3.2.4. Scanning Electron Microscopy Study of Co-precipitated Iron Oxide Catalysts

ABSTRACT

Iron oxide Fischer-Tropsch catalysts were prepared using a sol-gel method to incorporate varying amounts of silica (SiO_2) and a constant amount of potassium oxide (K_2O) promoters. The sol-gel slurries containing different Fe/Si ratios were dried using a spray dryer. The spray-dried materials were calcined at 300^{o}C prior to the use as catalysts for the Fischer-Tropsch reaction. Scanning electron microscopy (SEM), combined with energy dispersive X-ray spectroscopy (EDS) and elemental dot mapping (EDM) techniques, was utilized to characterize the structural morphology for these promoted iron oxide catalysts. The results indicate that the promoters (SiO_2, K_2O) are evenly distributed throughout the catalysts, and no agglomerated regions of iron, silica or potassium could be observed. Thus, the sol-gel preparation, followed by spray drying produces industrial catalysts of fine particle morphology and a uniform distribution of the promoters.

INTRODUCTION

The Fischer-Tropsch process has attracted a great deal of attention in terms of catalytic activity and selectivity to produce higher carbon number hydrocarbons by reacting carbon monoxide and hydrogen at high pressures in the presence of catalysts (Fischer and Tropsch (1923)). Shortly after the initial discovery, Fischer and Tropsch developed more active catalysts for indirect liquefaction. The product distribution resulting from the Fischer-Tropsch synthesis (FTS) varies widely depending upon the catalysts, the temperature and pressure of reaction, pretreatment conditions, etc. It is always desirable to improve the selectivity while maintaining the activity intact. One approach to achieving this task is the addition of promoters such as oxides of K, Mn, Ti, Mo, Ni, and Co, etc. It was observed that most of these promoted catalysts exhibit an increase in selectivity to higher hydrocarbons (Barrault, *et al.* (1988); Ledford, *et al.* (1987); Takhashi, *et al.* (1988); Baker and Clark (1987)). For example, the addition of thoria as a promoter to cobalt-kieselguhr catalysts resulted in an enhanced yield of C_5^+ hydrocarbons (Storch, *et al.* (1951)). Even a small amount of thoria promoter (~0.4 wt.%) addition to Co/ZSM-5 causes a remarkable increase in the conversion, shift activity, and C_5^+ selectivity (Rao, *et al.* (1985)). Thoria added as a promoter to a precipitated iron oxide catalyst appears to decrease wax selectivity (Dry (1981)). It is generally believed that the factors such as dispersion effects of rare earth oxides (Ledford, *et al.* (1987); Rao, *et al.* (1985); Dry (1981); Anderson (1956); Mok, *et al.* (1983)), the redox properties (Barrault, *et al.* (1988); Takhashi, *et al.* (1988)), and the basic properties of rare earth oxides and (Takhashi, *et al.* (1988); Rao, *et al.* (1985)), greatly influence the activity and selectivity.

The FTS reaction is very exothermic and handling the heat generated during the synthesis has presented significant problems in developing processes for the synthesis. One approach to handling the excess heat of reaction is to utilize a slurry reactor. In order to utilize this approach, it is necessary to effect catalyst/wax separation. As heavy wax builds up in the reactor during synthesis, the liquid level will rise. To maintain a constant liquid level in the reactor, slurry must be withdrawn, catalyst and wax separation effected, and the catalyst is returned to the reactor. For effecting a uniform slurry in the reactor and for many solid separation techniques, it is advantageous to have the catalyst with a spherical shape with a narrow size distribution. One way to obtain this type of catalyst is to utilize spray drying to develop spherical catalyst particles with a narrow size distribution. This technique has been utilized in this study.

Iron oxide and oxyhydroxide catalysts can be synthesized following various preparation methods. The current investigation describes the preparation and characterization by electron microscopy of the iron oxyhydroxide catalysts promoted by silicon and potassium.

EXPERIMENTAL METHODS

(a) Catalyst Preparation

A 15 kg batch of the catalyst was made by a continuous precipitation technique. The slurry (containing 5 at.% silicon based on Si and Fe content corresponding to 3.8 wt.% SiO_2) was divided into three portions, as outlined in Figure 1. The first portion was directly spray-dried. The product was then dried at 100^oC for 27 hours. This dried sample was designated as **RLS5.0Si-I**.

The second portion of the catalyst sample was mixed with a slurry containing sufficient potassium silicate (K_2SiO_3) to add 0.5 wt.% potassium and hydrolyzed tetraethylorthosilicate (TEOS) in an amount to provide a total of 7.5 wt.% SiO_2 in the finished catalyst. This slurry was then spray-dried. While spray-drying this sample, it was found that the initial product was too damp because of a high feed rate; hence the feed rate was reduced and a drier product was then obtained, as shown in Figure 1. Both the damp and drier products were then dried at 100^oC for 27 hours. The damp product and the drier products were consequently designated as **RLS5.0Si-II-A** and **RLS5.0Si-II-B**, respectively.

The third portion of the catalyst was treated the same way as the second except the amount of TEOS was sufficient to produce 12.2 wt.% SiO_2. This sample was designated as **RLS5.0Si-III.** Portions of the spray-dried products were, after drying at 100°C for 27 hours, calcined at 200°C for 15 hours or at 300°C for 23 hours.

(b) Description of the Spray Dryer

The drying chamber consists of a ten foot tall cylinder with a diameter of four and one-half feet and has a two foot conical section attached to the bottom of the cylinder. Hot gases at 600-650°F (combustion by-products from a gas burner) are blown by a fan into the top of the chamber and exit the bottom of the chamber, while the catalyst slurry is pumped through an atomizer nozzle at the bottom of the chamber (the nozzle is inserted through the conical section at the bottom of the chamber). The catalyst travels vertically upwards (countercurrent flow) with enough velocity so that it almost hits the top of the chamber, then it is entrained in the hot gas in a downward motion (cocurrent flow) towards the bottom of the chamber. This countercocurrent flow yields an effective chamber height of about 20 feet. Attached to the bottom of the chamber (i.e., the bottom of the conical section) is a collection device for capturing the dried catalyst. Exhaust gases exit the bottom of the chamber and are sent to a cyclone for removal of catalyst fines and then the exhaust gases pass through filters and are vented to the atmosphere.

(c) Scanning Electron Microscopy

A Hitachi S-2700 scanning electron microscope was used with a spatial resolution of about 3.5 nm. Secondary electron images, qualitative energy dispersive X-ray spectra as well as elemental distribution maps, were obtained from the catalysts under investigation. This scanning electron microscope was outfitted with a Princeton Gamma Tech IMIX-II Omega SLS (Sealed Light Element Spectrometer), which is a

Si(Li) detector utilizing an ultra-thin window, sensitive to all elements with an atomic number of boron and higher.

The spray—dried powders were spread on a flat aluminum holder and this was coated with carbon to minimize charging effects. The carbon-coated specimens were then mounted into the microscope for analysis.

RESULTS AND DISCUSSION

Electron micrographs were obtained from powder specimens of the catalysts under investigation at various magnifications. An electron micrograph obtained from catalyst RLS5.0Si-I depicts several agglomeration of particles (Figure 2). Under high magnification, each agglomeration is shown to consist of many small particles. If the powders were ultrasonically dispersed in an organic compound such as acetone or alcohol before the specimen preparation, the agglomerates were no longer present, and only small particles appeared in the microscopic examination. Hence, the specimen preparation for microscopy is very important, and it should not be allowed to distort the true morphology of the specimens. All the electron micrographs presented in this investigation were prepared from the as-dried powders without any ultrasonic treatment.

An energy dispersive X-ray spectrum obtained from one agglomerate is presented in Figure 3. X-ray lines corresponding to FeKα, Kβ, and Lα are observed. In addition to Fe lines, a Si Kα line also appeared exhibiting a minor fraction of SiO_2. The intensity ratio of FeKα to SiKα is 8.67. This sample contains about 5 at.% silicon relative to Si and Fe contents in the starting slurry (see Figure 1).

Samples RLS5.0Si-IIA and RLS5.0Si-IIB were obtained from the second portion of the starting slurry to which 0.5 wt.% K and 4 wt.% SiO_2 were added prior to spray-drying. A scanning electron micrograph obtained from sample RLS5.0-Si-IIA is shown in Figure 4. The morphological features are quite similar to those of the previous sample. An EDS spectrum obtained from this sample (Figure 5), shows a minor fraction of potassium in addition to the Fe and Si Kα x-ray lines. Examination of sample RLS5.0Si-IIB revealed similar morphological features. Elemental dot maps from one of these two catalysts are shown (Figures 6), along with the image from the region where the dot map data were collected. The maps show that the potassium and silica promoters are distributed very uniformly in the catalyst. X-rays emanating from each element present in the illuminated area were collected for a timed interval.

A scanning electron micrograph of catalyst RLS5.0Si-III, dried at 100°C, (Figure 7), shows that the agglomerate size is greatly reduced compared to the samples described above. Several EDS spectra obtained from this catalyst at different locations indicated the presence of Fe, Si, K, and O. An elemental dot map obtained from the dried sample of RLS5.0Si-III clearly showed the potassium and silicon promoters to be uniformly distributed on the catalyst surface. Similar morphological features were observed for the sample RLS5.0Si-III, dried at 300°C.

The characteristic morphological features from these spray-dried catalysts were examined at various locations of the samples and at various magnifications. It was observed that the agglomerates consisted of very small particles. The sizes of the agglomerates were measured and plotted for the series of catalysts dried at 100°C (Figure 8(a)), and those at 300°C (Figure 8(b)). The sizes of these agglomerates range up to about 100 microns.

The relationship between the mean agglomerate size and the silica content is presented in Figure 9. The two samples with the lowest silica contents have agglomerate sizes that are essentially the same as an iron sample prepared by the same procedure that did not contain silica, and the maximum in the size distribution occurs for agglomerates in the 40-60 μm range. With increasing silica content the agglomerate size decreases. Thus, the agglomerate size for the 7.5 wt.% silica sample is smaller than the one containing 3.8 wt.% SiO_2. The sample containing 12.2 wt.% SiO_2 has a particle size centered at 20-40 μm. A similar sample that contained 30 wt.% SiO_2 had a particle size centered at about 10 μm. Thus, the agglomerate size of the material dried at 100^{o}C depends upon the silica content with the size decreasing with increasing SiO_2 content as shown in Figure 9. All slurry drying runs were conducted using similar slurry compositions, temperatures, slurry and atomizing gas feed rates, and drying gas rates. It appears that the silica present either on the surface of the individual particles and/or incorporated in the bulk of the material that ultimately form the agglomerates permits the formation of smaller drops during the atomization process. If this was not the case, it would be necessary for the initial droplets to further divide during the drying process, and this does not seem to be likely.

Calcination at 300^{o}C produces a surprising result. For the two samples with the lowest silica content there is some increase in agglomerate size following calcination, but it is very slight. For both of these samples the maximum for the agglomerate size is in the range of 40-60 μm as it was in these samples that had been only dried at 100^{o}C. However, the agglomerate size for the catalyst containing 12.2 wt.% SiO_2 had increased appreciably to show a maximum in the 40-60 μm range, whereas the dried sample exhibited a maximum in the 20-40 μm range. It therefore appears that silica enhances agglomerate size growth during the calcination process.

ACKNOWLEDGMENT

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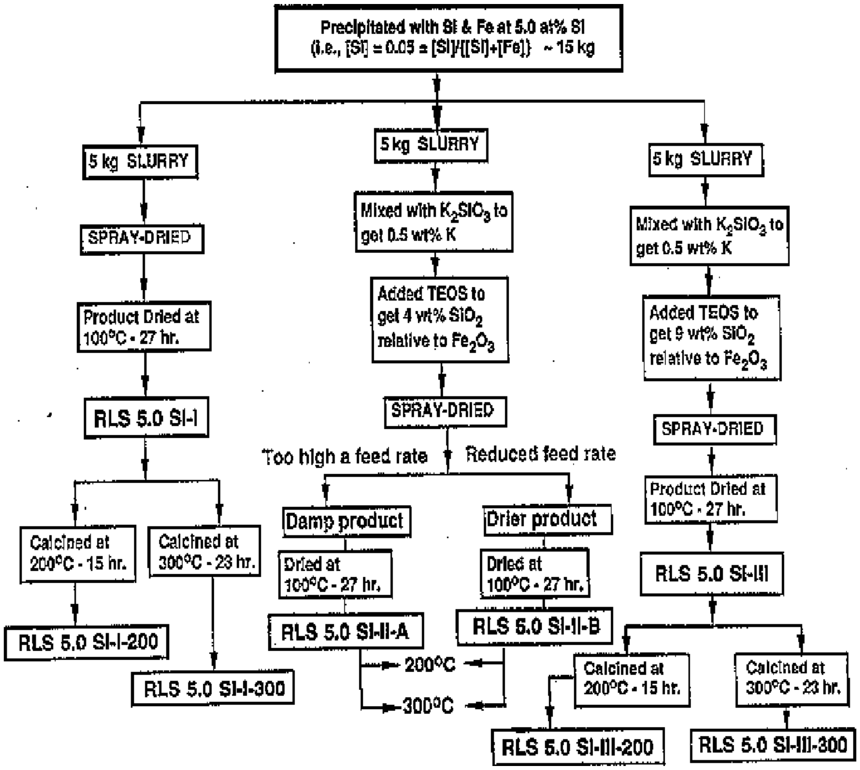

Figure 1. Synthesis routes showing the schematics of the procedure followed for making a 15 kg batch of promoted iron oxide catalysts.

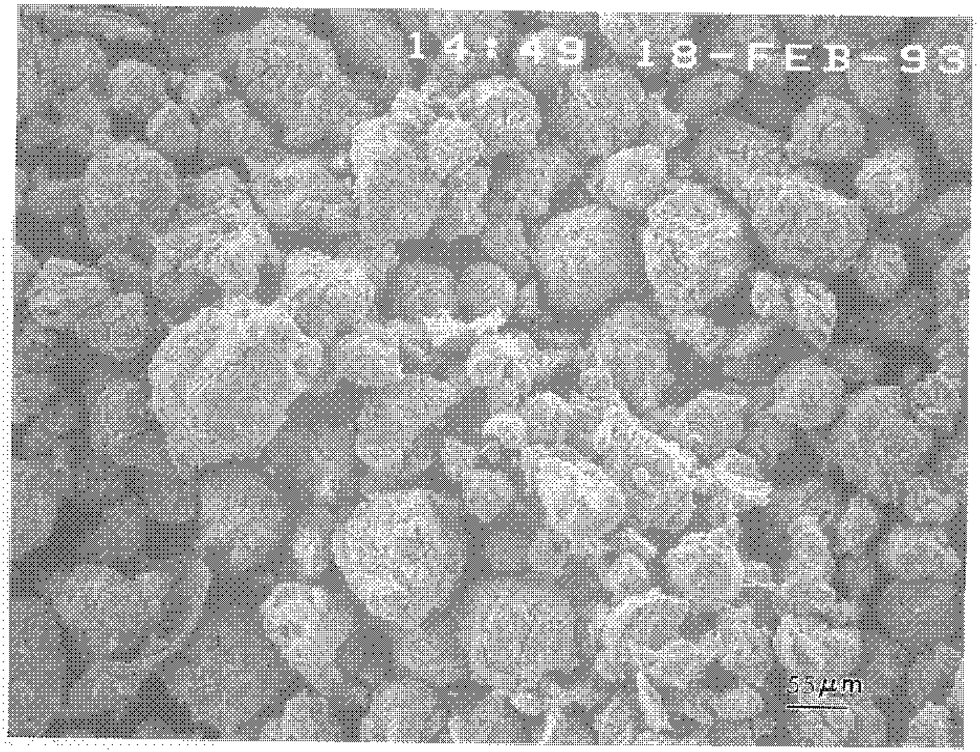

Figure 2. Scanning electron micrograph from the sample RLS5.0-Si-I, dried at 100°C for 27 hours.

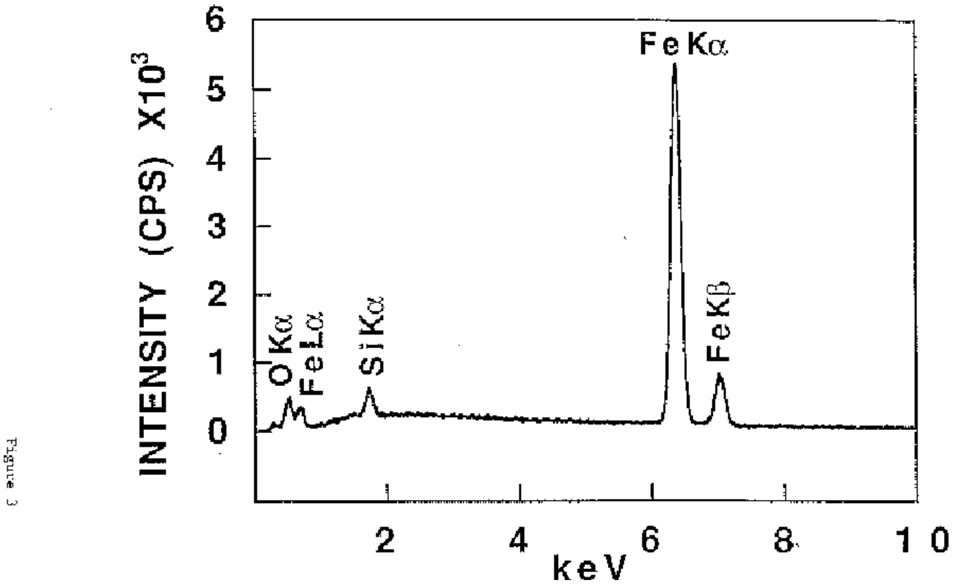

Figure 3. Energy dispersive X-ray spectrum from an agglomerate shown in Figure 2.

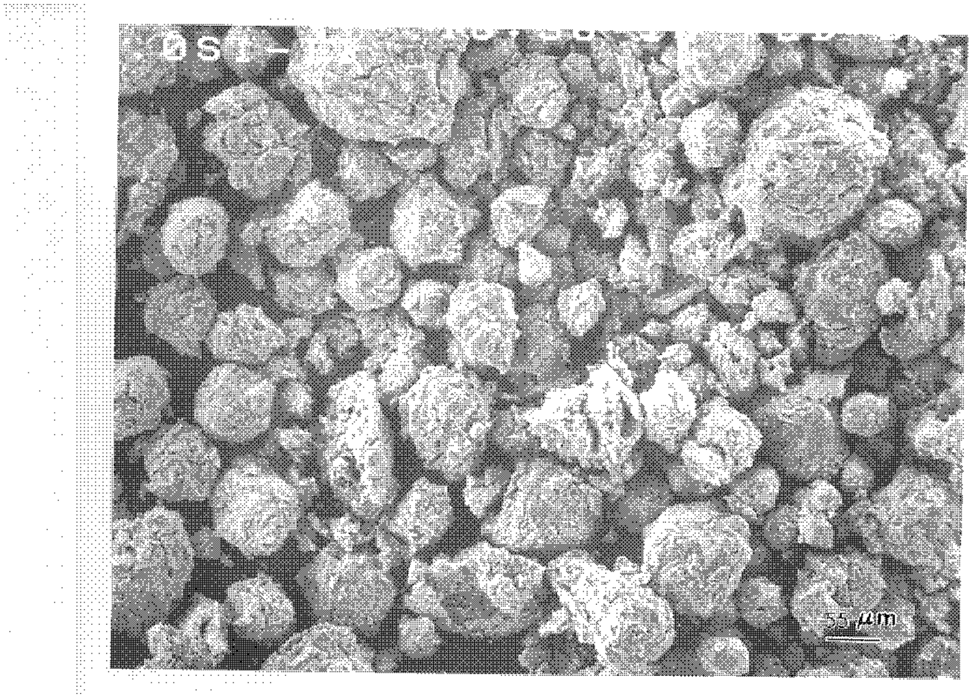

Figure 4. Scanning electron micrographs from RLS5.0-Si-IIA, dried at 100°C for 27 hours.

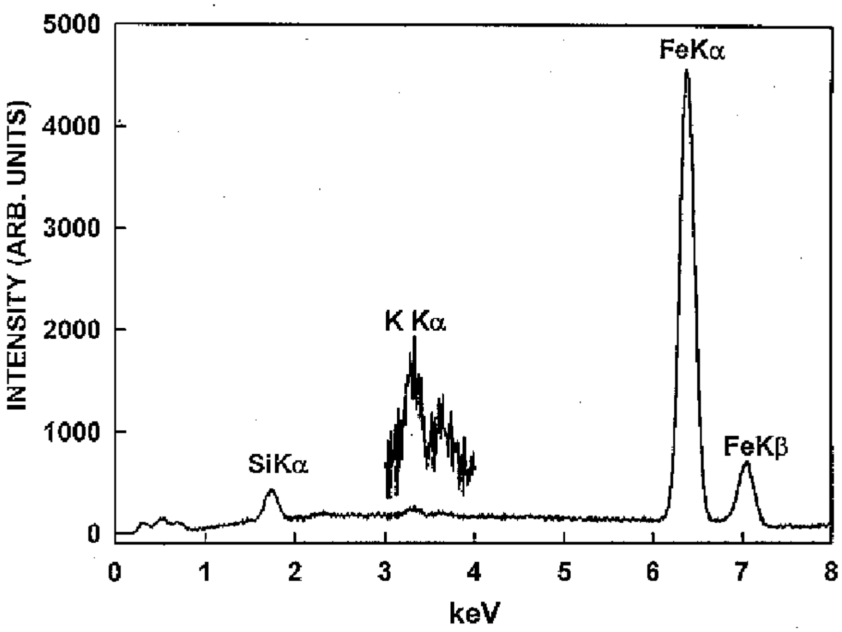

Figure 5. Energy dispersive X-ray spectrum from the sample RLS5.0Si-IIA, showing Fe, Si, K, O lines. These lines are indicated in the figure.

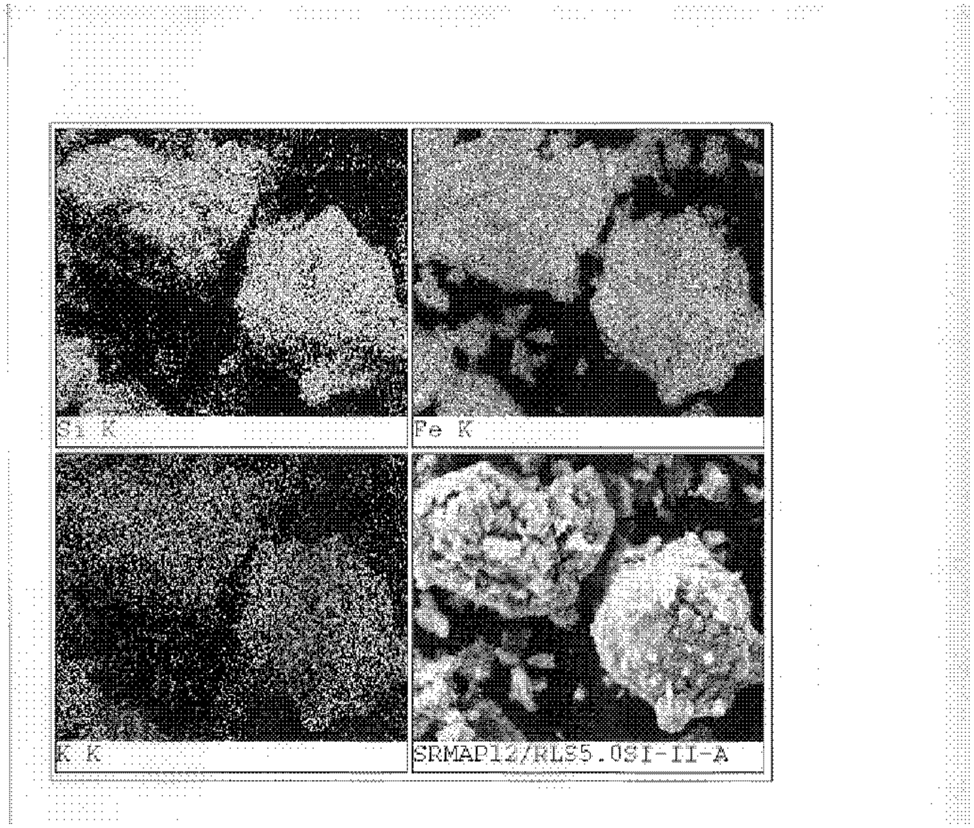

Figure 6. Elemental dot maps for the catalyst RLS5.0Si-IIA dried at 100°C. The last square is the image from which the dot map data were collected.

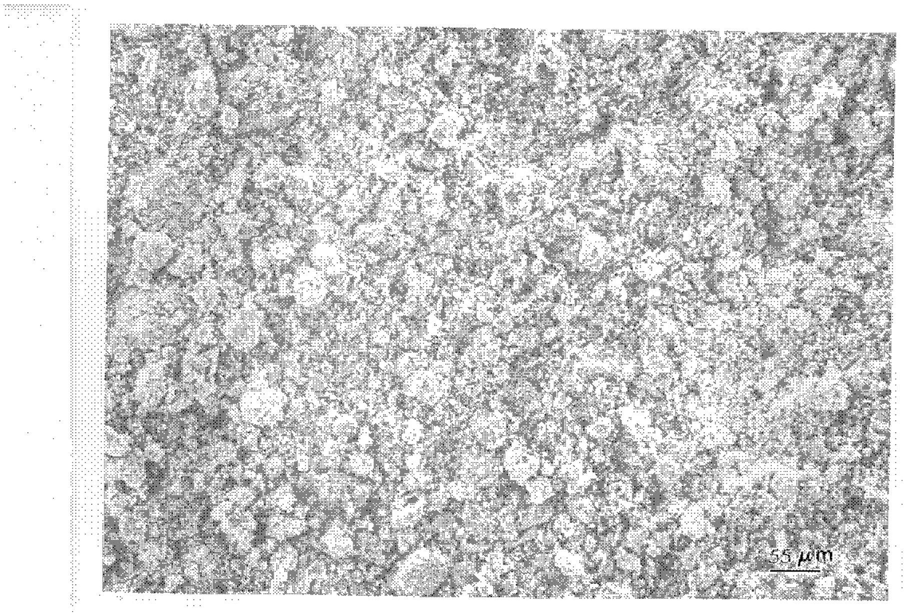

Figure 7. Electron micrographs from the catalyst RLS5.0Si-III, dried at 100°C.

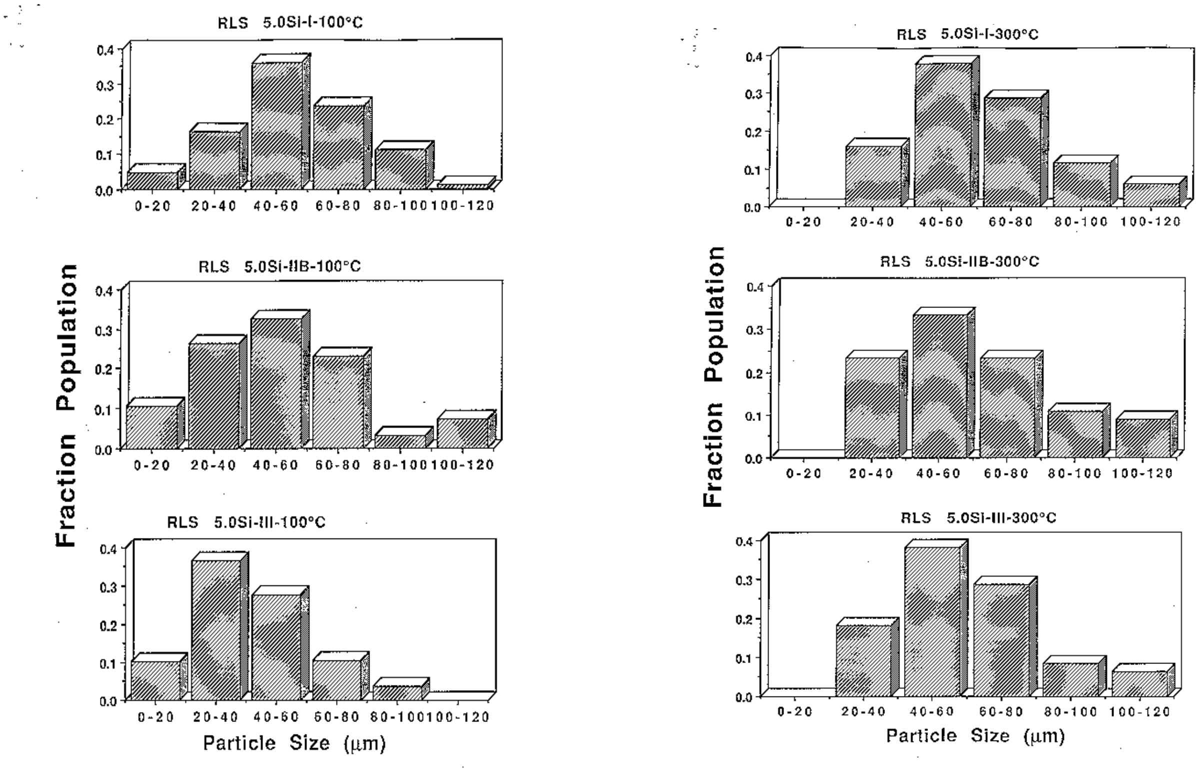

Figure 8. Size distribution for the agglomerates for the three catalysts (a) 100°C and (b) 300°C.

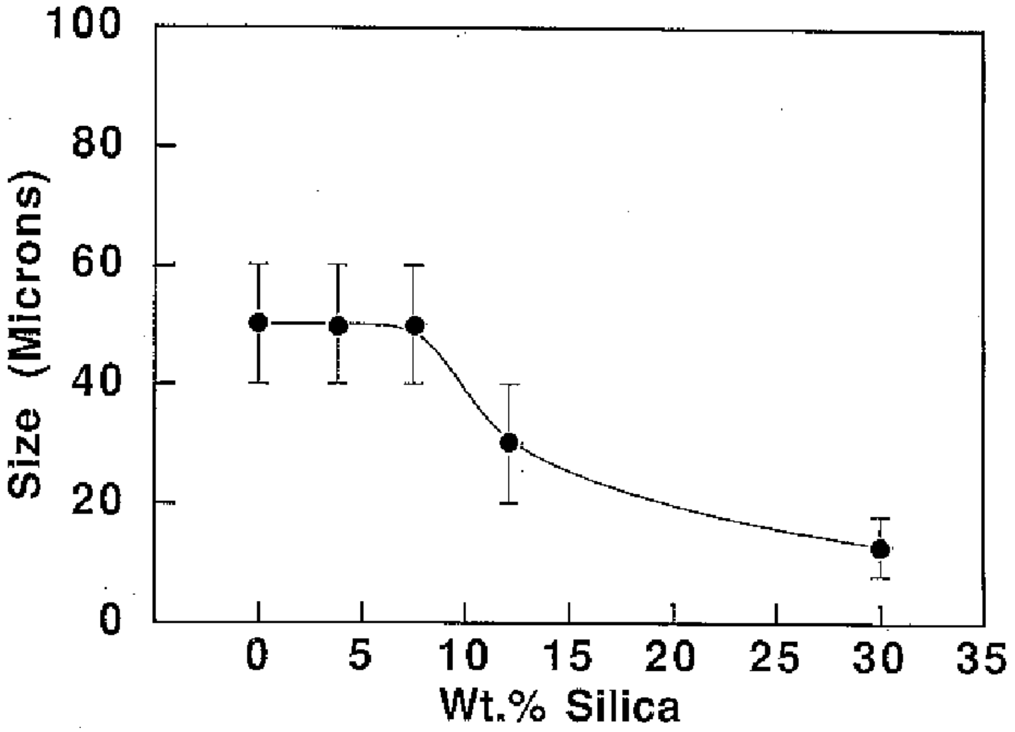

Figure 9. Agglomerate size (in microns) of iron oxide catalysts dried at 100^{o}C containing varying amounts of SiO_2.