

Development of Attrition Resistant Iron-Based Fischer-Tropsch Catalysts

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Abstract

The Fischer-Tropsch (F-T) reaction provides a way of converting coal-derived synthesis gas ($\text{CO}+\text{H}_2$) to liquid fuels. Since the reaction is highly exothermic, one of the major problems in control of the reaction is heat removal. Recent work has shown that the use of slurry bubble column reactors (SBCRs) can largely solve this problem. The use of iron-based catalysts is attractive not only due to their low cost and ready availability, but also due to their high water-gas shift activity which makes it possible to use these catalysts with low H_2/CO ratios. However, a serious problem with use of Fe catalysts in a SBCR is their tendency to undergo attrition. This can cause fouling/plugging of downstream filters and equipment, makes the separation of catalyst from the oil/wax product very difficult if not impossible, and results in a steady loss of catalyst from the reactor.

Recently, fundamental understanding of physical attrition is being addressed by incorporating suitable binders into the catalyst recipe. This has resulted in the preparation of a spray dried Fe-based catalyst having aps of 70 μm with high attrition resistance. This Fe-based attrition resistant, active and selective catalyst gave 95% CO conversion through 125 hours of testing in a fixed-bed at 270°C, 1.48 MPa, $\text{H}_2/\text{CO}=0.67$ and 2.0 NL/g-cat/h with C_5^+ selectivity of >78% and methane selectivity of <5%. However, further development of the catalyst is needed to address the chemical attrition due to phase changes that any Fe-catalyst goes through potentially causing internal stresses within the particle and resulting in weakening, spalling or cracking.

The objective of this research is to develop robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry bubble column reactor. Specifically we aim to develop to: (i) improve the performance and preparation procedure of the high activity, high attrition resistant, high alpha iron-based catalysts synthesized at Hampton University, (ii) seek improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modifications in catalyst preparation steps and (iii) investigate the performance in a slurry reactor.

The effort during this reporting period has been devoted to more attrition study of the iron-based catalysts. Precipitated silica appeared to decrease attrition resistance of spray-dried iron FT catalysts. Spray-dried Fe catalysts were prepared having a composition of 100 Fe/5 Cu/4.2 K but with varying amount of precipitated SiO_2 . The results show that the use of small amounts of precipitated SiO_2 alone in spray-dried Fe catalysts can result in good attrition resistance. All catalysts investigated with SiO_2 weight percentages ≤ 12 produced fines less than 10 wt % during the jet cup attrition test, making them suitable for long-term use in a slurry bubble column reactor. Thus, concentration rather than type of SiO_2 incorporated into the catalyst has a more critical impact on the catalyst attrition resistance of spray-dried Fe catalysts. Lower amounts of SiO_2 added to a catalyst give higher particle densities and, therefore, higher attrition resistances. To produce a suitable SBCR catalyst, however, the amount of SiO_2 added has to be optimized to provide adequate surface area, particle density, and attrition resistance.

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Development of Attrition Resistant Iron-Based Fischer-Tropsch Catalysts

Introduction

Fischer-Tropsch Synthesis (FTS) is the reaction of CO and H₂ (syngas) to form a wide variety of hydrocarbons, typically using iron- or cobalt-based catalysts. Currently there are two commercial FTS plants: SASTECH produces synthetic fuels and chemicals from coal (including recent expansions), and Shell is using FTS to convert natural gas to high value products in Malaysia. There are other units in the planning or construction stage: China plans to make town gas via FTS; Williams Company is constructing a pilot plant to determine the economics of underground coal gasification; and Exxon is evaluating the possibility of locating a large natural gas-based FTS plant in Qatar. These activities clearly show that improvements and innovations in FTS are underway. This process is also strategically important to the U.S. because of its vast coal reserves, and because FTS represents the best means to make high quality transportation fuels and liquid products from coal. In addition to other technical challenges, one of the major problems in control of the reaction is heat removal. Recent progress in this area has focused on the use of a slurry bubble column reactor (SBCR). These reactors offer simple designs and low costs while still permitting high catalyst and reactor productivity. It is generally thought that this will be the reactor of choice for commercial, coal-based FTS in the United States.

Since modern coal gasification plants produce a syngas that is relatively lean in H₂ (H₂/CO = 0.5-0.7), a catalyst which is active for the FTS reaction ($\text{CO} + 2 \text{H}_2 \rightarrow -\text{CH}_2- + \text{H}_2\text{O}$) and the water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) is required. The overall reaction on these catalysts is thus $2\text{CO} + \text{H}_2 \rightarrow -\text{CH}_2- + \text{CO}_2$. This allows the efficient use of low H₂/CO syn gas. Iron-based catalysts, which are active shift catalysts, are thus preferred over cobalt-based catalysts, which are not. Iron is also much less expensive than cobalt.

F-T products are very desirable from an environmental point of view. Because F-T catalysts are very sulfur sensitive, the feed must be completely sulfur free which means that the product is also sulfur free. In addition to being sulfur free, the product is also nitrogen and aromatics free. F-T diesel fuel has a very high cetane number. Although

raw F-T naphtha has a low octane number, it can be processed into high quality gasoline. F-T distillate also makes excellent ethylene plant feedstock.

Catalyst development activities have involved an extensive effort to improve the performance of iron catalysts. Iron catalyst development work has been carried out by the Center for Advanced Energy Research (CAER) and FETC's Office of Science and Technology (OST). These efforts have resulted in iron catalysts with much higher activities than previous catalysts. A problem with iron catalysts is that they tend to have low structural strength with the result that attrition tends to produce very small catalyst particles during slurry operations. This attrition causes plugging, fouling, difficulty in separating the catalyst from the wax product, and loss of the catalyst. This is due to the low attrition resistance of the Fe catalyst and the significant breakage of the Fe particles. Fe catalysts are subject to both chemical as well as physical attrition in a SBCR. Chemical attrition can be caused due to phase changes that any Fe catalyst goes through ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe} \rightarrow \text{Fe carbides}$) potentially causing internal stresses within the particle and resulting in weakening, spalling or cracking. Physical attrition can result due to collisions between catalyst particles and with reactor wall. Catalyst particles of irregular shapes and non-uniform sizes produced by conventional methods are subject to greater physical attrition.

Another inherent complication associated with the iron-based catalyst is the catalyst pretreatment. Before synthesis, a catalyst precursor is pretreated to convert the catalyst into an active form. The pretreatment of Fe is not as straight forward as that for Ru, Co or Ni. Although pretreatment includes reduction of the iron particles, other processes are also involved. The pretreatment of iron FT catalysts is not clearly understood. Part of the confusion stems from the fact that the nature and composition of iron catalysts change during reaction. These changes depend on the temperature, time of exposure to the reactant feed, nature of the reactor system, and composition of the feed, and activation conditions (time and temperature). The common pretreatment conditions employed in the case of iron catalysts are H_2 reduction, CO reduction (and carbiding), or reduction in the reactant syngas. Work at the Federal Energy Technology Center has focused on the effect of catalyst pretreatment and the impact of the liquid starting medium on syngas conversion in a stirred tank slurry reactor.

Several phases of iron are known to exist when iron-based catalysts are subjected to F-T synthesis conditions. These include metallic iron (α -Fe), iron oxides (hematite, α -Fe₂O₃; magnetite, Fe₃O₄ and Fe_xO), and iron carbides, of which at least five different forms are known to exist. These include O-carbides (carbides with carbon atoms in octahedral interstices, ϵ -Fe₂C, ϵ' -Fe_{2.2}C, and Fe_xC) and TP-carbides (carbides with carbon atoms in trigonal prismatic interstices, χ -Fe_{2.5}C and Fe₃C). The formation and distribution of these phases depend on the reaction conditions, reaction times, and state of the catalyst (reduced/unreduced, supported/unsupported, etc.). However, the role of each of these phases during the reaction has not been resolved.

Potassium and copper are typically used as chemical promoters for iron FT catalysts. The adsorption of CO on iron results in a net withdrawal of electrons from the metal, whereas hydrogen adsorption tends to donate electrons to the metal. Potassium and the associated O²⁻ donate electrons to the metal, enhancing CO adsorption while weakening H₂ adsorption. This leads to decreased hydrogenation and increased chain growth during the synthesis reaction, yielding higher molecular weight products (i.e., a higher α). More lower olefins are also produced. Potassium also decreased CH₄ production and increases WGS activity. Copper on the other hand is introduced to facilitate reduction of the iron itself. Copper is more effective in increasing the FTS reaction rate than potassium. Also the average molecular weight is increased in the presence of copper.

The objective of this research is to develop robust iron-based Fischer-Tropsch catalysts that have suitable activity, selectivity and stability to be used in the slurry bubble column reactor. Specifically we aim to develop to: (i) improve the performance and preparation procedure of the high activity, high attrition resistant, high alpha iron-based catalysts synthesized at Hampton University, (ii) seek improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modification in catalyst preparation steps and (iii) investigate the performance in a slurry reactor.

EXPERIMENT

Catalyst

A series of spray-dried Fe FT catalysts having compositions of 100/Fe/5Cu/4.2K/ x SiO₂ was used in this study. Six catalyst composition in this series were prepared with precipitated SiO₂ at different levels: 0, 3, 5, 8, 10, and 12 wt% based on total catalyst weight. Fe/P(y) is used to refer to each catalyst composition according to its precipitated SiO₂ content incorporated; for instance, Fe/P(5) refers to the catalyst composition with 5 wt% precipitated SiO₂ added. The concentrations of Cu and K relative to Fe remained identical for all catalyst compositions; therefore, they are not used in the catalyst nomenclature. The details of catalyst preparation can be found elsewhere. In brief, a solution containing the desired ratio of Fe(NO₃)₃ • 9 H₂O, Cu(NO₃)₂ • 2.5 H₂O, and Si(OC₂H₅)₄ (added to give precipitated SiO₂) was precipitated with ammonium hydroxide. An aqueous potassium promoter KHCO₃ was added to a slurry of the precipitate. The slurry was spray-dried at 250°C in a Niro spray drier and was then calcined at 300°C for 5 hours in a muffle furnace. The calcined catalysts were sieved between 38-90 µm before attrition testing and other characterizations.

Catalyst Characterization

Attrition tests were conducted using a jet cup system. The details of the system configuration as well as test procedure have been extensively described previously. In the jet cup test, 5g of each calcined catalyst sample was evaluated for attrition resistance under identical testing conditions using an air jet flow of 15 l/min with a relative humidity of 60 ±5% at room temperature and atmospheric pressure. After one hour time-on-stream, the air jet flow was stopped and the weight of fines collected by the downstream filter was determined. “Weight percentage of fines lost” was calculated and used as one of the attrition indices. Particle size distribution before and after attrition testing was determined with a Leeds & Northrup Microtrac laser particle size analyzer and used to calculate “net change in volume moment”, the other attrition index used in our attrition studies. Volume moment is a measure of the average particle size.

A Philips XL30 Scanning Electron Microscope (SEM) was used to observe the morphology of the catalyst particles, before and after attrition, and also the structure of the precipitated SiO₂ network in the catalyst particles, after acid leaching. Elemental analysis was carried out to determine surface composition and distribution of each element on cross-sectional surfaces of catalyst particles using Energy Dispersive X-ray Spectroscopy (EDXS). Powder XRD patterns of the catalyst samples was determined using a Philips X'pert Diffractometer. Catalyst BET surface areas and pore volumes were measured using a Micromeritics ASAP 2010 automated system. Each catalyst sample was degassed under vacuum at 100°C for one hour and then 300°C for three hours before BET surface area and pore volume measurements. Average particle density (particle mass divided by its volume) of each catalyst was determined using low-pressure mercury intrusion.

RESULTS

Catalyst Attrition

Attrition results for all the catalysts studied are summarized in Table 1 and the plot of the two attrition indices, “weight percentage of fines lost” and “net change in volume moment” versus total silica concentration is shown in Figure 1. Weight percentage of fines lost was calculated based on the ratio of the weight of fines collected from the exit filter of the jet cup and the total weight of all particles recovered after the jet cup test. Net change in volume moment average particle size change during the attrition test. Since the average particle size decreases during attrition, net change in volume moment is always a positive number. Volume moments of the attritted catalysts were calculated based on both fines generated and particles remaining in the jet cup. Therefore, net change in volume moment is calculated by $\{[\text{volume moment of fresh} - \text{volume moment of attritted (average bottom and fines)}]/[\text{volume moment of fresh}]\} \times 100$. Detailed calculations and significance of attrition indices have been given elsewhere. High values of attrition indices indicate low attrition resistances of catalysts.

Table 1. Jet Cup Attrition Results

Catalyst	Total SiO ₂ Concentration (wt%)	Fines Lost (wt%) ^(a,b)	Net Change in Volume Moment (5) ^(c,d,e)
Fe/P(0)	0.0	3.2	6.0
Fe/P(3)	2.7	6.4	18.4
Fe/P(5)	5.2	7.5	23.4
Fe/P(8)	7.6	8.6	27.1
Fe/P(10)	9.9	9.3	30.1
Fe/P(12)	12.1	7.7	27.8
Fe/P(16)	16.1	24.5	--
Fe/P(20)	19.8	29.9	--

(a) Wt% fines = weight of fines collected/weight of total catalyst recovered x 100%

(b) Error = $\pm 10\%$ of the value measured.

(c) Net change in volume moment was determined with reference to the particle size distribution before attrition testing.

(d) Net change in volume moment (VM) = [(VM of sample after attrition test – VM of sample before test) / VM of sample before test] x 100%.

(e) Error = $\pm 5\%$ of the value measured.

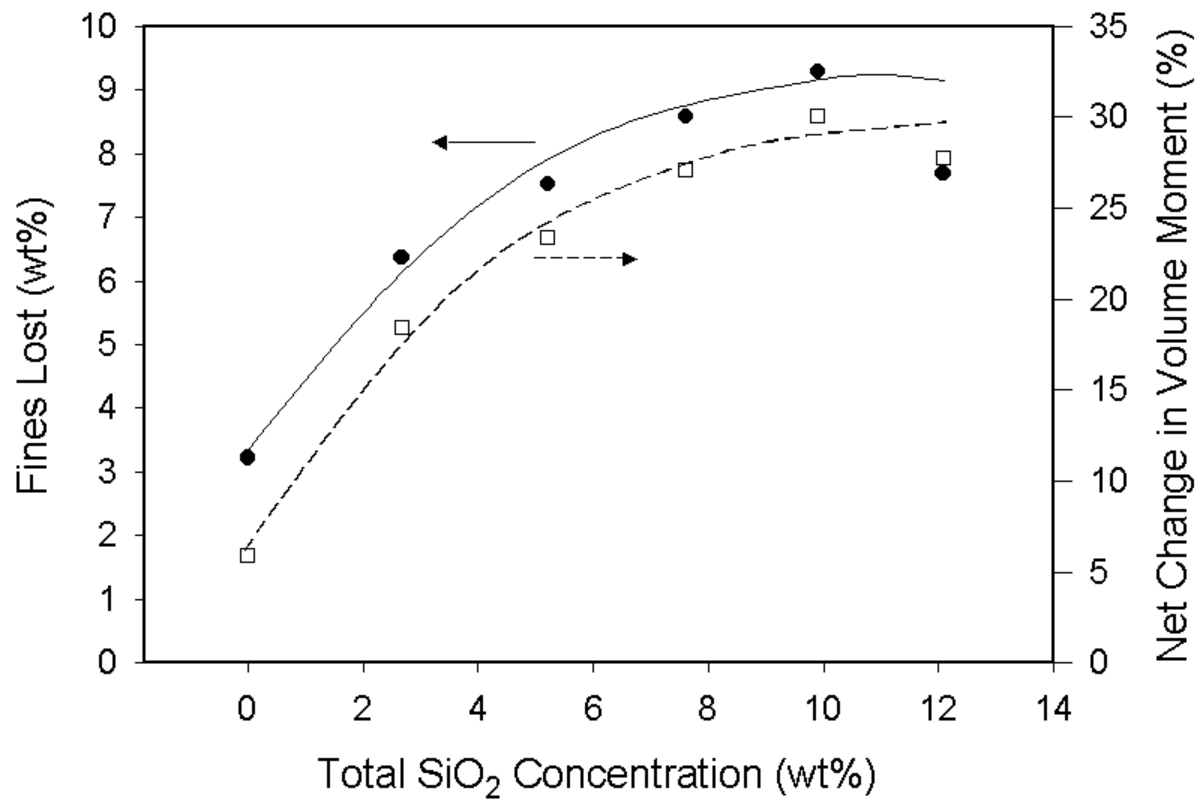


Figure 1. Jet Cup Attrition Results

As shown in Figure 1, the catalyst without precipitated SiO₂ (Fe/P(0)) showed the highest attrition resistance (least attrition) among all the catalysts tested, while the lowest attrition resistance (highest attrition) was exhibited by the catalysts with the highest concentration of precipitated SiO₂. Figure 1 shows clearly that both attrition indices had similar trends with varying concentration of precipitated SiO₂. Effect of fluidization differences (as a result of particle density differences) on catalyst attrition in the jet cup has been considered and proved to be negligible by using an ultrasonic attrition test, an attrition test with no fluidization involved. Attrition results from the ultrasonic test were found to be comparable and reproducible within experimental error to those obtained with the jet cup test.

Catalyst Particle Properties

The BET surface areas and pore volumes (micro- and meso-pores) of the catalysts, measured by N₂ physisorption, are summarized in Table 2. It can be seen (Table 2) that BET surface areas fluctuated with the total concentration of SiO₂, and no relationship between these two parameters can be drawn. It should be noted that the experimental error of BET surface area measurement is $\pm 5\%$ based on multiple runs of the same sample. However, this error is increased to ca. $\pm 10\%$ by an added sampling error due to potential partial segregation of different particle sizes and densities within a powder sample. In addition, surface area of catalysts may fluctuate somewhat due to slight variations in a number of preparation parameters (especially precipitation pH). As expected, the catalyst with 0% SiO₂ had the lowest BET surface area. However, BET surface areas of all the catalysts tested did not change significantly during attrition, except for Fe/P(5) and Fe/P(8). The pore volumes of this catalyst series did not vary significantly with total SiO₂ content and remained essentially unchanged after attrition.

The XRD patterns of all the catalysts tested before and after attrition were found to be identical and confirmed that iron existed mainly as hematite (Fe₂O₃). Other components including precipitated SiO₂ were not detectable. The attrition process did not change the XRD patterns of hematite significantly. Thus, as to be expected, attrition affected only physical properties of the catalyst particles and not chemical ones.

Table 2. BET Surface Area and Pore Volume of the Iron Catalysts Studied.

Catalyst	BET Surface Area (m ² /g) ^(a)		Pore Volume (cm ³ /g) ^(b)	
	Fresh	Attritted	Fresh	Attritted
Fe/P(0)	24	23	0.08	0.08
Fe/P(3)	69	63	0.12	0.11
Fe/P(5)	83	115	0.12	0.16
Fe/P(8)	48	69	0.11	0.14
Fe/P(10)	41	44	0.11	0.11
Fe/P(12)	76	84	0.11	0.12

(a) Error = $\pm 5\%$ of the value measured.

(b) Error = $\pm 10\%$ of the value measured.

Particle density (particle mass divided by its volume including all pore volumes) has been suggested to strongly govern attrition resistance of our spray-dried Fe FT catalysts in calcined, reduced, and carburized forms. Particle density was determined based on low-pressure mercury intrusion in order to prevent mercury from penetrating into the pores of the particles. Mercury porosimetry was used to measure macro pore volumes of the catalyst samples. Particle density and macro pore volume results are summarized in Table 3. It can be seen that macro pore volumes of the selected samples were essentially similar within experimental error. The catalyst with no precipitated SiO₂ (Fe/P(0)) had the highest particle density. Particle density decreased as the concentration of precipitated SiO₂ increased.

Catalyst Morphology

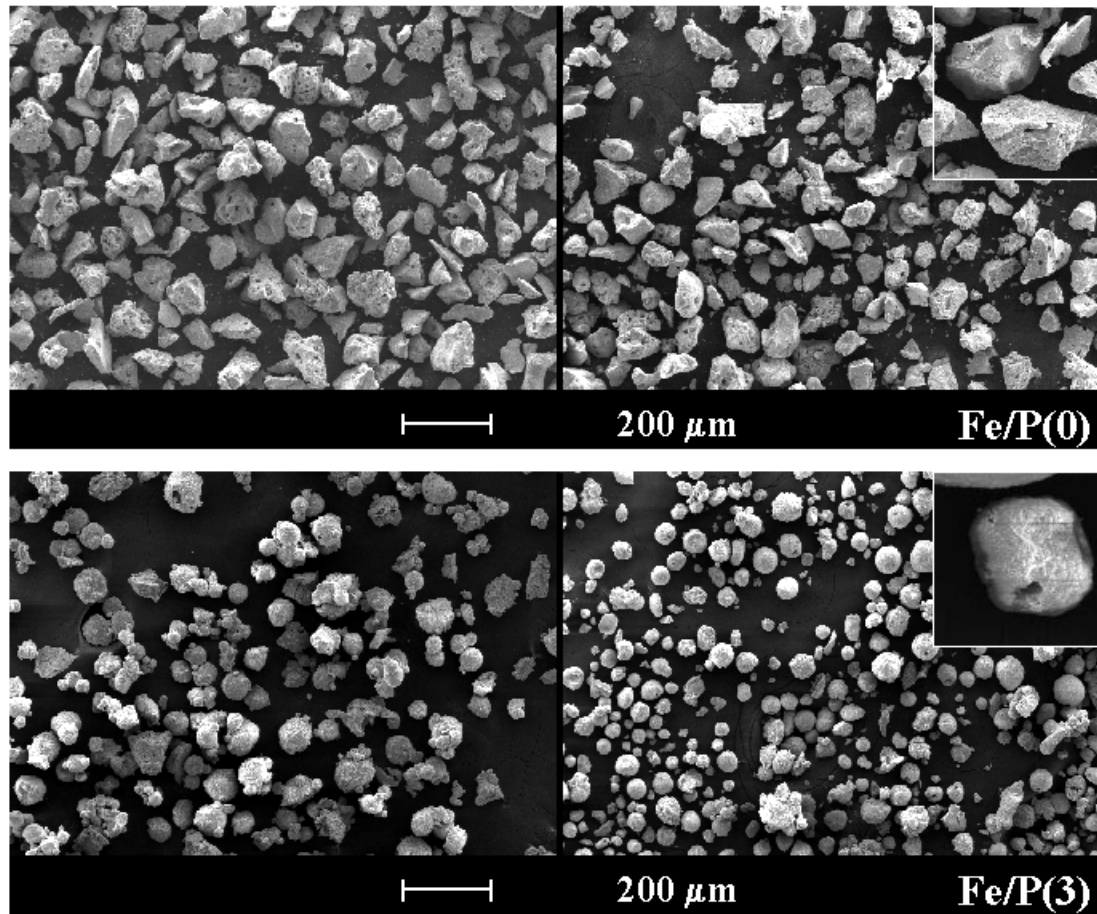
SEM micrographs of all the catalyst samples before and after attrition are shown in Figures 2A-C. The catalyst with no precipitated SiO₂ (Figure 2A/Top) shows clearly non-spherical particles while the other catalysts with addition of precipitated SiO₂ have particles somewhat more rounded in shape and agglomerated. The figures show that breakage during attrition was mostly a break up of particle agglomerates since there was an obvious decrease in numbers of agglomerates after attrition. There was no evidence for the actual breakage of distinct catalyst particles. The presence of small chips and pieces caused by abrasion was observed in the fines collected at the top exit of the jet cup. Degree of breakage increased as the amount of precipitated SiO₂ incorporated increased, which is in good agreement with changes in the attrition indices. It can also be observed that some particles had interior holes, seen only as dark spots on particles at higher magnification in Figures 2A-C. Such holes, which have also been found for the spray-dried Fe catalysts studied previously, were probably produced because of the lower efficiency of a laboratory scale spray drier. Only a small minority of these catalyst particles had holes but they provided a means to determine if the silica structure was maintained during acid leaching of the catalyst particles, discussed in detail later.

Table 3. Macro Pore Volume and Particle Density of Selected Iron Catalysts.

Catalyst	Macro Pore volume (cm ³ /g) ^(a)	Particle Density (g/cm ³) ^(b)
Fe/P(0)	0.25	1.64
Fe/P(10)	0.26	1.40
Fe/P(12)	0.24	1.44
Fe/P(16)	--	0.81
Fe/P(20)	--	0.79

(a) Measured using mercury porosimetry, error = $\pm 10\%$ of the value measured.

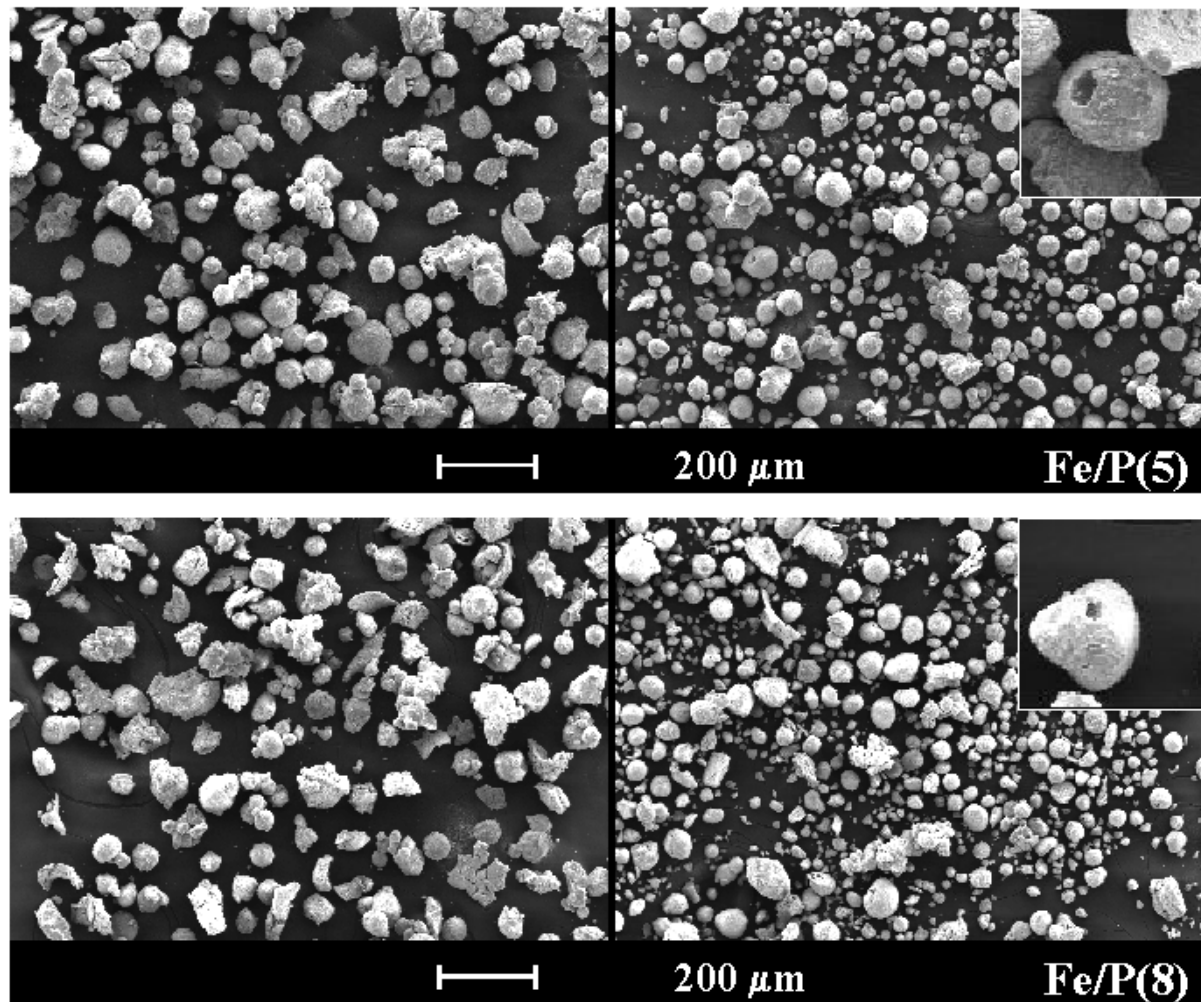
(b) Determined using low-pressure mercury displacement, error = $\pm 5\%$ of the value measured..



Before Attrition

After Attrition

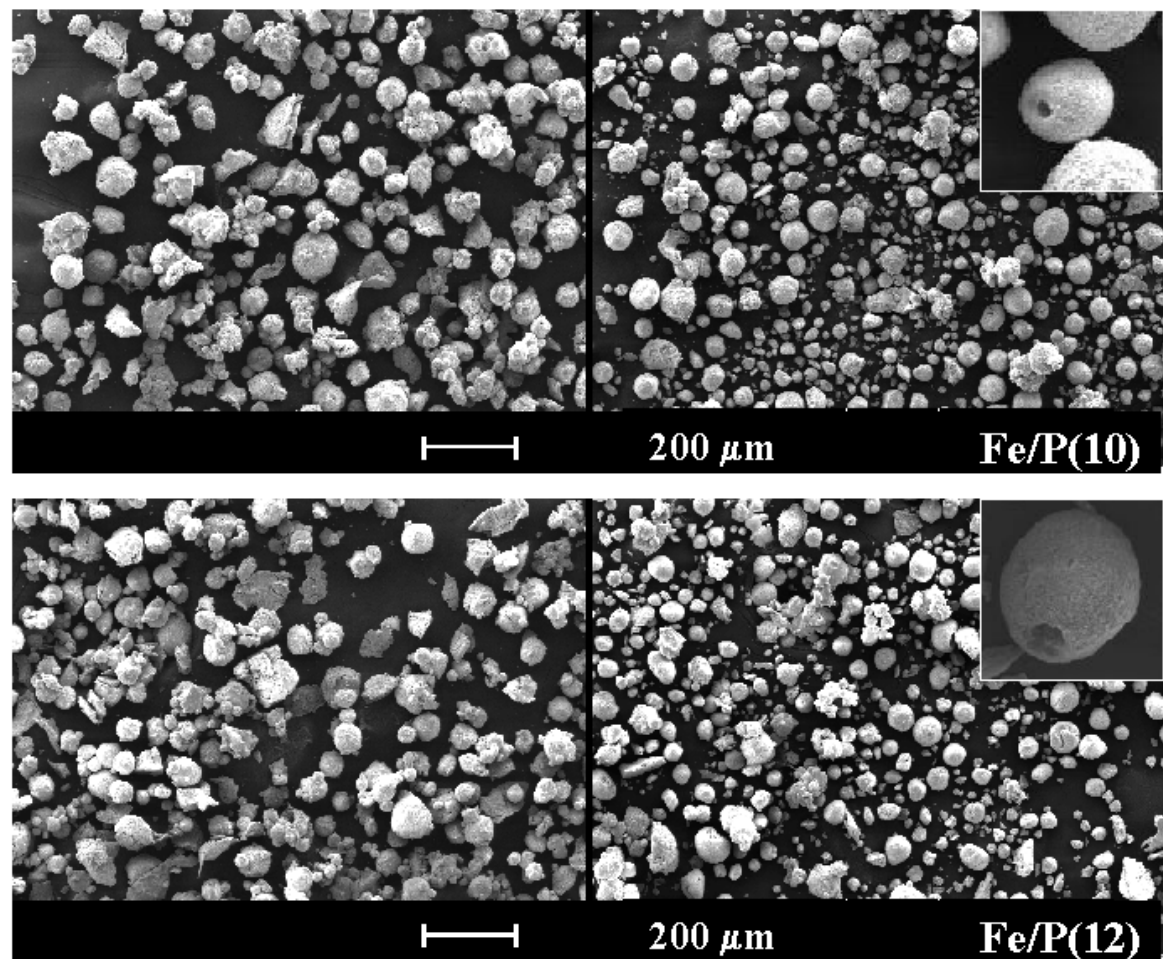
Figure 2a. SEM micrographs of Fe/P(0) and Fe/P(3) before and after attrition.



Before Attrition

After Attrition

2b. SEM micrographs of Fe/P(5) and Fe/P(8) before and after attrition.



Before Attrition

After Attrition

Figure 2c. SEM micrographs of Fe/P(10) and Fe/P(12) before and after attrition.

To obtain a better understanding of the factors affecting attrition resistance, catalyst inner structure as well as distribution of each element in the catalyst particles are important to determine. The distribution of each element in the catalyst particles was determined using EDXS to analyze the cross-sectional area of catalyst particles prepared by microtoming. The elemental mapping results, an example being shown in Figure 3, were found to be similar for all catalyst compositions containing precipitated SiO₂. Iron, Cu and precipitated SiO₂ were found to be evenly distributed throughout the catalyst particles. Potassium, on the other hand, was found in higher concentration at catalyst surfaces as seen on the outer edge of the cross-sectioned particles.

The precipitated SiO₂ network incorporated in the catalysts can be seen by SEM after acid leaching, which dissolves Fe, Fe oxide, Cu, and K and leaves mainly the SiO₂ structure. Catalyst particles were treated with 30% HCl solution (pH=1) for 48 hours to ensure that those elements were leached out. The residue was washed thoroughly with deionized water under vacuum filtration and dried under vacuum at room temperature to avoid agglomeration by heating. Figure 4 shows typical SiO₂ structures seen with and without interior holes. Both structures showed a smoother texture of SiO₂ surface at this magnification, which differs from the more porous SiO₂ structures seen in spray-dried Fe catalysts prepared earlier with either binder or binder + precipitated SiO₂.¹ The SiO₂ structures obtained by leaching catalysts after attrition were identical, consistent with the fact that there was not a great deal of attrition and most was due to a break up of agglomerates (Figures 2A-C).

DISCUSSION

Catalyst Attrition Resistance

Although 'weight percentage of fines lost' and 'net change in volume moment' are both used as attrition indices, they have different physical meanings. While weight percentage of fines lost is a representative of the amount of fines generated and elutriated (ca. <22 μm), net change in volume moment represents a change of volume mean average particle size, weighted mostly towards the larger particles.² Therefore, a

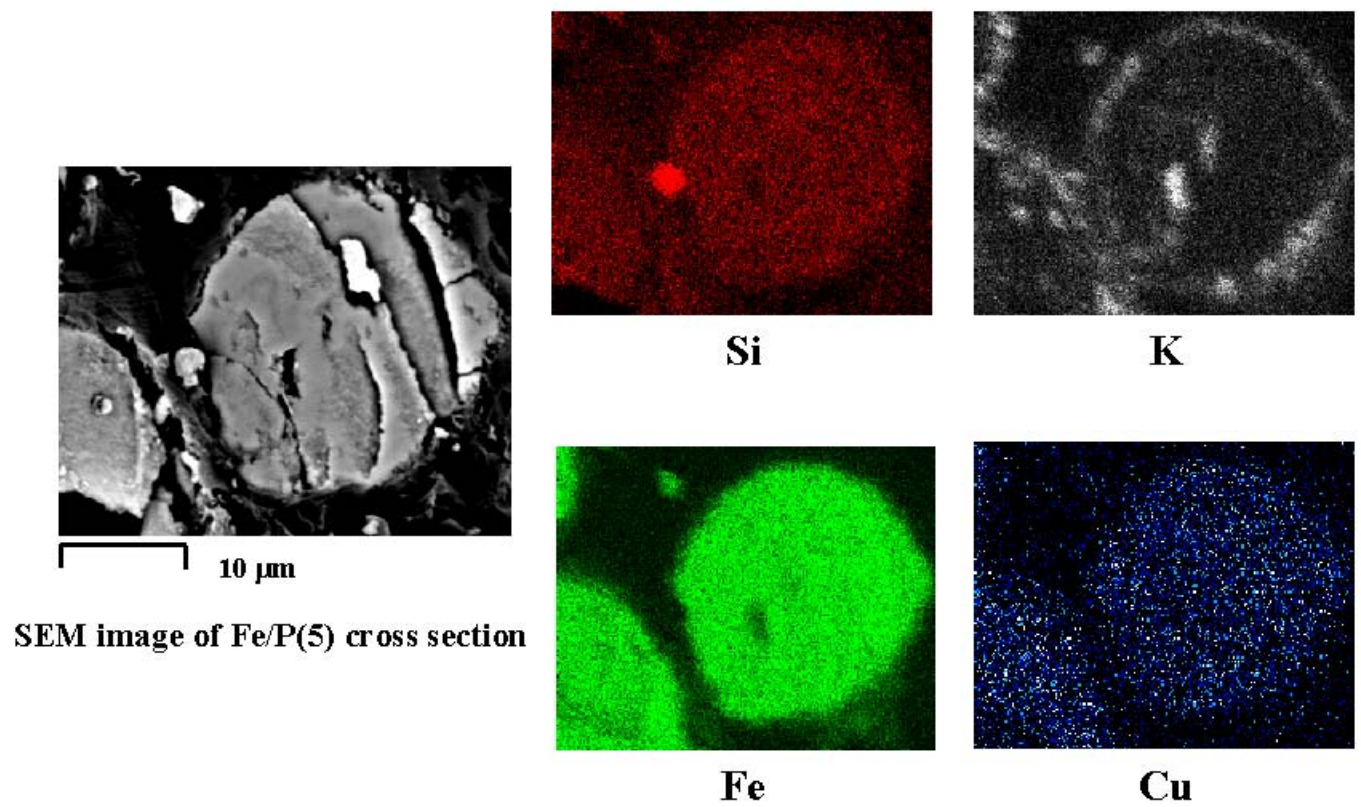


Figure 3. EDXS results for the cross section of a typical Fe/P(5) particle.

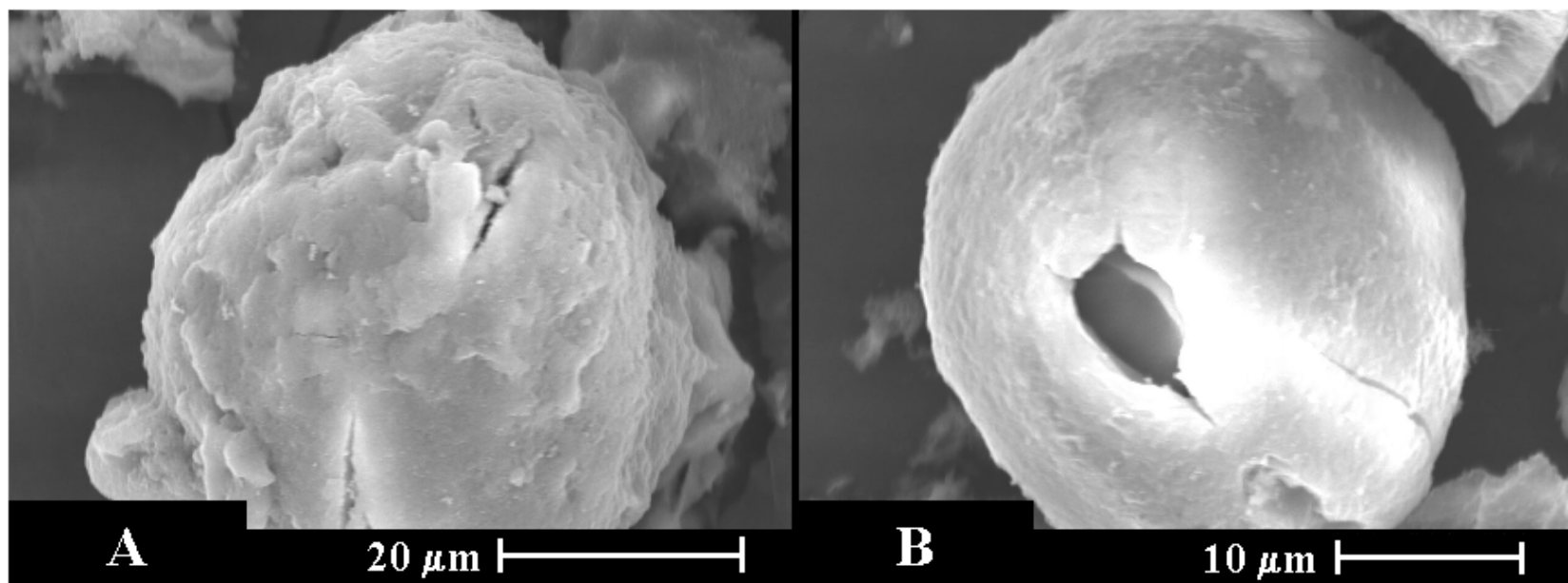


Figure 4. SEM micrographs of typical SiO_2 structures after acid leaching [Fe/P(12)]: (A) typical structure, (B) particle with interior.

combination of these two attrition indices have been used in our attrition studies to help delineate physical attrition both by fracture (generating large broken particles) and abrasion/erosion (generating fines). Due to the difference in their physical meanings, it would not be surprising if the values of these two parameters were not identical with each other. However, for this spray-dried Fe catalyst series prepared with precipitated SiO₂ only, both attrition indices show similar trends in their relationship to the amount of precipitated SiO₂ added (Figure 1). These results suggest that the change in average particle size (mostly large particles) occurred in a similar degree as fines generated and possibly that the breakage of large particles facilitated the generating of fines. Weight percentage of fines lost is, however, considered the most important attrition index in our studies since fines generated cause the aforementioned problems in SBCR operation and since these catalysts were developed for SBCR usage.

In our previous study² to determine the effect of SiO₂ type (binder vs. precipitated + binder) and concentration on attrition resistance of spray-dried Fe catalysts, the catalyst having only binder SiO₂ (Fe/P(0)/B(11)) at the moderate concentration of ca. 11 wt% SiO₂ showed the highest attrition resistance (least attrition). Addition of precipitated SiO₂ to this composition (Fe/P(y)/B(10)) was found to reduce attrition resistance sharply. The use of precipitated silica alone at high loadings (20-25 wt%) is well known to result in poor attrition resistant Fe catalysts. However, the effect of having only precipitated SiO₂ at lower concentrations, especially in spray-dried Fe catalysts, was not determined. Thus, it is useful to compare the attrition results of the catalysts in this study (which had the same Fe/Cu/K ratios as those previously studied but were prepared with only precipitated SiO₂) with those from the previous study² (see Figure 5). Catalysts with only precipitated SiO₂ at concentrations <12 wt% showed significantly improved attrition resistance than other catalyst compositions. At a moderate total SiO₂ concentration about 11 wt%, the curves for the three catalyst series essentially intersect, indicating that some particle property of these spray-dried iron catalysts prepared with similar amounts but different types of SiO₂ could possibly have an influence on their attrition resistances.

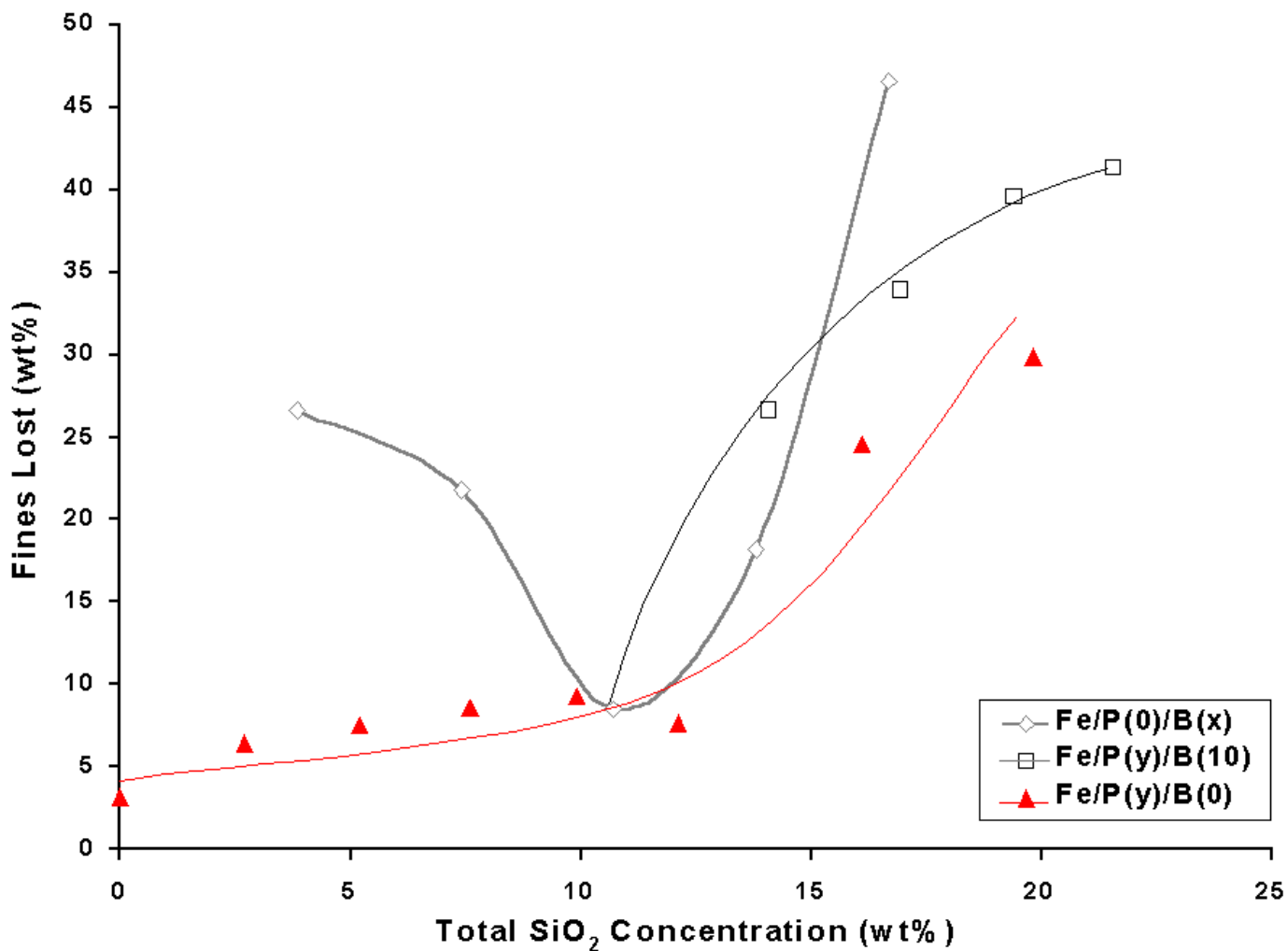


Figure 5. Weight percentage of fines lost vs. total concentration of SiO₂ for different series of spray-dried Fe FT catalysts: B refers to binder SiO₂; P refers to precipitated SiO₂; x and y refer to the amount of binder and precipitated SiO₂ added, respectively. [Data for Fe/P(0)/B(x) and Fe/P(y)/B(10) from ref. 1].

The two catalysts having the lowest concentrations of binder SiO₂ seem to have had somewhat different attrition properties than the rest of the catalysts (Figure 5). This was possibly due to their being prepared at different solution pH and/or drying temperature, which may have caused lower particle densities than otherwise expected. This effect has been shown to be reproducible.

In the earlier studies,^{2,3} we found that catalyst attrition depended greatly on catalyst particle density and that this was not due to a bias in the attrition test. Figure 6 shows % fines lost versus particle density for catalysts prepared with only precipitated SiO₂ and for catalysts prepared with only binder SiO₂ or with binder + precipitated SiO₂.² The results for the catalysts having only precipitated SiO₂ are completely consistent with the previous data and therefore confirm the strong relationship between these two parameters. Thus a catalyst with a high particle density exhibits low attrition or, in other words, has high attrition resistance. On the other hand, too dense catalysts, however, may not be fluidized well enough to obtain a good dispersion in a reactor slurry, leading to poor contact between reactants and catalyst particles.

Thus, attrition resistance is not only the important factor in catalyst design for SBCR usage. High surface area and proper particle density are also needed to obtain high catalytic activity and good fluidization, respectively. The presence of SiO₂ in Fe FT catalysts enhances their active surface areas but lowers the density of the catalyst as well as their attrition resistances. Therefore, the amount of SiO₂ added must be optimized to obtain high catalytic activity, high attrition resistance, and good fluidization of catalyst particles when used in SBCRs.

SiO₂ Structure

After acid leaching, precipitated SiO₂ particles (Figure 4) were not found significantly changed in either size or shape from the original catalyst particles. Moreover, those particles with interior-hole structures maintained the same structure (with holes) after being acid leached. All these observed structures after acid leaching as well as the EDXS results suggest that the structure of precipitated SiO₂ in the catalyst particles was a continuously network (skeleton). There is no evidence that suggests the SiO₂ existed as discrete, non-continuous parts in the original catalyst particles that

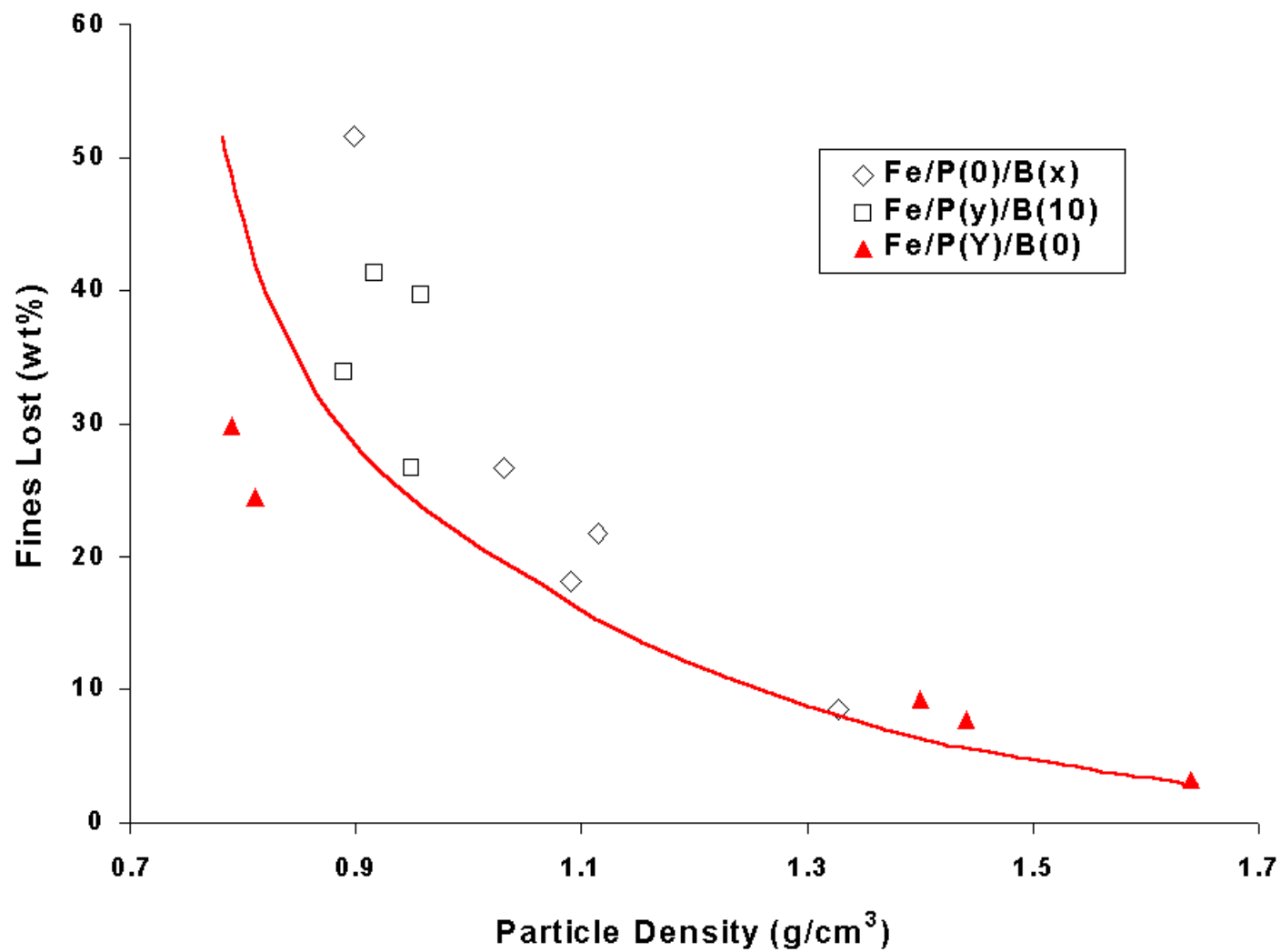


Figure 6. Weight percentage of fines lost vs. average particle density of calcined Fe/P(y), Fe/B(x), and FE/P(y)/B(10) catalysts.

somehow agglomerated during acid leaching. Although some SiO₂ particles were found to have interior holes, in no way did they have an ‘egg shell’ structure. Precipitated SiO₂ was evenly distributed, as shown by EDXS (Figure 3), throughout the particles, similarly to Fe.

The surface morphology of the acid leached precipitated SiO₂ particles (Figure 4) both with and without interior holes was relatively more smooth compared to the porous SiO₂ structures resulting from acid leaching of the catalysts prepared with binder SiO₂ or binder + precipitated SiO₂.² However, the difference in this morphology did not seem to be a major factor for the physical strength of the catalysts (Figure 5).

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