PHYSICAL AND CHEMICAL PROPERTIES OF $Fe(CO)_5/Al_2O_3$ CO-HYDROGENATION CATALYSTS.

M. Rameswaran and C. H. Bartholomew.

BYU Catalysis Laboratory, Department of Chemical Engineering, Brigham Young University, Provo, UT 84602.

Introduction

Carbonyl-derived catalysts (CDCs), ie catalysts prepared by the decomposition of metal carbonyls on catalyst carriers, have attracted recent attention because of their unusually high dispersions (fractions exposed to the surface) and high extents of reduction [1,2] . While conventional preparation methods may lead to metal contamination with S or Cl or may result in support decoration [3,4], it may be possible to produce "clean" particles by decomposing carbonyl complexes on carefully dehydroxylated supports. Thus, effects of metal loading, and crystallite size may be investigated in the absence of these contaminants using this class of catalysts.

The objective of this study was to investigate the effects of metal loading and support dehydroxylation temperature on the physical and chemical properties of Fe CDCs.

Experimental

Alumina (DISPAL M,) was dehydroxylated under vacuum at 473-1073 K for 16 hours and stored in a dry box. A dehydroxylation temperature of 923 K was used in the preparation of most of the catalysts in this study. About a two fold excess of $Fe(CO)_5$ to achieve a given Fe loading was mixed with pentane. The dehydroxylated alumina was then impregnated to incipient wetness using this solution. The pentane solvent was removed by evacuation at room temperature. About 10 g of the catalyst thus prepared was reduced in flowing hydrogen and stored in a dry box and the remainder was sealed and stored in a refrigerator. Total hydrogen adsorption capacities and oxygen titration uptakes (upon oxidizing the reduced catalyst at 723 K) were measured using a volumetric apparatus and procedures described elsewhere [5]. The reactor system used for obtaining the activity/selectivity properties are described elsewhere[6].

Results and Discussion

Figure 1 depicts the effect of reduction temperature on the dispersion and the extent of reduction of a 4.6 %Fe/alumina catalyst. The dispersion goes through a maximum while the extent of reduction reaches 100% as the temperature of reduction is increased from 473-773 K. Garten [7] reported that in the case of Fe/alumina catalysts prepared by aqueous impregnation, up to 1.5% Fe (300

μmoles per gram catalyst) was irreducible even at very high reduction temperatures due to strong interaction of iron oxide with the support. However, the results from this study indicate that the Fe/alumina prepared via carbonyl decomposition can be easily reduced to the Fe(0) state at relatively mild reduction conditions. The significant decrease in dispersion at higher reduction temperatures suggests that the carbonyl-derived species are mobile at higher temperatures in reducing atmosphere. Since the maximum dispersion was obtained at 573 K, this temperature was used for reducing all the catalysts in this study.

Data showing the effects of metal loading on the physical properties of carbonyl-derived Fe/alumina reduced at 573 K are tabulated in Table 1. Although dispersion decreases with increasing metal loading, neither the hydrogen uptake nor the extent of reduction follow any clear trends. Nevertheless, the dispersions and extents of reduction for these catalysts are much higher than obtainable for catalysts prepared by other method with similar metal loadings.

Table 2 illustrates effects of support-dehydroxylation temperature on the physical properties of Fe/alumina CDS's. All the catalysts listed in Table 2 contain 4.0-4.8 wt.% iron. However the amount of hydrogen adsorbed per gram of catalysts varies significantly with dehydroxylation temperature. The extent of reduction and the %D for the catalyst with the support dehydroxylated at 473 K were not obtained due to the inability to measure any significant oxygen uptake by the conventional methods. Hence it can be safely assumed that the impregnated carbonyl was fully oxidized. However, the catalyst with the support dehydroxylated at 1023 K was easily reduced. Thus, it is seen that the extent of reduction (or the ease of reduction) increases with decreasing surface OH concentration. This observation is consistent with that of Brenner and Burwell [8], who proposed that the surface OH groups act as anchors for the carbonyls by causing their partial oxidation.

The activity of iron/alumina dehydroxylated at 923 K increases with decreasing metal loading or increasing dispersion. This observation is opposite to that observed for Co/alumina prepared by aqueous impregnation [9] and Ru/alumina prepared from carbonyls on partially dehydroxylated alumina [10]. However, the selectivities of these Fe/alumina CDC catalysts were independent of metal loading or dispersion (Table 3). The 1 and 1.5% Fe/alumina catalysts deactivated rapidly at temperatures above 473 K, hence accurate measurement of activation energies was not possible. Although Fu and Bartholomew [9] observed a trend of decreasing activity with decreasing metal loading or increasing dispersion for Co catalysts prepared by aqueous impregnation with cobalt nitrate, they also observed that a 3% Co/alumina CDC catalyst was at least twice as active as 3% Co/alumina prepared by impregnation. Their results suggest that the conventional impregnation method leads to crystallite decoration and thus lower activity. Hence the results

TABLE 1.
Effects of Metal Loading on the Physical Properties of Fe/ Alumina[a] Catalysts.

Wt % Fe	H_2 uptake (μmoles/g)	% Dispersion[b]	Extent[c] of Reduction
1.0	45.1	75	33.6
1.5	31.5	40	58.6
4.6	72.6	31	55.1

a. Support dehydroxylated at 923 K under vacuum, catalyst reduced at 573 K.

b. $\%D = \frac{\text{\#of exposed atoms of Fe measured by hydrogen adsorption}}{\text{Total \# of reduced Fe atoms.(From oxygen titration and AA)}} \times 100$

c. Measured by O_2 titration at 673 K.

Table 2
Effects of Support Dehydroxylation Temperature on the Physical Properties of ~4.5 Fe/Alumina[a].

Dehydroxy-lation Temp. (K)	H_2 uptake (μmoles/g)	% Dispersion[b]	Extent[c] of Reduction
473	8.9	--[d]	--[d]
923	72.6	31	55.1
1073	55.9	16	95.4

a. Catalyst reduced at 573 K.

b. $\%D = \frac{\text{\#of exposed atoms of Fe measured by hydrogen adsorption}}{\text{Total \# of reduced Fe atoms.(From oxygen titration and AA)}} \times 100$

c. Measured by O_2 titration at 673 K.

d. Unable to measure oxygen uptakes.

TABLE 3.

Effects of Metal Loading on Activity/Selectivity Properties.
(H_2/CO = 2, 1 atm, 473 K)

Wt % Fe	TOF[a] x10^{-3} (sec^{-1})	% HC in[b] product Stream	HC Selectivity[c]				O/P[d]
			CH_4	C_2-C_4	C_5-C_{11}	C_{12+}	
1.0	0.36	87.2	26.2	40.8	33.0	0	1.6
1.5	0.13	83.8	28.3	42.4	29.3	0	2.5
4.6	0.05	87.2	21.7	40.1	38.1	0	2.5

a. Based on total H_2 adsorption.

b. Mole percent based on carbon balance; the remainder of the C apppeared as CO_2.

c. Wt.% hydrocarbon in product.

d. $O/P = \sum_{n=3}^{7} C_n^{=} / C_n$

observed for catalysts prepared by conventional methods [9] are probably due to a secondary structure-sensitivity [ie. decoration of the crystallites by support species] while the results in this study reflect either a primary structure sensitivity or changes in the electronic properties of the small metal clusters in the well-dispersed Fe/alumina. In a study by Kellner and Bell [10] of highly dispersed Ru/alumina prepared from the carbonyl, their observation of a decreasing activity with increasing dispersion may be a result of incomplete dehydroxylation of the support leading to crystallite contamination in the more highly dispersed catalysts.

The results of this study show that the support dehydroxylation temperature has a greater influence on the activity/selectivity properties than does dispersion (Table 4). The activity, selectivity for CH_4 and C_2-C_4 hydrocarbons, and the O/P ratio decrease with increasing dehydroxylation temperature, while the C_5-C_{11} fraction increases. Figure 2 indicates that the activation energy also increases with increasing dehydroxylation temperature. These effects of dehydroxylation temperature may be due to changes in the concentration of surface OH groups.

Conclusions

1. It is possible to produce highly dispersed and highly reduced catalysts by decomposing $Fe(CO)_5$ on dehydroxylated alumina.

2. The specific activity decreases with increasing metal loading (or decreasing dispersion). This effect may be due to a primary structure sensitivity on "clean" metal crystallites. The independence of selectivity with metal loading supports this hypothesis.

3. The significant changes in activity/selectivity with support dehydroxylation temperature may be a function of support hydroxyl group concentration, a significant concentration leading to support contamination of the metal surface and oxidation of the metal.

Acknowledgments

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References.

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TABLE 4.

Effects of Dehydroxylation Temperature on Activity/Selectivity Properties of ~4.5 % Fe on Al_2O_3.
(H_2/CO = 2, 1 atm, 473 K)

Dehydro-xylation Temp.(K)	TOF[a] $\times 10^{-3}$ (sec^{-1})	% HC in[b] product Stream	HC Selectivity[c] CH_4	C_2-C_4	C_5-C_{11}	C_{12+}	O/P[c]
473	0.2	77.0	43.0	56.0[e]	0	0	∞[f]
923	0.05	87.2	21.7	40.1	38.1	0	2.5
1073	0.02	87.4	21.7	39.0	39.7	0	2.3

a. Based on total H_2 adsorption.

b. Mole percent based on carbon balance; the remainder of the C apppeared as CO_2.

c. Wt.% hydrocarbon in product.

d. $O/P = \sum_{n=3}^{7} C_n^{=} / C_n$

e. C_2 and C_3 only

f. C_2: no parafins; C_3: O/P=1.54

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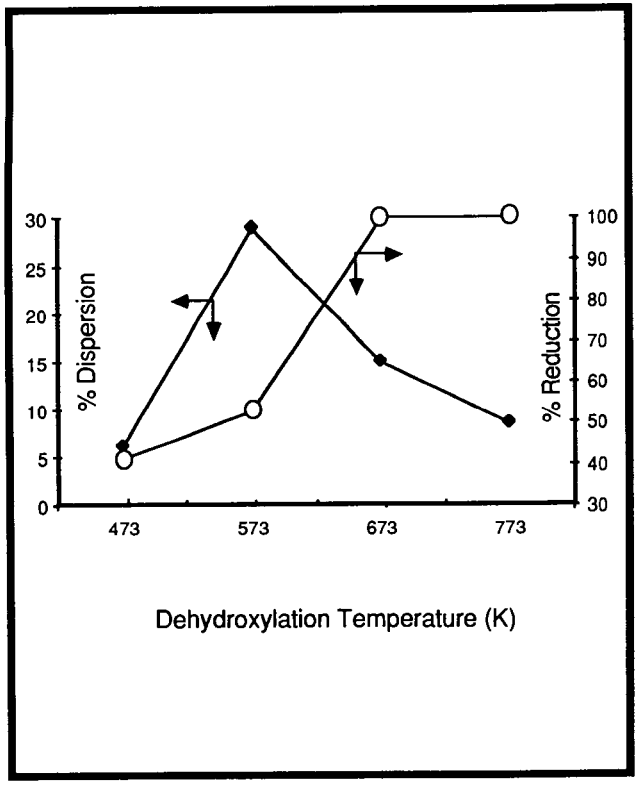

Figure 1. Reduction Temperature vs % Reduction and % Dispersion

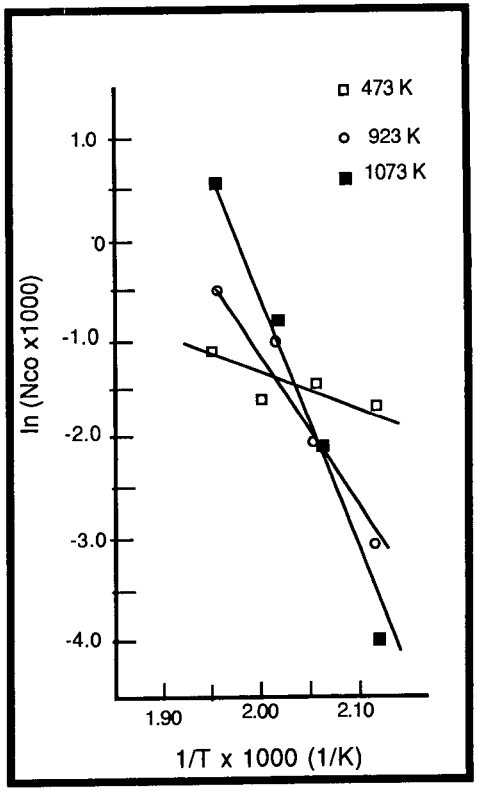

Figure 2. Effect of Dehydroxylation Temperature on Activation Energy for CO Hydrogenation