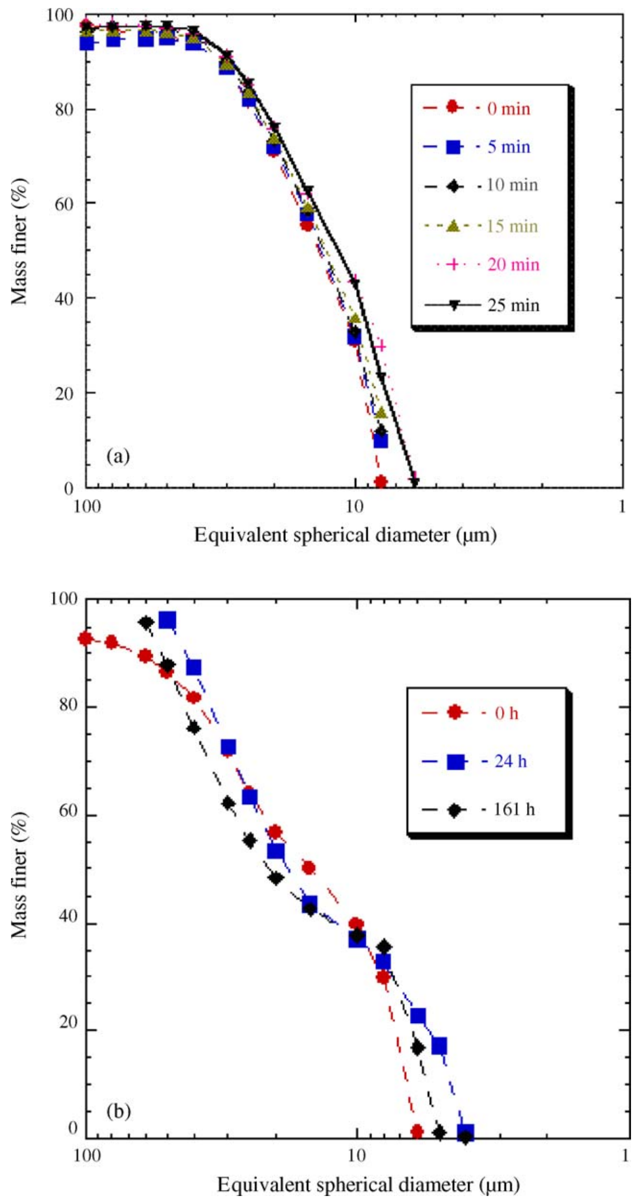

Fig. 4. PSD of $100Fe/3Cu/4K/16SiO_2$ catalyst during: (a) ultrasound irradiation test and (b) STSR test. Reprinted from Appl. Catal. A, 266, D.B. Bukur, V. Carreto-Vazquez, H.N. Pham, A.K. Datye, Attrition properties of precipitated iron Fischer–Tropsch catalysts, pp. 41–48, Copyright 2004, with permission from Elsevier.

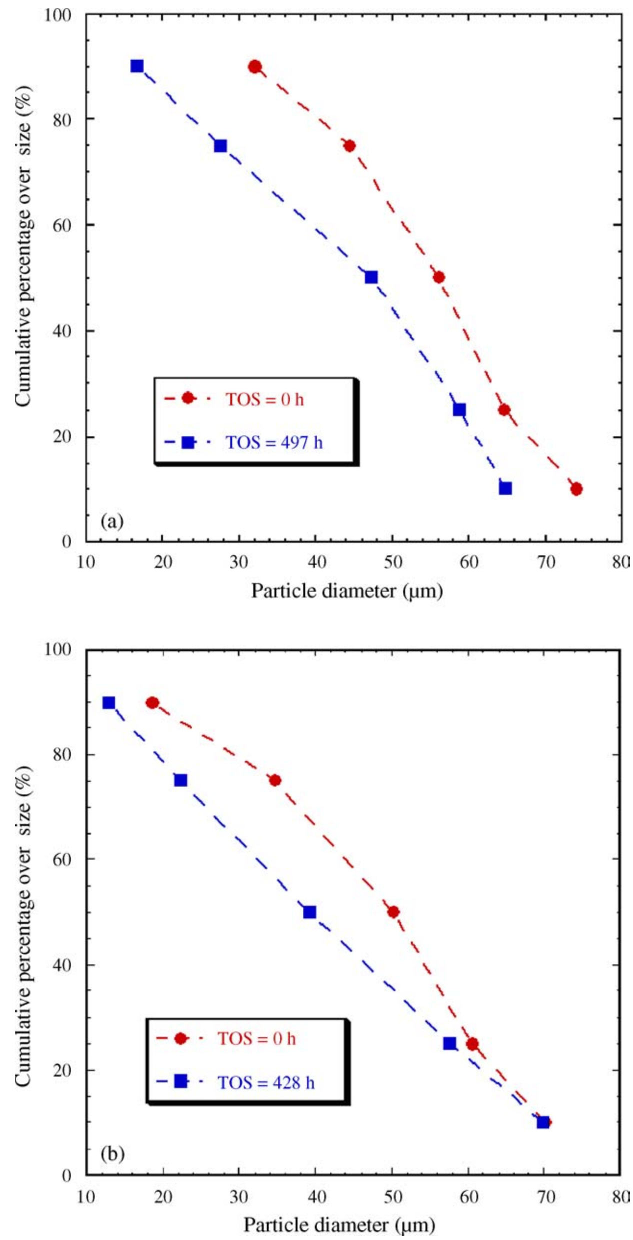

Fig. 5. PSD of precipitated Fe catalysts before and after F–T synthesis in the STSR: (a) $100Fe/3Cu/5K/16SiO_2$ and (b) Ruhrchemie ($100Fe/4.3Cu/4.1K/25SiO_2$). Reprinted from Top. Catal. 32 (2005) pp. 135–141, Attrition studies with precipitated iron Fischer–Tropsch catalysts under reaction conditions, D.B. Bukur, W. Ma, V. Carreto-Vazquez, Copyright 2005, with permission from Springer Science and Business Media.

attrition strength of this material appears to be higher than that of the various support materials tested in our laboratory.

3.2. Attrition tests in a STSR under reactive (F–T synthesis) conditions

Attrition properties of four representative Fe F–T catalysts were determined during reaction studies in the STSR reactor. Two of the catalysts were prepared by conventional precipitation method (commercial Ruhrchemie catalyst and $100Fe/3Cu/5K/16SiO_2$ catalyst prepared at TAMU), which produces irregularly shaped particles and the other two by spray drying method, which yields nearly spherical particles. The Ruhrchemie catalyst ($100Fe/4.3Cu/4.1K/25SiO_2$ in pbw) was used initially in commercial fixed-bed reactors at Sasol in South Africa.

Catalysts were sieved to 170–325 mesh size (45–90 μm) prior to loading into the STSR filled with Durasyn-164 oil. Catalysts were reduced in situ with CO ($H_2/CO = 2/3$ in the case of Ruhrchemie catalyst) at 280 °C, 0.8 MPa, 3 NL/(g of catalyst h) for 8 h. After the reduction, the catalysts were tested at 260 °C, 1.5 and 2.2 MPa in a CO rich synthesis gas

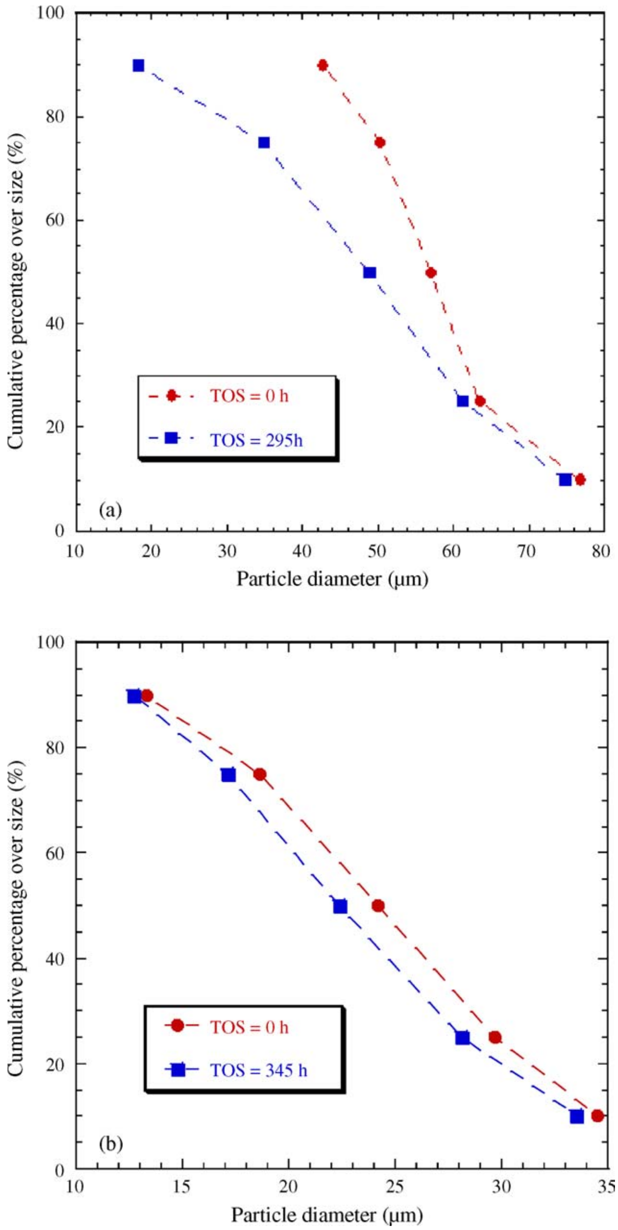

Fig. 6. PSD of spray-dried Fe catalysts before and after F–T synthesis in the STSR: (a) 100Fe/5Cu/6K/24SiO_2 (reprinted from Top. Catal. 32 (2005) pp. 135–141, Attrition studies with precipitated iron Fischer–Tropsch catalysts under reaction conditions, D.B. Bukur, W. Ma, V. Carreto-Vazquez, Copyright 2005, with permission from Springer Science and Business Media); (b) 100Fe/3Cu/5K/16SiO_2.

(H_2/CO = 2/3) for several hundreds of hours on stream. Slurry samples were withdrawn from the reactor before the reduction (time on stream, TOS = 0 h) and at the end of the test (295–97 h). After separation of the catalyst, particles from the slurry medium PSD was measured by Coulter counter multisizer.

Results from PSD measurements are shown in Figs. 5 and 6. These plots show volumetric percent of the sample that is greater than a given particle diameter. Shift in PSD to the left (relative to data at TOS = 0 h) is due to reduction in particle size by fracture and erosion. The two precipitated catalysts

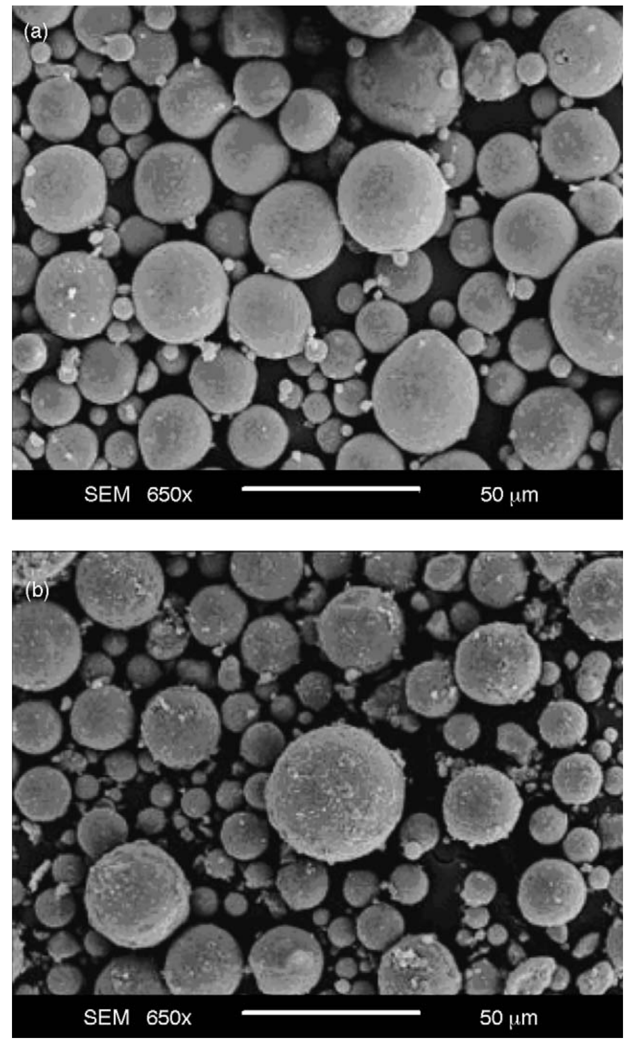

Fig. 7. SEM images of spray-dried 100Fe/3Cu/5K/16SiO_2 catalyst (a) before F–T synthesis and (b) after 345 h of F–T synthesis in the STSR.

(Fig. 5) and the 100 e/5 u/6 /24 SiO_2 catalyst (Fig. 6a), prepared by spray drying of dry precursor [13], had experienced moderate particle size reduction. The extent of particle reduction was very small with spray-dried 100 e/3 u/5 /16 SiO_2 catalyst (Fig. 6b).

The latter catalyst was prepared using silica binder as the silica source, and the particles withdrawn from the reactor at TOS = 0 h were spherical with smooth texture (Fig. 7a). SEM micrograph of the catalyst particles after 345 h on stream shows that they have retained their spherical shape (Fig. 7b). The other three catalysts were not spherical, but their morphology did not change significantly after relatively long exposure to the synthesis gas in the STSR [13].

From the PSD measurements, one can calculate parameters that quantify the extent of particle size reduction. The most commonly used parameters to characterize mean value of PSD are: Sauter mean diameter ($d_{3,2}$) and volumetric mean diameter ($d_{4,3}$). Reduction in either the Sauter mean or volumetric mean diameter reflects the

Table 1
Results from attrition resistance measurements in the STSR under reaction conditions

Catalyst ID	TOS = 0 h			TOS = t			% change		
	$d_{3,2}$ (μm)	$d_{4,3}$ (μm)	F (<10 μm)	$d_{3,2}$ (μm)	$d_{4,3}$ (μm)	F (<10 μm)	$\Delta d_{3,2}$	$\Delta d_{4,3}$	ΔF
A	47.1	53.1	0.3	30.8	43.2	3.0	34.6	18.6	2.7
B	20.6	24.1	4.1	19.2	22.8	4.8	6.8	5.4	0.7
C	34.1	46.9	3.3	25.8	40.2	5.9	24.3	14.3	2.6
D	48.3	57.3	1.0	33.1	48.1	3.3	31.5	16.1	2.3

Catalyst A (100Fe/3Cu/5K/16SiO_2, conventional precipitation); Catalyst B (100Fe/3Cu/5K/16SiO_2, spray-dried); Catalyst C (100Fe/4.3Cu/4.1K/25SiO_2, conventional precipitation); Catalyst D (100Fe/5Cu/6K/24SiO_2, spray-dried); t = 497 h (A); 345 h (B); 428 h (C) and 295 h (D).

particle size reduction in general and is weighted toward the larger particles. On the other hand, increase in fraction of fines generated is a critical parameter for slurry phase reactor applications, since difficulties with catalyst/wax separation and product contamination are caused by small particles. Reduction in the Sauter (or volumetric mean) diameter is expressed as percentage of the initial value: $\Delta Y = [(Y\,(0\text{ h}) - Y(t\text{ h}))/Y\,(0\text{ h})] \times 100$; where: $Y = d_{3,2}$ or $d_{4,3}$ and t = test duration in hours. Increase in fraction of particles smaller than 10 μm, is calculated as: $\Delta F = F(t\text{ h}) - F\,(0\text{ h})$, where F represents a fraction of particles less than 10 μm. Results for all four catalysts are given in Table 1, together with their designations (ID code).

Overall reduction in the catalyst particle size, measured by changes in the Sauter mean and volumetric mean diameter, was moderate and generation of particles smaller than 10 μm was small (0.7–2.7%) for all four catalysts tested in the STSR under reaction conditions. Catalyst B prepared by spray drying (micro-spherical particles) had the highest attrition strength (reduction in volumetric mean diameter of 5.4 and 0.7% increase in fraction of fine particles). Its attrition strength was better than that of Catalyst A, which has the same nominal composition but was prepared by conventional precipitation method (irregularly shaped particles). Catalyst C (precipitated Fe obtained from Ruhrchemie AG and prepared by conventional precipitation) and Catalyst D (spray drying of material prepared by conventional precipitation) have similar compositions (amounts of Cu and K promoters and SiO_2) and their attrition strengths were comparable (Table 1). Catalyst D particles, although prepared by spray drying, were not spherical and its attrition strength was similar to that of catalysts prepared by conventional precipitation (Catalysts A and C).

Detailed information on attrition properties of F–T catalysts during slurry phase operation is rather limited. Davis and co-workers at the University of Kentucky [8,9] reported that spray-dried Fe F–T catalysts (in the form of micro-spherical particles) easily disintegrate during stirring in a STSR. Apparently, these catalysts are much weaker than precipitated Fe catalysts prepared in our laboratory (both catalysts prepared by conventional precipitation and spray-dried catalysts). O'Brien et al. [9] studied attrition behavior of several supported Fe F–T catalysts under reaction conditions in the STSR. Based on qualitative examination of SEM images of catalysts before and after F–T synthesis, they concluded that some of these materials showed no evidence of attrition.

Goodwin and co-workers [4,6] studied attrition behavior of several alumina and silica-supported Co catalysts in a small SBCR (2.5 cm in diameter). They reported reductions in the volumetric mean particle diameter after 240 h of F–T synthesis. Reductions in the volumetric mean diameter ranged from 1.6 to 8.4% in experiments with alumina-supported catalysts (Catapal-B from Condea/Vista) and 8.1–14.2% in experiments with silica-supported catalysts (Davison 952 silica). Catalysts evaluated in our study under reaction conditions had experienced reduction in the mean diameter of 5.4–18.6%, which are somewhat higher than those reported by Goodwin and co-workers (1.8–14.2%). However, it should be noted that our catalysts were exposed to more severe hydrodynamic conditions in the STSR than those tested in a SBCR, and that test durations were longer (295–497 h) than in the SBCR tests (240 h). Also, quantitative comparisons between our results and those of Goodwin and co-workers [4,6] are difficult to make due to the fact that Goodwin and co-workers employed different method of PSD measurements (laser beam technique) and they did not account for particles smaller than 10 μm (due to their loss through a metal filter during the SBCR operation).

4. Conclusions

Attrition properties of precipitated Fe F–T catalyst (100Fe/3Cu/4K/16SiO_2) were evaluated using ultrasound irradiation test and STSR test under non-reactive conditions. Catalyst attrition by fracture and erosion was small in both types of tests, and attrition strength of this catalyst was higher than that of several alumina and silica supports, which were evaluated under the same conditions.

Attrition properties of four Fe F–T catalysts prepared by either conventional precipitation or spray drying were evaluated in the STSR under F–T synthesis conditions. Catalyst B prepared by spray drying (micro-spherical particles) had the highest attrition strength (reduction in volumetric mean diameter of 5.4 and 0.7% increase in fraction of fine particles). The attrition indices for the other three catalysts were: reduction in the mean diameter of 14.3–18.6% and increase in fraction of fine particles 2.3–2.7%.

Acknowledgements

This work was supported by the US Department of Energy under Grants DE-FG26-98FT40110 and DE-FG26-00NT40822. The author is grateful to Drs. L. Nowicki, W. Ma, H.N. Pham (University of New Mexico) and Mr. V. Carreto-Vazquez who performed all experiments, Dr. A.K. Datye (University of New Mexico) for PSD measurements of various supports, S. Gregory (Food and Protein Research Center at TAMU) for use of a spray drier, and Microscopy & Imaging Center at TAMU for assistance with SEM measurements.

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