Appendix A
Improving the Attrition Resistance of Slurry Phase Heterogeneous Catalysts

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Abstract

Slurry phase heterogeneous catalysts for processes such as Fischer-Tropsch synthesis must exhibit a high degree of attrition resistance. The precipitated Fe-Cu catalyst used for F-T synthesis is quite weak, in its as-prepared state. Spray-drying yields spherical particles which show some improvement in attrition resistance. However, the formation of fines (< 5 μm) in this powder shows that it is not suitable as a slurry phase catalyst. In this paper we report on the use of silica binders to improve the strength of spray-dried agglomerates. The attrition resistance was measured using ultrasonic fragmentation followed by sedigraph particle size analysis. The attrition strength of the iron oxide catalyst agglomerates was compared to that of a commercial alumina powder, which was used as a reference material. The role of calcination (before or after spray-drying) and the method of silica binder addition (before or after spray-drying) was investigated.

Introduction

This work is directed towards synthesis of iron oxide catalysts for Fischer-Tropsch synthesis, a reaction that allows conversion of coal or natural gas into liquid fuels. For coal conversion, Fe catalysts are preferred since they can operate at the lower H_2/CO ratio in coal-derived syngas. These iron oxide catalysts are prepared by co-precipitation of iron and copper salts. Potassium is used as a promoter to improve catalyst selectivity. The preferred reactor type is a slurry phase bubble column which requires spherical catalyst agglomerates 50-70 μm in diameter. Since the products of F-T synthesis are liquid hydrocarbon waxes, separation of product from the catalyst requires that the catalyst agglomerates be attrition resistant.

In a previous study (1), we reported a comparison of two approaches used for measuring the attrition strength of catalyst agglomerates. Ultrasonic fragmentation coupled with particle size distribution measurements was found to be more sensitive to differences in catalyst strength than the conventional approach involving uniaxial compaction. Using the ultrasonic fragmentation approach (2,3), we were able to show that a plate-like kaolin binder did not impart any additional strength to a precipitated iron catalyst, that was otherwise weak and easily susceptible to attrition.

As revealed by TEM, the kaolin and Fe F-T catalyst occurred as two distinct phases, and that both had plate-like structures which did not connect to create strong interlocking forces between them.

We have therefore explored the role of other binder morphologies to provide improved attrition resistance for Fe F-T catalysts. We have worked with silica because it is the preferred choice as a support for obtaining better product selectivity and activity in F-T synthesis. We report here a study of factors that determine the strength of spray-dried agglomerates. When agglomerates are formed, binders are often used for the process. Binders play several roles, such as in controlling the release of drugs via a coating process, or in strengthening brittle materials. For example, Nikolic *et al*. (4) used a sol-gel silica coating (5) to strengthen an alumina substrate.

Several factors can have an effect on the strengths of agglomerates. Horisawa *et al*. (6) found that for their sample powders with polymer binders, the surface polarities of both powders and binders, as well as the degree of polymerization of the binder were important factors in determining the strength of granules. Bortzmeyer *et al*. (7) investigated three different $CaCO_3$ powders and found that no correlation was observed between the attrition rate and the mechanical properties (tensile strength, fracture energy, etc.). However, a correlation between attrition rate and surface roughness was observed. The factors we have explored in this study include the method of silica addition, and the effect of calcination on the strength of spray-dried agglomerates prepared from precipitated iron oxide.

Experimental

A precipitated Fe-Cu catalyst in its wet form (labeled PRFECU-ED20-124) was used for the experiments. The starting materials were the nitrates of Fe and Cu, and NH_4OH. Solutions of Fe-Cu nitrate and NH_4OH were mixed in a continuous flow through mixer causing the iron hydroxide to precipitate out. The product catalyst was discarded until the pH was between 6.8 and 7.2. The catalyst was then collected in a filter funnel, and the filter cake was pumped down to being wet but not cracked. Samples of the filtrate were obtained; a pH and brown ring test were performed for each sample to ensure that the pH remained near 7.0 and that traces of NH_4OH were removed from the catalyst, respectively. The cake was removed and then resuspended in hot water. After filtering the slurry, samples of the filtrate were obtained for pH and brown ring testings. After the brown ring test was negative, the filter cake was pumped moist. Finally, once the precipitated Fe-Cu catalyst was dry enough to remove it off the filter, the catalyst was suspended in deionized H_2O.

In a typical run, 100 ml of the precipitated Fe-Cu catalyst was ultrasonicated at an amplitude of 20 for 2 min to break up any loose agglomerates. A Tekmar 501 ultrasonic disrupter (20 kHz $\pm$ 50 Hz) equipped with a V1A horn and a ½" probe tip was used for the ultrasonication process. The sample was then mixed with 11 ml of potassium silicate solution (KASIL$^®$#1; PQ Corp.), with a silica loading of 25 wt%. Dilute Nitric acid (0.1 N; J.T. Baker) was added dropwise while the slurry was stirred until the pH was about 7. The mixture was stirred for a further 20 min and then filtered using a Buchner funnel. Deionized water was then added to prepare 250 ml of slurry. A Buchi 190 Mini Spray Dryer was used to spray-dry the slurry. The inlet temperature of the spray dryer was over 200°C with the outlet being maintained over 100°C. The powder was collected in

a cyclone trap and then analyzed using a Sedigraph 5100 particle size analyzer and scanning electron microscope (SEM).

In another run, 200 ml of PRFECU-ED20-124 was ultrasonicated at an amplitude of 20 for 2 min. Deionized water was then added to prepare 250 ml of slurry. The slurry was spray-dried, and the dried Fe-based catalyst was collected in a cyclone trap. The sample was then mixed with 11 ml of potassium silicate solution. The procedure and subsequent analyses were the same as in the previous run.

Other runs involved performing the same procedure from the first run, followed by calcining the sample at 320°C to see if there was any additional strength imparted to the sample, or calcining the SiO_2-containing sample first followed by adding deionized water to prepare 250 ml of slurry, and then spray-drying the slurry to see if there was any additional strength imparted to the sample.

Our synthesized precipitated Fe F-T catalysts were then compared to a VISTA alumina powder (VISTA-B-965-500C). The starting alumina from VISTA was sieved and calcined in air at 500°C. While this alumina is not prepared by spray-drying, it is useful as a reference material since it was being considered as a support for Fe-Cu catalysts in the work of McDonald *et al.* (8).

Results and Discussion

Figure 1 shows a cumulative mass distribution plot of mass finer (%) vs. equivalent spherical diameter for the precipitated Fe-Cu catalyst, as-prepared. Also shown in this plot is the influence of ultrasonic irradiation on the particle size distribution. This catalyst is weak with a broad particle size distribution. Both fracture and erosion occur during ultrasonic fragmentation, and the generation of fine particles below 5 μm may not be acceptable for slurry F-T reactors. Figure 2 shows a cumulative mass distribution plot for the same catalyst which was spray-dried, but without a binder. Spray-drying improves the attrition resistance of the Fe catalyst, and there is a more uniform particle size distribution. However, ultrasonication causes an increase in the fraction of particles below 5 μm, suggesting that the catalyst is still not resistant to erosion.

Figure 3 shows a cumulative mass distribution plot for a precipitated Fe-Cu catalyst/potassium silicate mixture that was directly spray-dried. The addition of the SiO_2 binder further improved the attrition resistance of the catalyst, and now we see little of the fine particles below 5 μm after 25 min of ultrasonic irradiation. Some of the particles between 5 μm and 10 μm may have re-agglomerated, as indicated by the shift in curves within this particle size range. The median particle size (~8 μm) is smaller than that desired for a commercial F-T process (50-70 μm); however, this represents a limitation of our bench-top spray dryer. Figure 4 shows a scanning electron microscope (SEM) image of the spray-dried agglomerates. It was found that the number average particle diameter from this image was smaller than the median size determined by sedigraph particle size analysis. This was traced to a bias in the SEM sampling procedure, which skews the particle size distributions to smaller sizes. Smaller size particles tend to stick to the carbon tape on the SEM stub more favorably than the larger size particles. The larger particles are more likely to come off the carbon tape when the SEM stub is shaken to remove excess particles. To verify the presence of larger particles, the catalyst was first sieved using a standard testing sieve having pore openings of 38 μm, and the remaining large size particles were used for the SEM analysis. Figure 5 shows an SEM image of the same catalyst. Large size particles are seen in Fig. 5 that are not

seen in Fig. 4. The larger particles in Fig. 5 are less spherical than the smaller particles in Fig. 4, probably due to the limitations of our spray dryer.

Figure 6 shows a cumulative mass distribution plot for a precipitated Fe-Cu catalyst/potassium silicate mixture that was spray-dried and then calcined at 320°C. Figure 6 is similar to Fig. 3, suggesting that calcination did not appear to significantly improve the strength of the catalyst. Figure 7 shows an SEM image of the spray-dried/calcined catalyst. These particles have rougher surfaces after calcination than those shown in Fig. 3. The median particle diameter for the spray-dried/calcined catalyst, according to Fig. 6, was smaller than that for the spray-dried catalyst. It is possible that the particles collected after spray-drying were not completely dried. The "wet" particles would lose some water during calcination, shrinking the catalyst particles. Removal of the water present in the catalyst is essential before the Fe F-T catalyst is activated for use in a reaction run. However, it is also important that the calcination temperature be low enough that no adverse chemical reactions (formation of interfacial silicate phases) occur between the Fe F-T catalyst and the SiO_2 support.

Figure 8 shows a cumulative mass distribution plot for a precipitated Fe-Cu catalyst/potassium silicate mixture that was first calcined at 320°C in its dried state before spray-drying. No erosion occurred below 5 μm after 25 min of ultrasonic fragmentation. For particle sizes between 10 μm and 100 μm, the amount (percentage) of fine particles generated were less than those from the other two catalysts, suggesting that the particle size of this catalyst was larger than the other catalysts. For example, the mass % of particle sizes finer than 20 μm was 62% for the catalyst that was calcined before spray-drying, whereas the mass % of particle sizes finer than 20 μm was 94% for the catalyst that was spray-dried without calcination. Figure 9 shows an SEM image of the calcined/spray-dried catalyst. The particles were not spherical after spray-drying, but instead were irregular shaped. The irregular shapes must have resulted when the catalyst was first calcined, with the particle shapes being preserved during spray-drying.

Figure 10 shows a cumulative mass distribution plot for a precipitated Fe-Cu catalyst that was initially spray-dried, potassium silicate solution added, and then spray-dried again. Some erosion was observed in this catalyst, suggesting that SiO_2 addition after initial spray-drying may not be as effective as the silica added before the powder is spray-dried. Figure 11 shows an SEM image of the catalyst. These particles looked similar to those in the catalyst that was spray-dried after SiO_2 addition (Fig. 4). It is clear that examination of the external structure alone is not sufficient for determining the strength of the catalyst.

Figure 12 shows a cumulative mass distribution plot for a VISTA alumina, which was used as a reference sample for comparison with the precipitated Fe F-T catalysts. The strength of this alumina was comparable to the catalyst shown in Fig. 9. However, both the VISTA alumina and the catalyst where silica was added after spray-drying (Fig. 10) were weaker than the other precipitated catalysts.

SEM image (Figure 13) of the VISTA alumina showed that it consisted of irregularly shaped agglomerates, since this alumina did not come from a spray-drying step. The morphology of the calcined catalyst (Fig. 9) is similar to that of the VISTA alumina; however, the calcined catalyst appears to be more attrition resistant than the alumina, since it shows no erosion during ultrasonic fragmentation. It is evident that attrition strength depends on the method of agglomerate

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formation, the particle-binder interaction, primary particle size and shape, as well as subsequent processing such as calcination temperature.

Although the calcined/spray-dried catalyst is not spherical, it is comparable in strength to the spray-dried and spray-dried/calcined catalysts. This suggests that the strength does not depend on the shape of the particles. However, particle shape may be very important for other reasons such as slurry hydrodynamics. Furthermore, in a stirred tank reactor, more erosion is likely to occur for non-spherical particles than for spherical particles, and the use of spray-dried particles may be an advantage. In future work, we plan to study the attrition behavior of these precipitated catalysts in various reactor configurations: stirred tank, bubble column, etc.

Table 1 gives surface areas for the precipitated Fe F-T catalysts, using a BET N_2 adsorption analyzer. Of the precipitated catalysts, the calcined/spray-dried catalyst had the highest surface area while the catalyst where silica was added after spray-drying had the lowest surface area. This is reasonable if the silica tends to block access to the interior pores of the catalysts. Catalysts with high surface areas would generally be preferred since the reaction takes place at the gas-solid interface. However, in the case of these iron oxide catalysts, they have to be first transformed into reduced iron phases, such as iron carbide which is thought to be the active phase for this reaction (9). The phase transformations accompanying catalyst activation result in a chemical attrition of the catalyst (10) which needs to be considered when characterizing the attrition properties of these catalysts. This will be the subject of future work.

Summary

The precipitated Fe-Cu catalyst, as-prepared, was weak compared to the same catalyst which was spray-dried. Spray-drying improved the attrition resistance of the Fe F-T catalyst. We have explored the role of silica binder addition and calcination to further improve the attrition resistance of these catalysts. The precipitated catalysts were compared to a VISTA alumina, representing a commercially available reference sample. Our results show that addition of the SiO_2 binder provided further attrition resistance for the Fe F-T catalysts. Cumulative particle size distributions showed that the alumina and the Fe catalyst that was initially spray-dried before addition of SiO_2 were comparable in strength, but both were weaker than the spray-dried, calcined/spray-dried, and spray-dried/calcined catalysts. Calcination of the catalyst after spray-drying did not impart any additional strength to the catalyst.

SEM images of the VISTA alumina support and the calcined/spray-dried catalyst showed that the agglomerates were irregular shaped. However, the calcined/spray-dried catalyst was more attrition resistant than the alumina support. The attrition strength must therefore depend on the method for synthesizing Fe F-T catalysts. Factors which may improve the attrition strength are particle-binder interaction, primary particle shape and size of the precipitated Fe-Cu precursor, type and morphology of binders, and calcination temperature. We found that the attrition strength as measured via ultrasonic fragmentation does not depend on the shape of the Fe F-T catalyst agglomerates being tested. On the other hand, the shape of the catalyst may be important when the catalyst is used in a slurry bubble-column reactor, since it may determine the slurry hydrodynamics.

Acknowledgments

References

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Table 1. BET surface area of the precipitated Fe F-T catalysts.

SAMPLE	BET SURFACE AREA (m^2/g)
PRFECU-ED20-124 + SiO_2 (calcined; spray-dried)	224.3
PRFECU-ED20-124 + SiO_2 (spray-dried)	127.5
PRFECU-ED20-124 + SiO_2 (spray-dried; calcined)	158.7
PRFECU-ED20-124 + SiO_2 (spray-dried PRFECU precursor, addition of binder, spray-dried mixture)	81.3
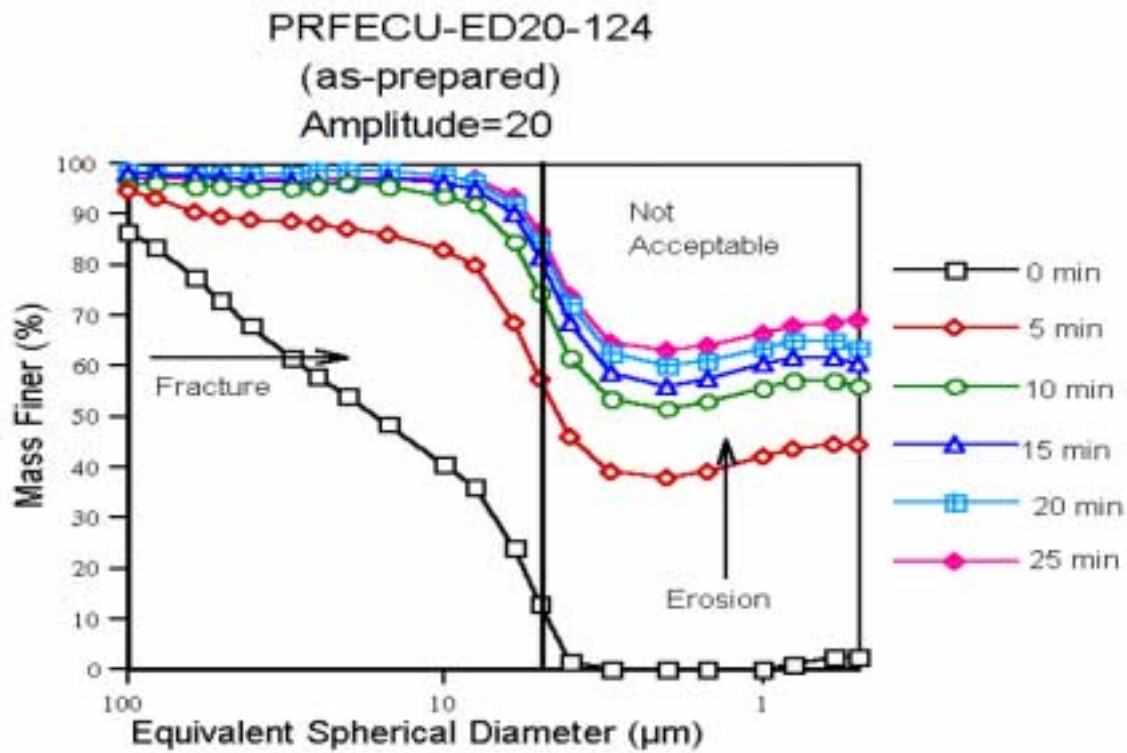
Figure 1.   Sedigraph particle size distribution of a precipitated Fe, Cu catalyst, as-prepared. There is both fracture and erosion of particles after 25 min of ultrasonic fragmentation, indicating that the catalyst is weak. Furthermore, the catalyst has a broad particle size distribution.
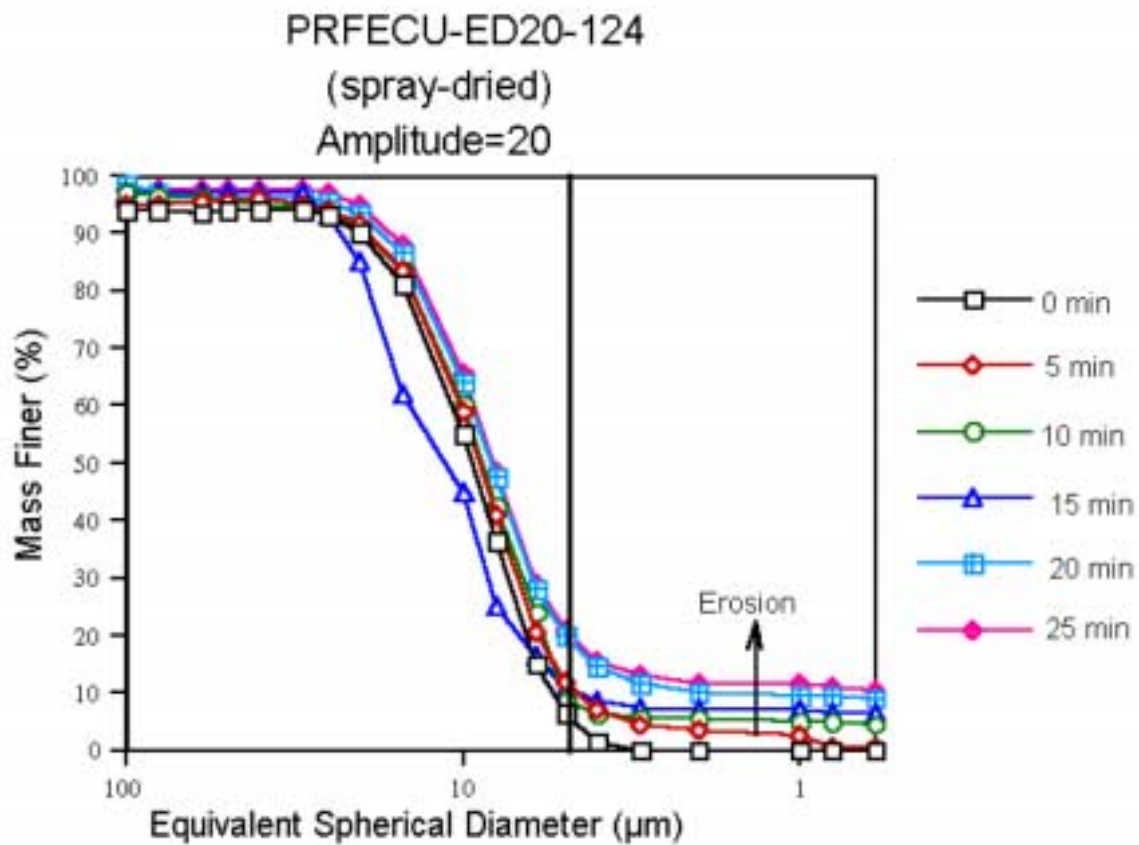
Figure 2.   Sedigraph particle size distribution of a spray-dried precipitated Fe, Cu catalyst. Spray-drying improves the attrition resistance of the catalyst, and there is a more uniform particle size distribution
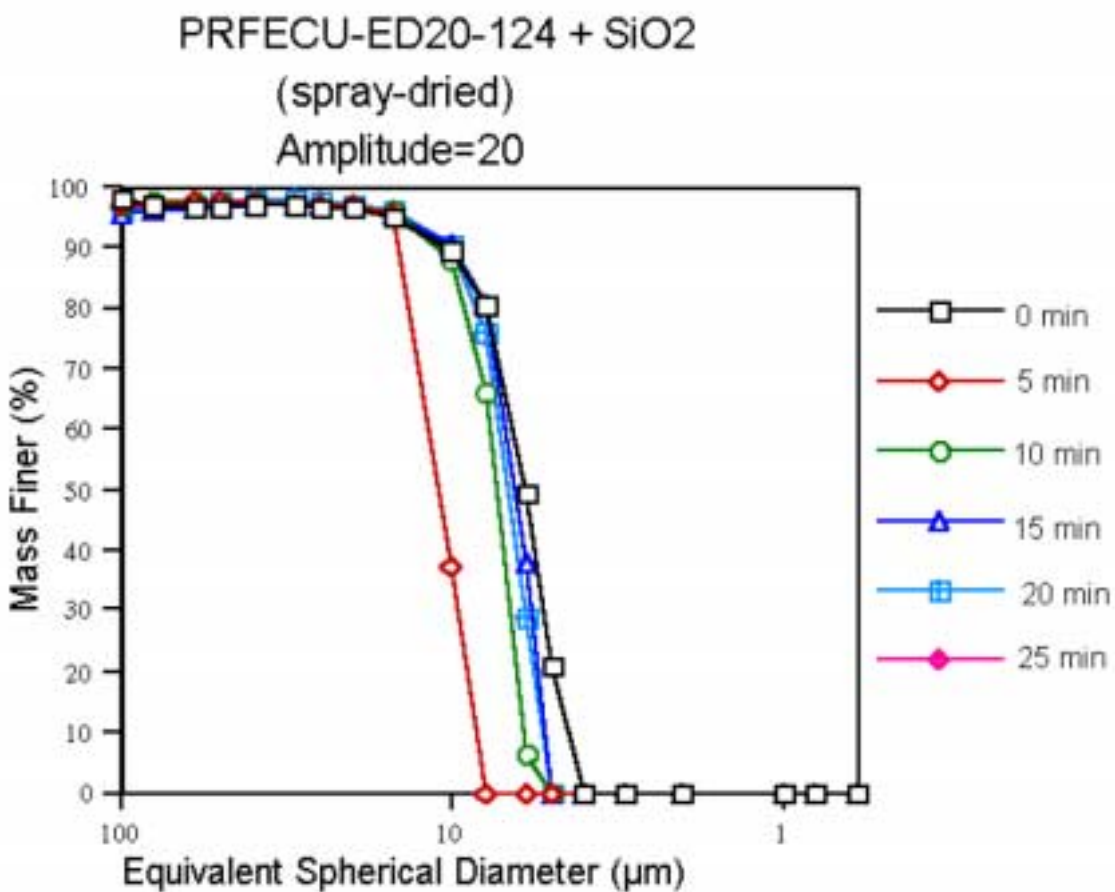
Figure 3.   Sedigraph particle size distribution of a spray-dried precipitated Fe, Cu catalyst containing silica. No erosion has occurred below 5 μm after 25 min of ultrasonic irradiation.

10.00 µm
X1200
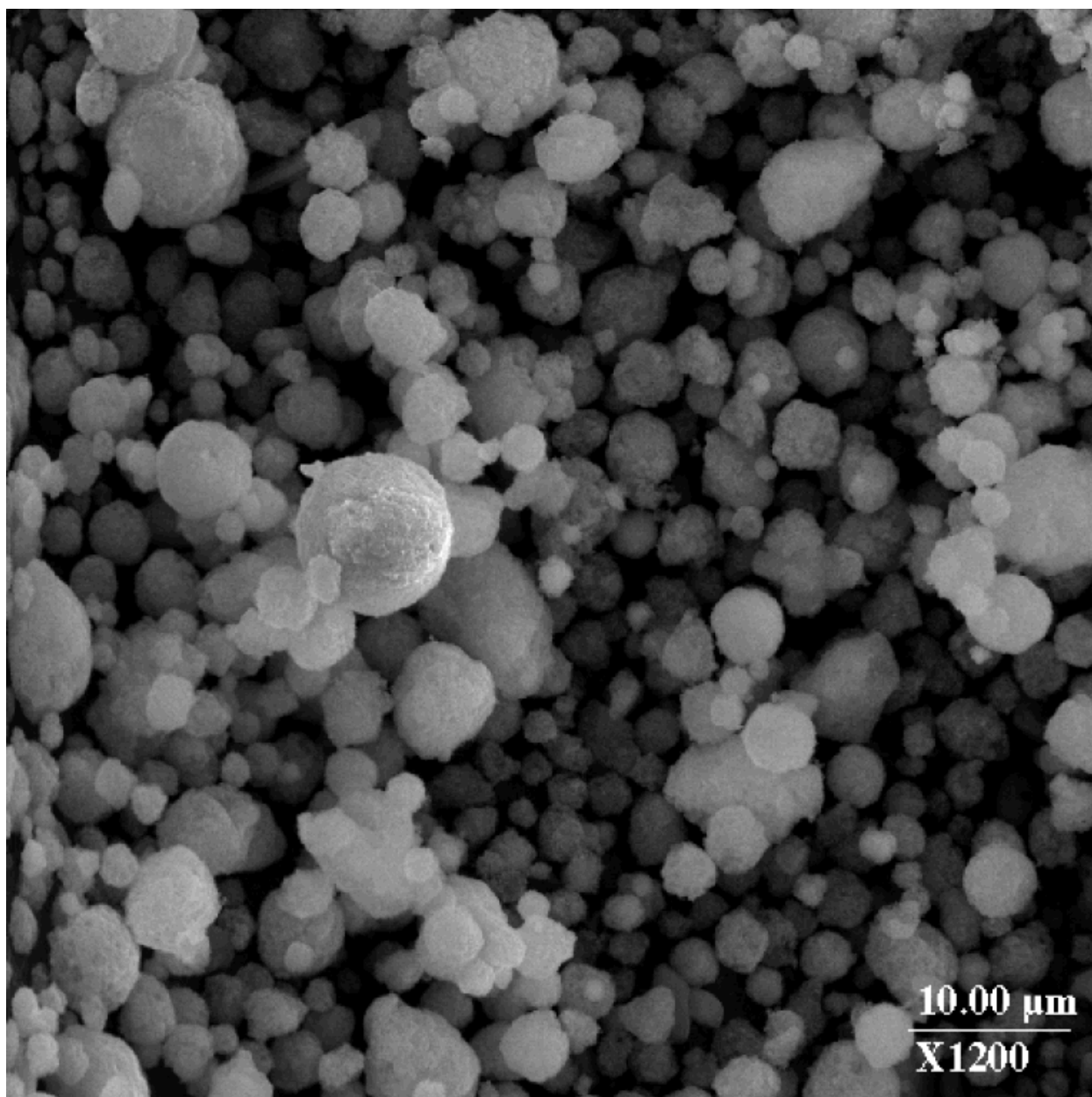
Figure 4.   SEM picture of the spray-dried precipitated Fe catalyst containing silica. Spherical particles are typical for a spray-dried powder, and are smaller than those desired for a commercial F-T process.

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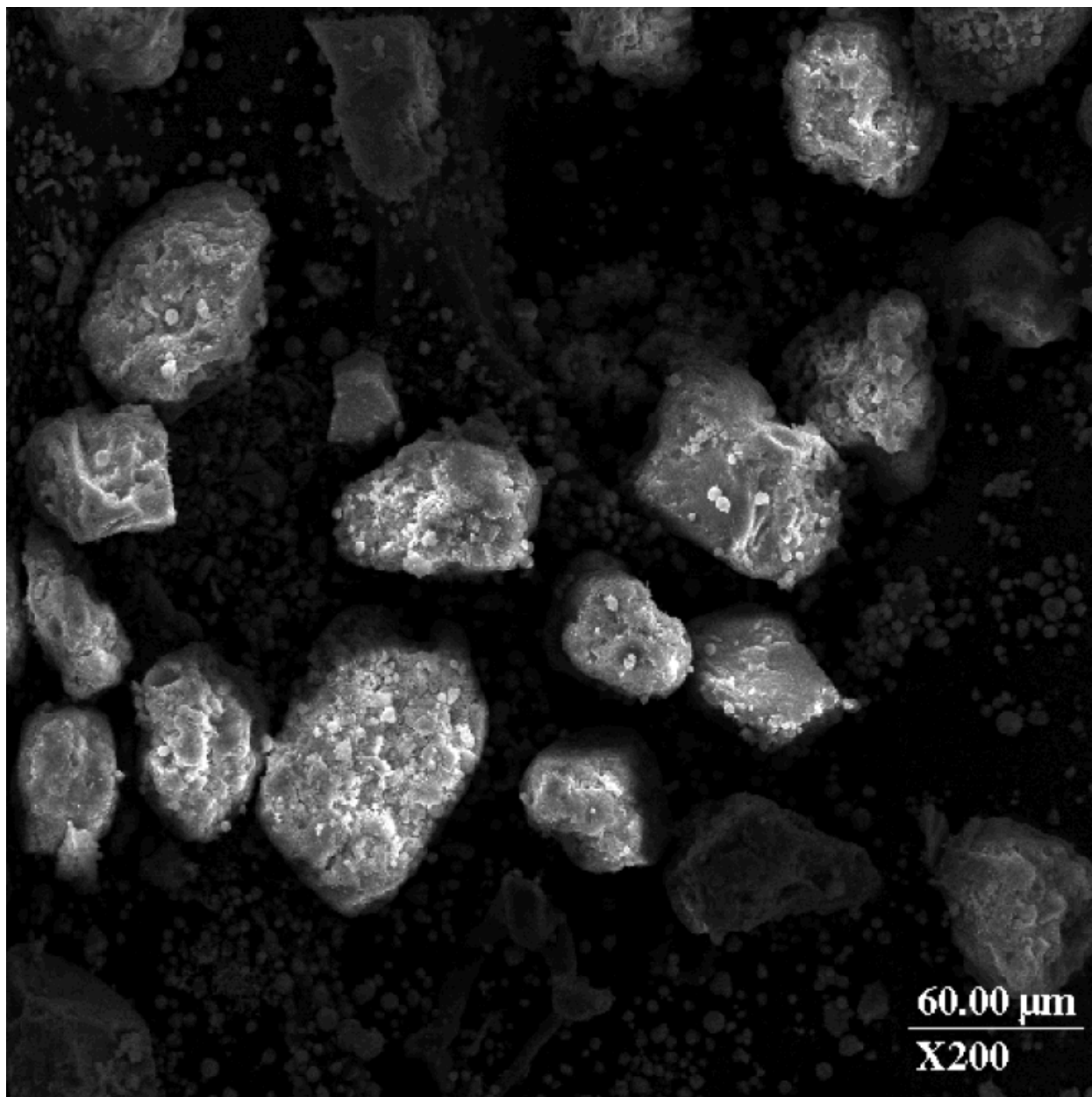
Figure 5.   SEM image of the spray-dried precipitated Fe, Cu catalyst containing silica. The large size particles were obtained by sieving with a standard testing sieve having pore openings of 38 μm. Also, the larger size particles are less spherical than the smaller size particles.
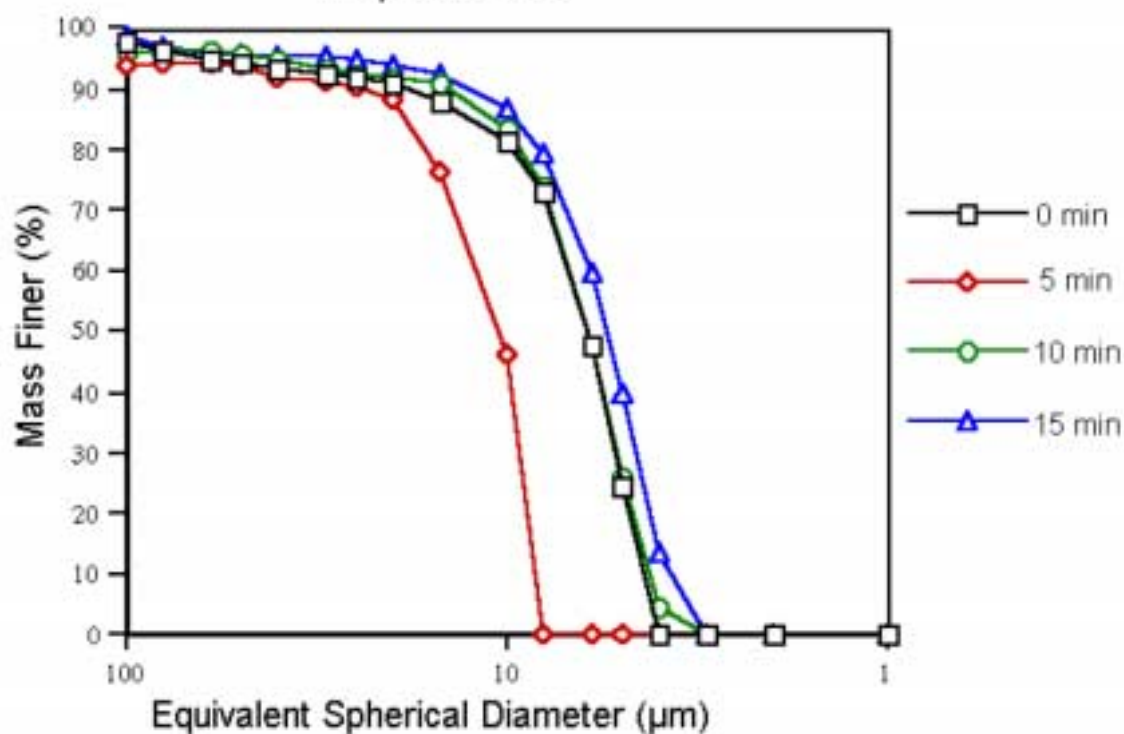
Figure 6.   Sedigraph particle size distribution of a precipitated Fe, Cu catalyst containing silica, which was spray-dried and then calcined at 320°C. Calcination does not appear to impart any additional strength to the catalyst.
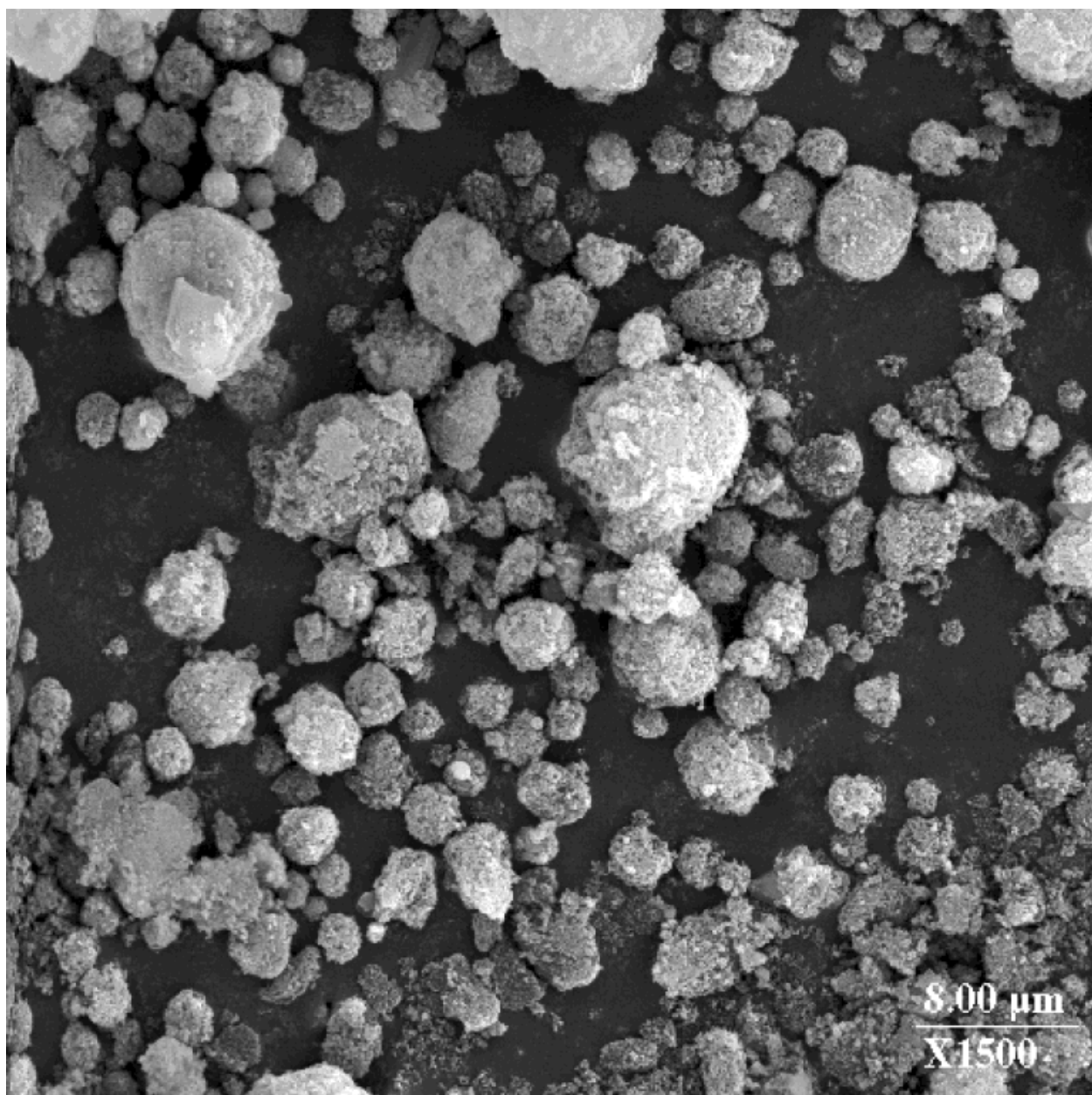
Figure 7.   SEM picture of a precipitated Fe catalyst containing silica, which was spray-dried and then calcined at 320°C. These particles are roughly spherical in shape, and the median particle diameter is smaller than the spray-dried Fe F-T catalyst.
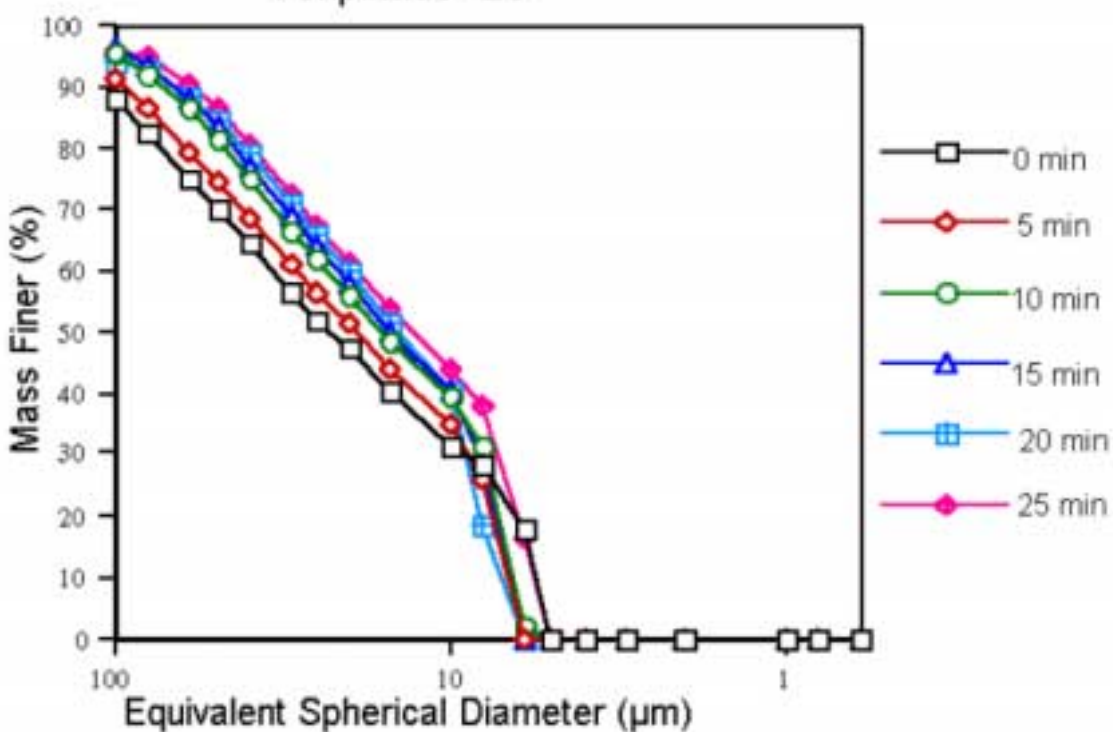
Figure 8.   Sedigraph particle size distribution of a precipitated Fe catalyst containing silica, which was calcined at 320°C in its dried state before spray-drying. No erosion has occurred below 5 μm after 25 min of ultrasonic irradiation.
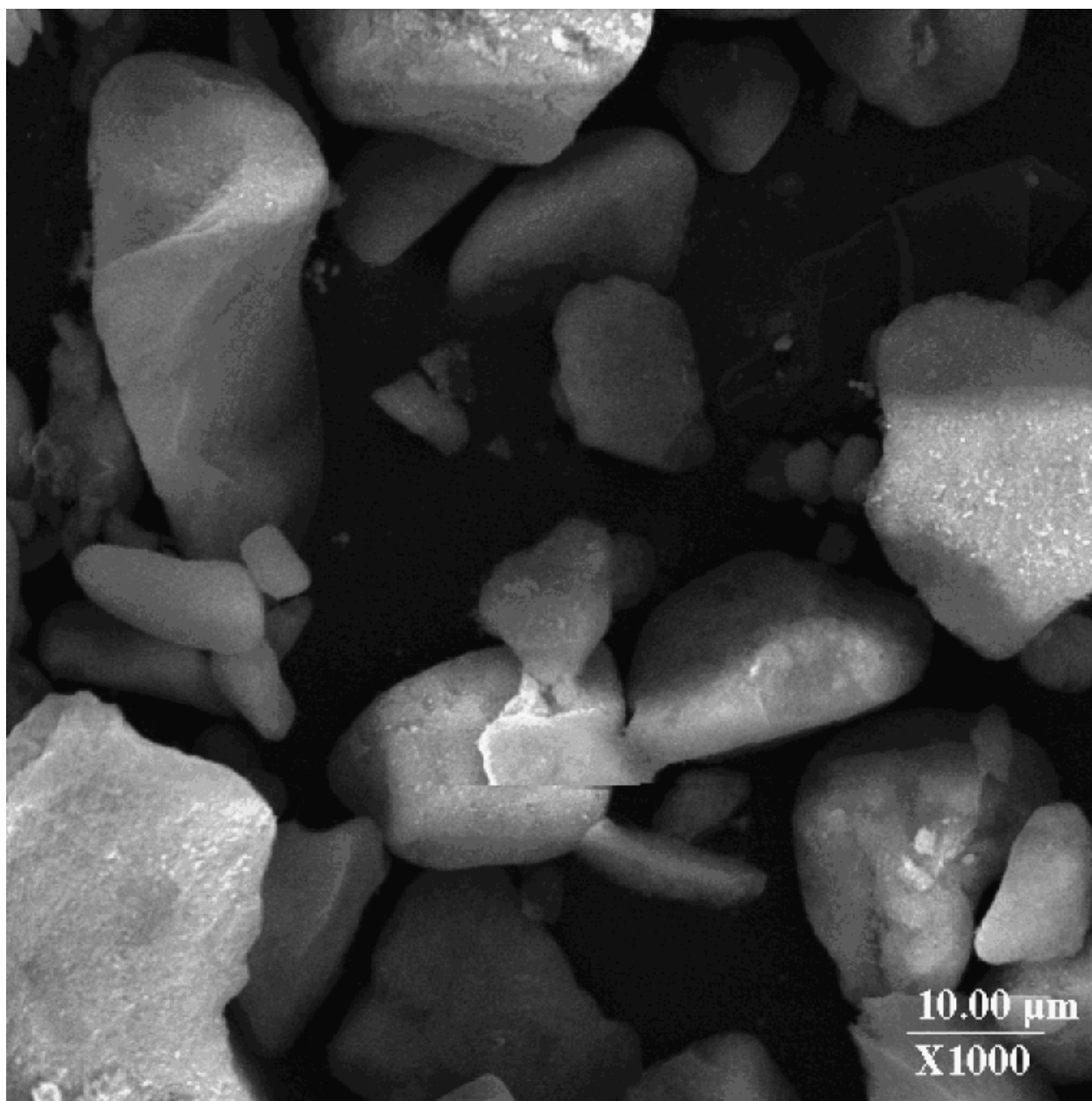
Figure 9.   SEM picture of a precipitated Fe catalyst containing silica, which was calcined at 320°C before spray-drying. These particles are not spherically-shaped, and are larger in size than the spherically-shaped spray-dried particles.
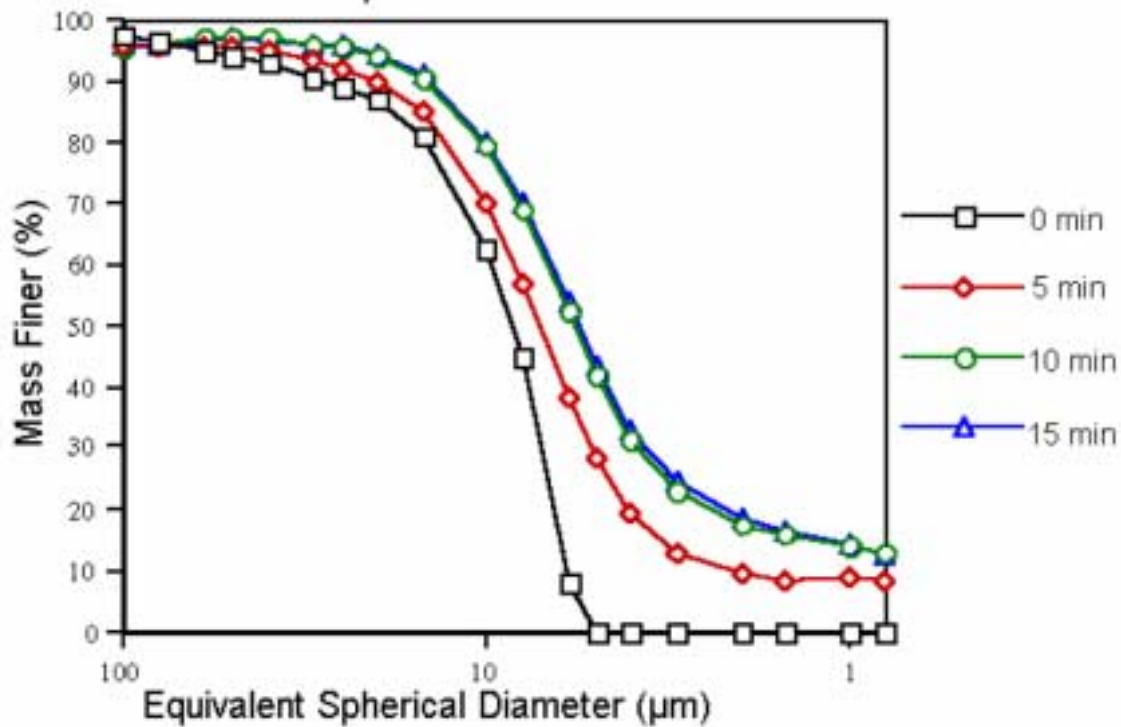
Figure 10.   Sedigraph particle size distribution of a precipitated Fe catalyst containing silica. The Fe precursor was spray-dried before adding silica, and then was spray-dried again. This catalyst is weaker than the other precipitated Fe F-T catalysts.
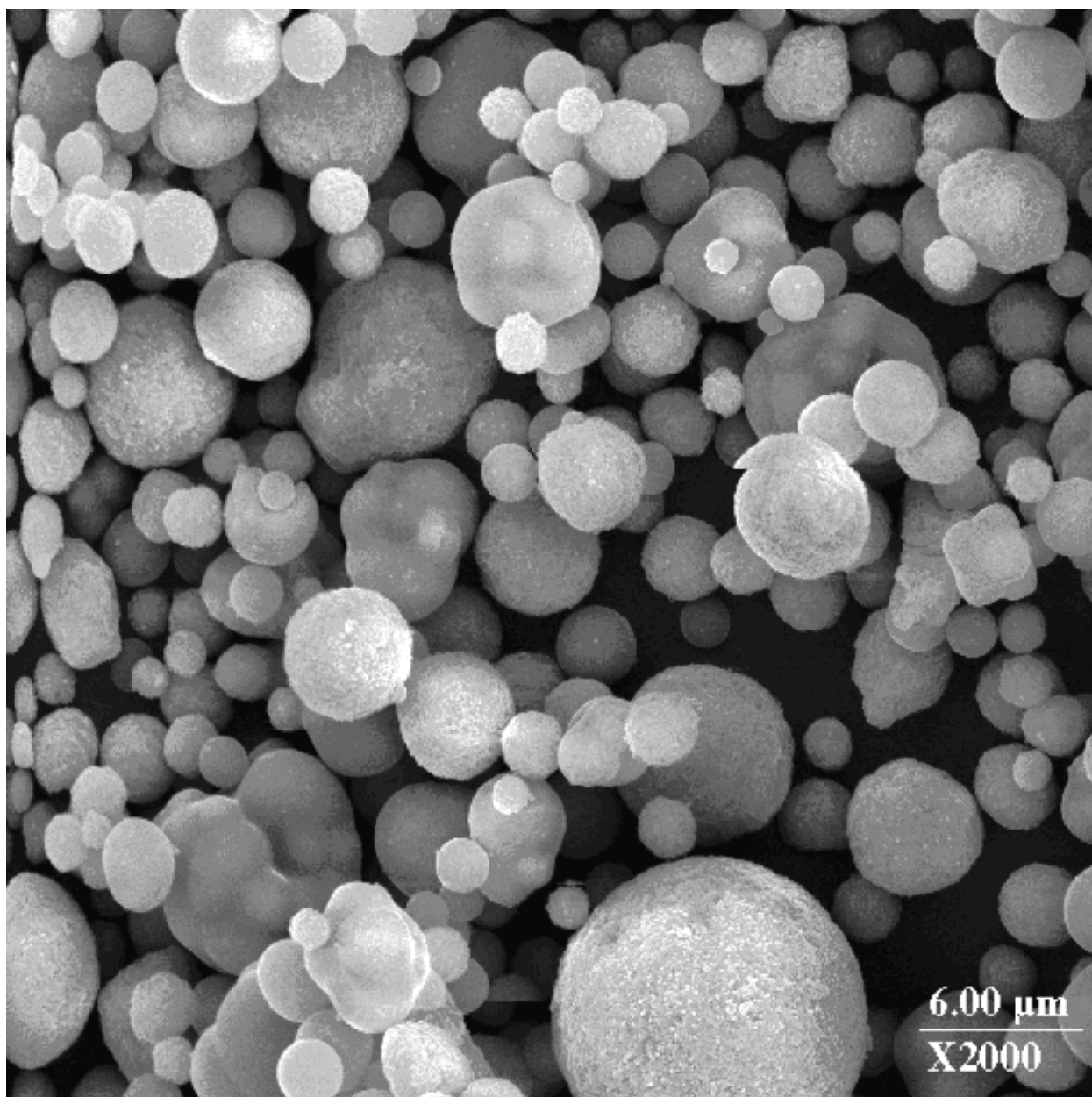
Figure 11.   SEM picture of a precipitated Fe catalyst containing silica. The Fe precursor was spray-dried before adding silica, and then was spray-dried again. These particles look similar to the spray-dried catalyst (Fig. 4).
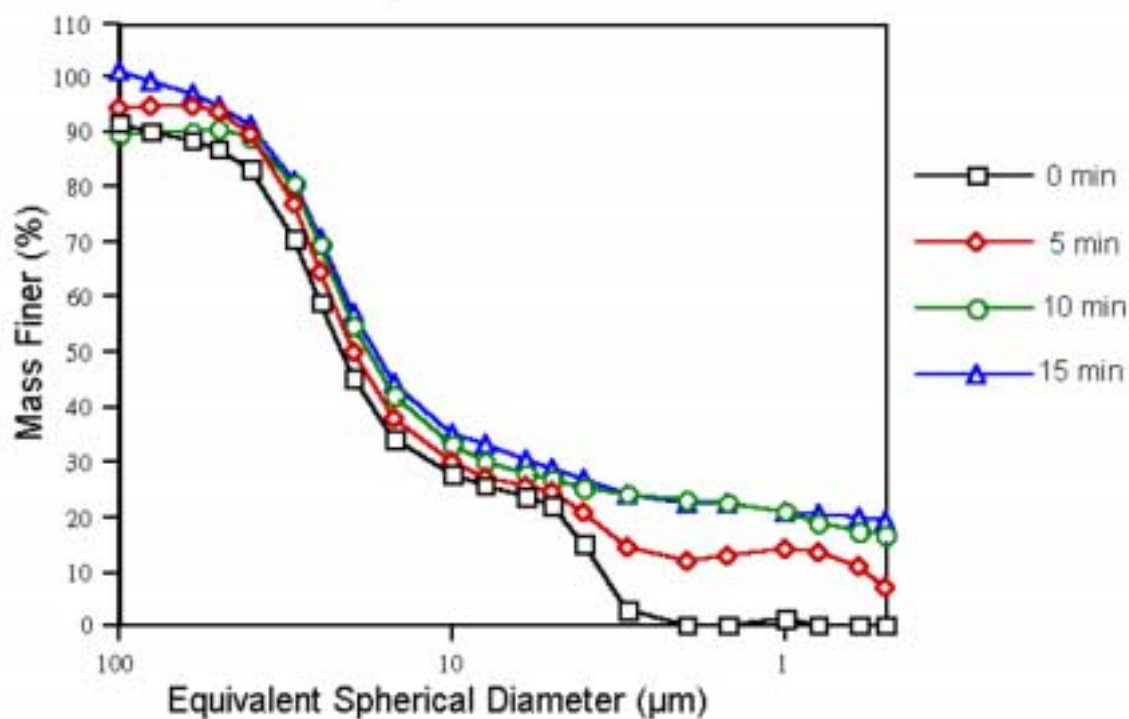
Figure 12.   Sedigraph particle size distribution of VISTA-B-965-500C sample. The starting alumina from VISTA was sieved and calcined in air at 500°C. Very little fragmentation occurs after 15 min of ultrasonic irradiation, although some erosion has occurred.
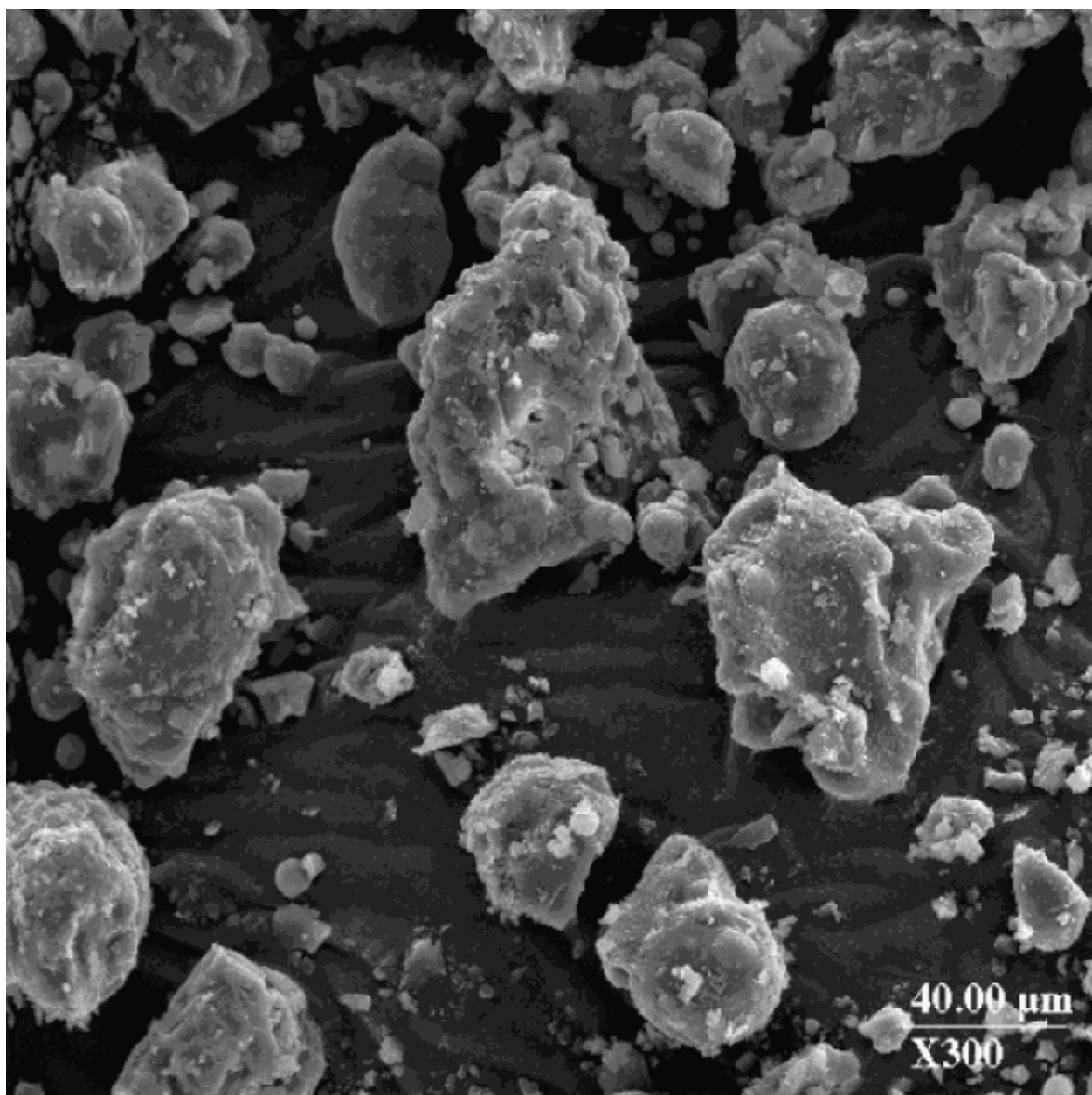
Figure 13.   SEM picture of a VISTA alumina support. The alumina is non-spherically-shaped since it is not spray-dried, and is larger in size than the spherically-shaped precipitated Fe F-T catalysts.

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