

VI.10. SURFACE AREA AND POROSITY CHANGES IN IRON CATALYSTS DURING ACTIVATION AND INITIAL USE IN THE FISCHER-TROPSCH SYNTHESIS (Diane R. Milburn, Robert J. O'Brien, Komandur Chary, and Burtron H. Davis).

VI.10.1. ABSTRACT

The impact on iron Fischer-Tropsch catalysts of the variables controlling the initial precipitation, subsequent aging and drying conditions has been detailed. Heat treatment of iron oxyhydroxides causes the surface area to decrease and the major pore size to increase as the temperature increases, both in air and in an inert atmosphere. A shift toward higher temperature stability is seen for the same iron oxyhydroxide when co-precipitated with 6% Al_2O_3 , SiO_2 , or ZrO_2 . Samples for characterization are withdrawn from the reactor at increasing time intervals during pretreatment and exposure to synthesis gas. Surface area decrease and pore size increase are also observed during pretreatment with CO at 260°C and 100 psi. and during the initial days of reaction under CO/H₂. The major changes appear to occur during pretreatment and in the very early stages of the reaction. The effects of added promoter(s) also impact the area and/or porosity of the materials. The area and pore size distributions have shown systematic changes during increasing exposure to synthesis gas.

VI.10.2. INTRODUCTION

Iron catalysts have been utilized in the Fischer-Tropsch Synthesis since the 1920's (VI.10.1). The catalyst is generally admitted to the reactor in an oxide form and is then converted to the carbide in a pretreatment step or during synthesis. It is

generally believed that the iron oxyhydroxide or oxide catalyst undergoes conversion to a carbide form during pretreatment and use (VI.10.2). Since the Fischer-Tropsch synthesis is highly exothermic, synthesis in a slurry reactor provides one means of managing the large heats of reaction. However, in a slurry reactor the catalyst is subjected to reducing conditions at the bottom of the reactor where the reaction gases enter, and oxidizing conditions at the top of the reactor where products, including water and CO₂, exit. It is therefore of interest to determine the composition and structure of the iron catalyst under a range of conditions. This study examines changes in the surface area and pore structure of a material obtained from precipitated iron oxyhydroxide precursors during pretreatment with CO and then in the initial stages of reaction with CO plus H₂.

VI.10.3. EXPERIMENTAL

VI.10.3.a. Catalyst Preparation

Iron catalysts were prepared by continuous precipitation from an aqueous solution with ammonium hydroxide (ca. 15M). Unpromoted iron catalysts were precipitated from aqueous ferric nitrate solution at 82°C and at pH=6.7. Zirconia promoted iron catalysts were coprecipitated at ambient temperature from ferric nitrate/zirconyl nitrate solution at pH=9.3. Silica and alumina promoted samples were coprecipitated from ferric nitrate solution at pH=10.0. The alumina was added as aluminum nitrate and the silica as hydrolyzed tetraethylorthosilicate. Metal oxide promoters were added to produce a final concentration of 6 wt% ZrO₂, Al₂O₃ or SiO₂, respectively. Following precipitation, the products were subjected to multiple filtration and washing cycles, then dried in flowing air at 100°C for 24 to 48 hours.

VI.10.3.b. Catalyst Characterization

Powder X-ray diffraction patterns were obtained using a Phillips APD X-ray spectrometer equipped with a Cu anode and Ni filter operated at 40 kV and 20 mA ($\text{CuK}\alpha=1.5418 \text{ \AA}$). Identification of iron phases in the catalyst was accomplished by comparing the XRD pattern of the sample with those in the standard powder XRD file compiled by the joint committee on powder diffraction standards published by the International Center for Diffraction Data.

Nitrogen sorption measurements were made with a Quantachrome Autosorb 6 instrument. Samples were outgassed at 80°C and less than 50 mtorr for at minimum of 12 hours prior to analysis. Care was taken not to exceed the sample's drying temperature during degassing to minimize the effects of temperature on physical structure. BET surface areas and pore size distributions were calculated from the adsorption and desorption data, respectively. The cylindrical pore model of Broekhoff-deBoer (VI.10.3) was used for pore size distributions due to better agreement with BET surface area and total pore volume as compared with other models (eg. Cohan's cylindrical pore model (VI.10.4), a packed sphere model (VI.10.5), or the BJH model (VI.10.6)). For comparison, the pore radii corresponding to maximum dV/dr calculated using the Broekhoff-deBoer model and the BJH method are listed for unpromoted iron oxyhydroxides in Table VI.10.1.

VI.10.3.c. Catalyst Activation and Reaction

A slurry containing 7% or 20 wt.% catalyst in a C_{30} -polyalphaolefins oil (Ethyl Corporation) was thoroughly mixed in a 300 mL autoclave operated as a continuous stirred tank reactor. Potassium t-butoxide was added directly to this slurry to prepare

the doubly promoted iron catalysts. The slurries were heated to 260°C or 270°C at 1.5 - 2.0° min⁻¹ at 100 or 175 psig while pretreatment gas (CO) was introduced into the reactor at a flow rate of 2.0 to 3.4 nL hr⁻¹ g⁻¹(Fe). After reaching 260 or 270°C, the flow of pretreatment gas was continued for 24 hr. Synthesis gas (H₂:CO = 1 or H₂:CO = 0.7) was then passed at a flow rate of 3.4 nL hr⁻¹ g⁻¹(Fe). Slurry samples (approximately 10 g each) were removed from the reactor at various times during the pretreatment and synthesis stages. CO and H₂ conversions were determined by analyzing the exit gas stream using a Carle gas analyzer. Soxhlet extractions, using toluene as the solvent, were performed on all samples to remove the accumulated wax. Toluene has been found to be the superior solvent for wax removal. XRD analysis on the spent catalysts reveals two peaks at low 2θ which are attributed to the presence of wax on the catalyst. Following extraction with toluene these peaks no longer appear; however, the possibility of small quantities of wax remaining cannot be eliminated. The catalyst samples were filtered and dried under vacuum at ambient temperature prior to characterization.

VI.10.4. RESULTS AND DISCUSSION

A strong temperature dependence on BET surface area and porosity was observed for all samples used in this study. The changes in surface area resulting from heating in air for the promoted FeOOH catalysts and an unpromoted iron catalyst are shown in Figure VI.10.1. The trend is clearly one of continuous loss in surface area with increasing temperature in air. An unpromoted sample was also seen to demonstrate this trend when heated in He.

The pore size distributions following heat treatments in air for an unpromoted iron oxyhydroxide are shown in Figure VI.10.2. A corresponding increase in the size of the pores providing the majority of the pore volume is observed with temperature increase. The sample which has been subjected to 800°C heating has very low pore volume and surface area as measured by nitrogen sorption.

Activities for the Fischer-Tropsch Synthesis (FTS) have been obtained using a slurry reactor for the iron catalysts. X-ray diffraction data show that all samples are nearly amorphous to x-ray with only traces of α -FeOOH prior to pretreatment and reaction. Following only 3 hours of pretreatment in CO, the XRD patterns are consistent with that of Fe₃O₄. After 24 hours of CO pretreatment, the patterns suggest the presence of Fe₃O₄ and a small amount of iron carbide. The carbide phase is evident due to an increase in the relative intensity of the 400 peak of Fe₃O₄.

Catalysts used in the following pretreatment and synthesis studies have been dried at 100°C and admitted to the reactors without further calcination other than that which occurs during pretreatment. The change in BET surface areas during pretreatment and synthesis are shown in Figure VI.10.3. As can be seen by comparing the surface areas for the fresh catalysts (Table VI.10.2) with those of the first samples taken during pretreatment, there was a substantial decrease on initial exposure to CO in every case. However, after this initial loss, only the sample promoted with Zr continues to show a decrease in surface area with reaction time. The unpromoted and Al promoted samples appear to show slight increases in surface area, whereas the samples to which K has been added in the reactor show a substantial increase in surface area following exposure to synthesis gas.

Pore size distributions for the unpromoted FeOOH are shown in Figure VI.10.4. This sample was also run with an initial 3 hour He pretreatment step prior to introduction of CO to the reactor in order to test any reported benefits in activity or stability. The pore size distributions, surface areas and conversions are essentially identical within experimental error after the first few hours of pretreatment in CO. Thus, all remaining reactions were made without pretreatment in He. Figure VI.10.4 illustrates the common trend seen in all of the iron catalysts tested, namely a rapid change toward larger pores and broader size distributions on exposure to CO pretreatment, then a more gradual broadening and increase to larger pores is seen with time on stream. Treatment in a CO/H₂ mixture produces an average pore size that is about twice as large as the samples pretreated in CO only.

Figures VI.10.5 through VI.10.8 show the pore size distributions calculated for the Zr, Al, Al + 0.5% K, and Si + 0.5% K promoted FeOOH catalysts, respectively. As compared with the unpromoted FeOOH, the 6% ZrO₂ promoted catalyst demonstrates less of an "aging" effect in its pore size distribution and shows smaller pores and less tendency for the distribution to broaden and move to higher radii (Figure VI.10.5). Pretreatment in CO and in CO/H₂ produce similar pore size distributions. Conversion data for both unpromoted and Zr-promoted samples shows relatively low and constant CO conversion with synthesis time (ca. 25% and 10%, respectively).

Pore size distributions for Al-promoted catalysts, shown in Figure VI.10.6, are similar to the trend shown with the unpromoted catalysts. The pore radii are broad and range from 100 Å upward. This sample also exhibited a relatively constant CO conversion at approximately 15%.

In contrast, the two runs using doubly promoted catalysts show increasing surface areas with time and increasing CO conversions. Adding 0.5% K to the Al-promoted catalyst (Figure VI.10.7) resulted in increasing the CO conversion from 15% to approximately 35% in the initial hours of reaction and to 55% by 71 hours on stream. The surface area (Figure VI.10.3) also increased throughout the synthesis.

FeOOH promoted with both Si and K also exhibit increasing surface areas and CO conversions with increasing reaction time, although to a lesser degree than for the Al doubly promoted samples. For 6% Si and 0.5% K, CO conversion increases steadily from approximately 20% to 40% from 3 hours to 72 hours under synthesis conditions. BET surface areas also increase, as shown in Figure VI.10.3 from $45 \text{ m}^2\text{g}^{-1}$ to $73 \text{ m}^2\text{g}^{-1}$. Pore size distributions (Figure VI.10.8) indicate some shift towards larger pores and broader size distributions with exposure to synthesis conditions.

All of the catalysts tested in this study experienced the greatest changes in pore structure (decrease in BET surface area and increase in pore size) during initial contact with the oil and CO. Further increases in pore size have been seen with increasing exposure to CO/H₂. The addition of a metal promoter such as Al, Si or Zr appears to lessen these effects during the synthesis reaction. The most striking changes were observed when a small concentration (0.5%) of potassium was added to the promoted iron catalyst. This resulted in a substantial increase in surface area and corresponding increase in conversion activity during the reaction. While the chemical effects of potassium promotion are certainly important in the increased activity and selectivity reported throughout the literature for iron catalysts in the Fischer-Tropsch reaction, Dry contends that the surface areas and pore size

distributions of the precursors and catalysts have a strong impact upon catalyst performance (VI.10.7). Further work is required to determine the optimum combination of promoters and to elucidate the underlying mechanism.

VI.10.5. ACKNOWLEDGEMENT

The authors acknowledge the financial support of this work by the Department of Energy contract No. DE-AC22-91PC90056 and by the Commonwealth of Kentucky.

VI.10.6. REFERENCES

- VI.10.1. A. Mittasch, *Advan. Catal.*, **2**, 82 (1950).
- VI.10.2. H. H. Storch, N. Golumbic and R. B. Anderson in "The Fischer Tropsch and Related Synthesis", Wiley & Sons, New York, NY (1951), p. 8.
- VI.10.3. (a) J. C. P Broekhoff and J. H. deBoer, *J. Catal.*, **9**, 9 (1967); (b) **9**, 15 (1967); (c) **10**, 153 (1968); (d) **10**, 368 (1968); (e) **10**, 377 (1968); (f) **10**, 391 (1968); (g) **11**, 46 (1968).
- VI.10.4. L. H Cohan, *J. Am. Chem. Soc.*, **60**, 433 (1938).
- VI.10.5. B. D. Adkins and B. H. Davis, *J. Phys. Chem.*, **90**, 4866 (1986).
- VI.10.6. E. P. Barrett, L. G. Joyner and P. P. Halenda, *J. Amer. Chem. Soc.*, **73**, 373 (1951).
- VI.10.7. M. E. Dry in "Catalysis. Science and Technology", (J. R. Anderson and M. Boudart, Eds.) Springer-Verlag, Berlin, Vol. 1, (1981), p. 159.

Table VI.10.1

Comparison of Pore Sizes Calculated Using the Broekhoff-deBoer (B-deB) and Barrett-Joyner-Halenda (BJH) Models for Unpromoted Iron Oxyhydroxides

Drying Temperature (K)	Pore Radius (A) B-deB Model	Pore Radius (A) BJH Model
150	19	23
300	25	31
400	62	68
500	90	97
800	N/A	N/A

Table VI.10.2

Comparison of Promoted and Unpromoted Iron Oxyhydroxides

Sample	BET Surface Area (m ² g ⁻¹)	Total Pore Volume (cm ³ g ⁻¹)
Unpromoted FeOOH	124	0.088
FeOOH / 6% ZrO ₂	257	0.200
FeOOH / 6% Al ₂ O ₃	160	0.130
FeOOH / 6% SiO ₂	284	0.226

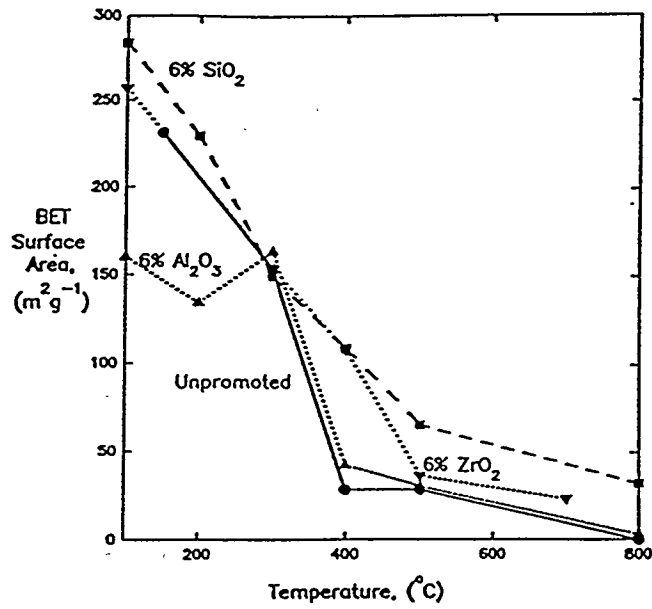


Figure VI.10.1. Effects of heating temperature on BET surface areas of FeOOH catalysts.

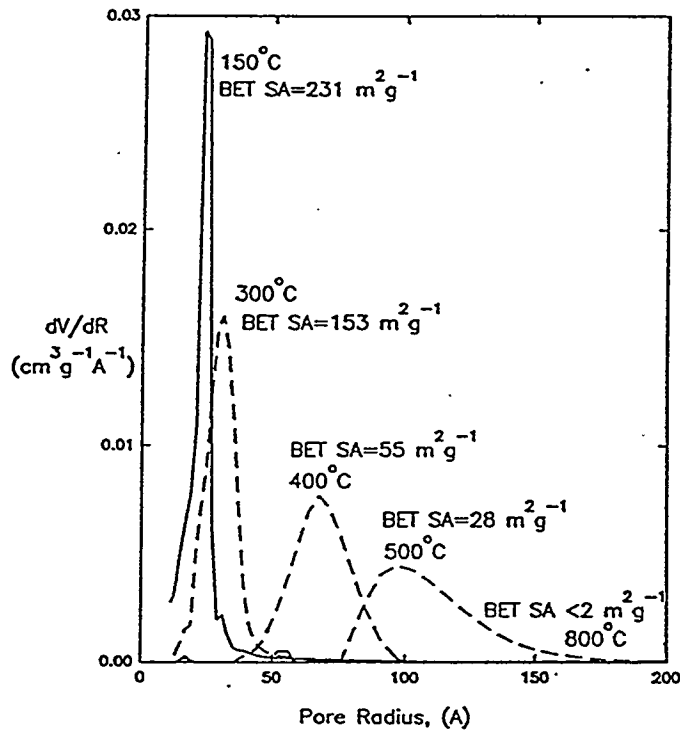


Figure VI.10.2. Pore size distributions for FeOOH catalysts heated in air.

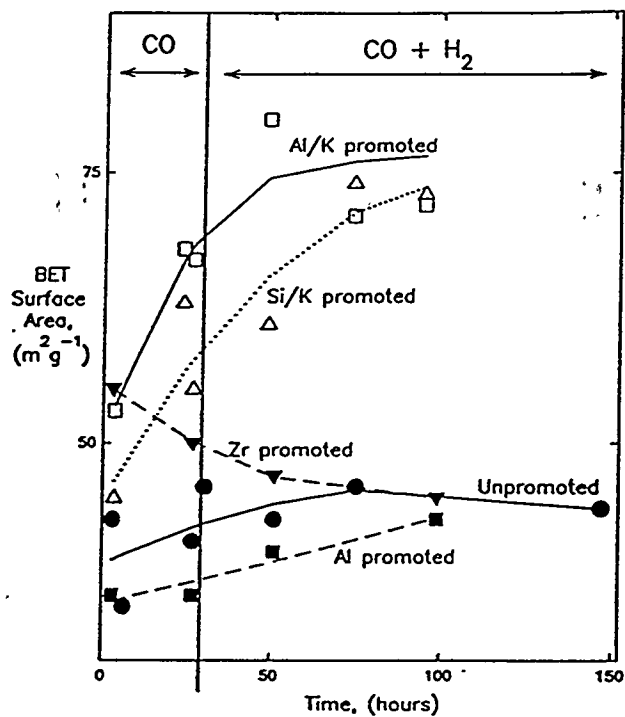


Figure VI.10.3. Effect of pretreatment and synthesis time on surface areas of FeOOH catalysts.

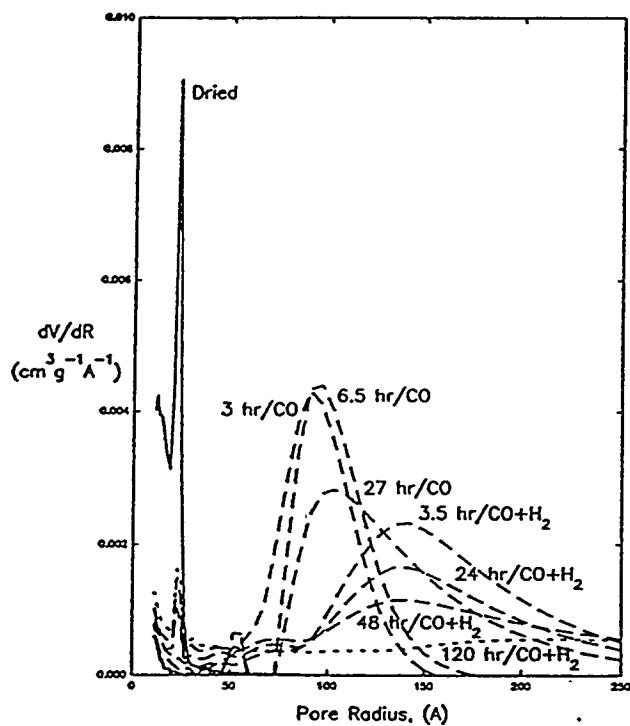


Figure VI.10.4. Effects of pretreatment and reaction on the pore size distributions of unpromoted FeOOH catalysts.

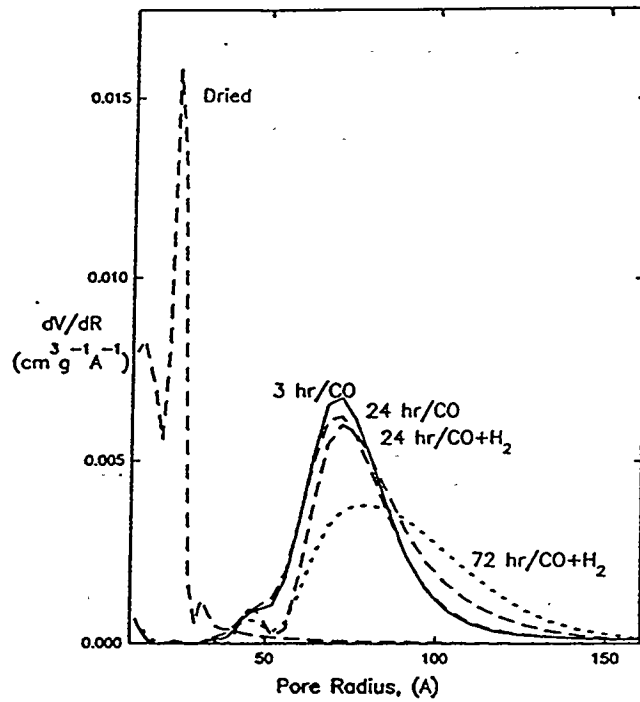


Figure VI.10.5. Effects of pretreatment and reaction on the pore size distributions for FeOOH/6% ZrO₂.

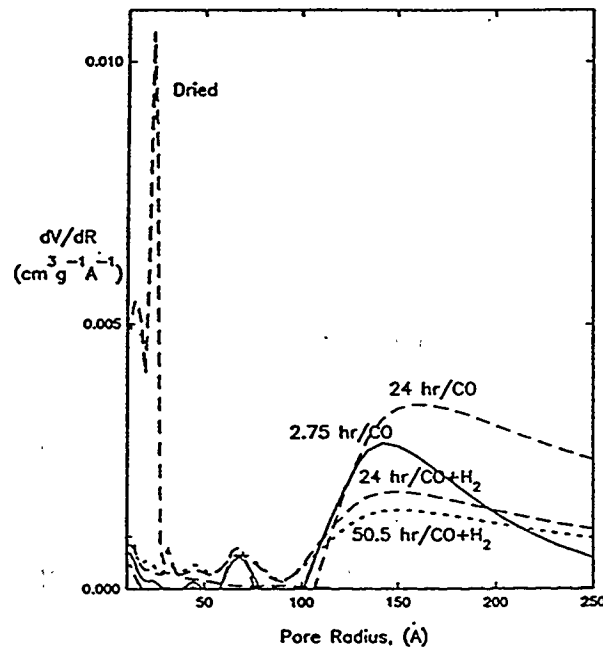


Figure VI.10.6. Effects of pretreatment and reaction on the pore size distributions of FeOOH/6% Al₂O₃.

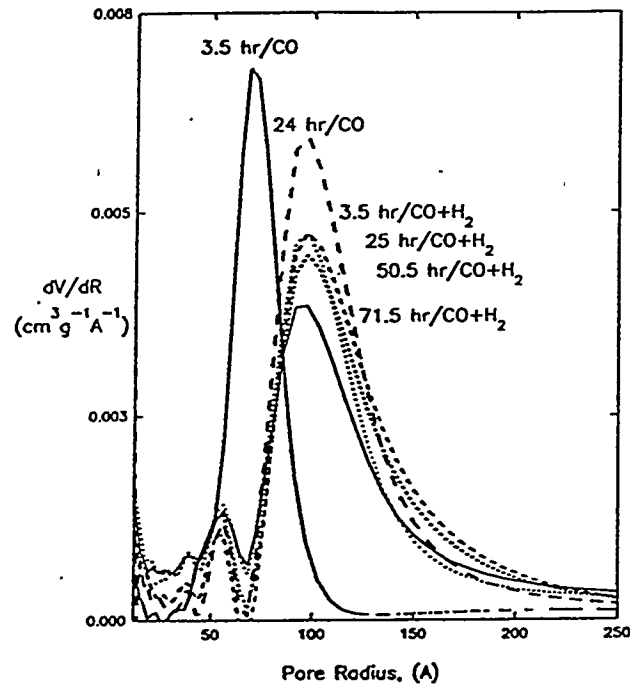


Figure VI.10.7. Effects of pretreatment and reaction on pore size distributions of FeOOH/6% Al₂O₃/0.5%K.

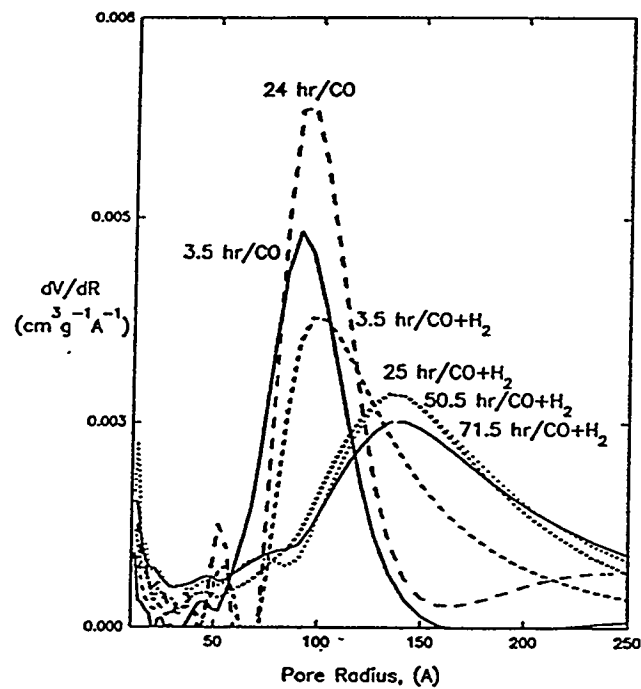


Figure VI.10.8. Effects of pretreatment and reaction on pore size distributions of FeOOH/6% SiO₂/0.5% K.