

Effect of Support and Promoter in Fischer-Tropsch Cobalt Catalysts

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The effect of support (kieselguhr) and promoter (ThO_2) in Fischer-Tropsch cobalt catalysts has been investigated using H_2 and CO adsorption, X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR) techniques. The extent of reduction is found to be 39% in the presence of kieselguhr due to its migration to the surface of cobalt oxide. Presence of ThO_2 increases the extent of reduction to 75% probably restricting the migration of kieselguhr. XPS results show the preferential segregation of ThO_2 on the surface thus preventing the encapsulation of cobalt oxide by kieselguhr. The CO/Co and H/Co values decrease with decrease in cobalt loadings indicating the possible interaction between cobalt and kieselguhr. During reduction, kieselguhr is found to stabilize CoO as revealed from TPR studies. © 1986 Academic Press, Inc.

1. INTRODUCTION

Industrial Fischer-Tropsch (FT) catalysts are normally multicomponent systems consisting of suitable supports and promoters in addition to the active metal component. The choice of the support and promoter depends on the required thermal stability and the extent of metal dispersion.

Kieselguhr, an inert support, used in the preparation of supported metal catalysts to improve the active metal surface area by virtue of increasing the bulk volume of the catalysts is a weakly interacting support material with metal under the normal heat-treatment conditions (1). However, the observed changes in the activity of kieselguhr-supported metal catalysts have been attributed to its influence on the structural modifications of the active particles (2). Hydrogen adsorption studies on silica- and alumina-supported cobalt catalysts have shown that the activation energy for desorption of hydrogen increases with decrease in metal loadings (3), indicating the definite effect of these supports on the active component, namely cobalt surface.

Promoters normally added to prolong the life of the catalysts also has an effect on the catalyst activity. For example, potassium added as promoter in the iron FT catalyst is

known to function as an electron donor to metal (4). The industrial cobalt FT catalysts consist of kieselguhr and thoria as support and promoter, respectively, with or without MgO (5). The addition of kieselguhr and thoria is known to increase the selectivity of high-molecular-weight hydrocarbon formation (6). In the present investigation, the cobalt FT catalysts with kieselguhr and thoria as support and promoter, respectively, have been characterized using H_2 and CO adsorption, XPS, and temperature-programmed reduction (TPR) studies to determine the interaction of support and promoter with cobalt. For comparison, studies have also been carried out on polycrystalline cobalt.

2. EXPERIMENTAL

Kieselguhr (Rideal-De Haen AG) was purified by digesting it with 10% nitric acid for 4 h, filtered, washed with hot water until the extract is free of Ca^{2+} , Fe^{3+} , SO_4^{2-} , and Cl^- ions, dried at 380 K and heated at 825 K for 8 h before use in the preparation of catalysts.

Thin slurry of kieselguhr and hot solution of potassium carbonate were simultaneously added to the boiling solution of metal (cobalt alone for catalyst A and cobalt and thoria for catalyst B) nitrates taken

in the proper proportions. The precipitate was filtered out while still hot and washed thoroughly with hot water. The cake thus obtained was dried at 380 K and a requisite amount was decomposed and reduced at 600 K for 48 h. The completion of reduction was checked by the reproducibility in the hydrogen adsorption on the reduced catalyst at the reduction temperature.

Kieselguhr-supported cobalt catalysts of compositions 3, 10, 15, 20, and 25% Co were prepared as per the above procedure. Polycrystalline cobalt was prepared by the reduction of Co_3O_4 using H_2 at 573 K for 48 h.

Freshly reduced catalyst surfaces were cleaned by evacuation at 670 K and at 10^{-6} Torr for 4 h. Hydrogen chemisorption was carried out according to the procedure of Bartholomew *et al.* (7) [i.e., hydrogen was allowed to the system at 570 K for adsorption and cooled very slowly to room temperature in hydrogen atmosphere] to determine the particle size. Adsorption measurements were carried out in an all-glass reactor where a high vacuum of 10^{-6} Torr was routinely obtainable. Adsorption was carried out at 200 Torr pressure for 12 h. CO-treated surfaces were regenerated by soaking it in hydrogen at 1 atm pressure and at 573 K. Fresh hydrogen was put into the system after evacuation at 10^{-2} Torr for 5 min for every 3-h interval for 4 or 5 times. Finally surface was evacuated at 10^{-6} Torr and at 670 K for 4 h. Extent of reduction of the catalysts was determined by reoxidizing the catalysts in oxygen atmosphere at 670 K for about 4 h. The oxygen uptake under this condition was measured for the conversion of Co to Co_3O_4 .

XPS measurements were made using ESCA-lab. 2 (VG Scientific Co., UK) at room temperature on the reduced catalysts A and B and at a typical pressure of 10^{-9} Torr.

The dry cake in the form of carbonate(s) was heated at 673 K in oxygen atmosphere for 4 h to oxidize cobalt to its oxidic form. X-Ray diffraction studies showed that

Co_3O_4 is the main oxide in the oxidized sample.

Purified hydrogen at the flow rate of 20 ml/min was passed first through a quartz reactor tube containing 1.5 ml of the oxidized sample, the ice-cold trap, and finally through a sensitive flowmeter (sensitivity ± 0.05 ml/min). The sample packing was loose enough to avoid any pressure development inside the system. During the temperature-programmed reduction, the change in flow rate of hydrogen was monitored and was taken as proportional to the reduction signal. The maximum change in flow rate was between 18 and 20 ml/min. The intensity of the reduction signal was normalized with respect to the amount of Co_3O_4 present in 1.5 ml of the sample.

3. RESULTS AND DISCUSSION

3.1 Effect of Kieselguhr and Thoria on the Adsorption of H_2 and CO on Cobalt FT Catalysts

Adsorption of hydrogen is found to be an activated process on polycrystalline cobalt, catalyst A and catalyst B. This observation is in agreement with the literature report (3). The results of room-temperature adsorption of H_2 and CO are summarized in Table 1. The stoichiometric adsorption ratio for CO on cobalt is estimated in terms of molecules of CO adsorbed per accessible cobalt atom. Number of accessible cobalt atoms were deduced from maximum hydrogen uptake obtained by Bartholomew's method instead of using equilibrium room-temperature adsorption and using a stoichiometry of one hydrogen atom per surface cobalt atom (8). (These samples were not initially oxidized in oxygen.)

Though the crystallite sizes are almost the same for catalysts A and B, the ratio of CO per cobalt atom are 0.83 and 0.56, respectively, and the extent of reduction is lower for catalyst A. The amounts of hydrogen and CO adsorption on catalysts A and B increased by the addition of kieselguhr indicating the increase of disper-

TABLE I

Values of Uptake of Hydrogen and Carbon Monoxide, Extent of Reduction, Dispersion, and Average Crystallite Size for Supported and Unsupported Cobalt Catalysts

Property	Catalyst		
	Polycrystalline cobalt	Catalyst A	Catalyst B
Total maximum hydrogen uptake, $\mu\text{mol/g}$	21.8	75.8	112.4
Percentage reduction	100	39	75
Percentage dispersion	0.26	6.86	5.70
Total hydrogen uptake at room temperature, $\mu\text{mol/g}$	18.7	70.4	96.8
Total CO uptake at room temperature, $\mu\text{mol/g}$	21.0	126.0	125.0
Average crystallite diameter from hydrogen adsorption, nm	284	14	17

Note. Metal crystallite size (d) and percentage dispersion (D) were calculated according to the procedure of Reuel and Bartholomew (8): $d = 6.59 s/\% D$, where s is the site density [= 14.6 atoms/nm² for supported crystallites (fcc) and 11.2 atoms/nm² for unsupported cobalt crystallites (hcp)]; and $\%D = 1.179 x/wf$, where x is the volume of hydrogen chemisorbed, expressed in $\mu\text{mol/g}$, w is the weight percent of cobalt, and f is the fraction of reduced metal.

sion of cobalt on support. This is in agreement with the earlier study of Anderson *et al.* (9) that the addition of kieselguhr increases both the surface area and the pore volume of the catalysts. However, the percentage reduction for catalysts A and B are only 39 and 75%, respectively. The lower percentage reduction in the case of catalyst A probably can be due to encapsulation of cobalt oxide particles by the support. The transport of SiO₂ in steam containing environments at elevated temperatures and pressure or even at atmospheric pressure has been deduced (10) from the studies of water-gas shift reaction over silica-supported Fe₃O₄ and by the AES study on the migration of SiO₂ over Fe₃O₄. It is therefore postulated that any reaction using or producing steam could cause the migration of SiO₂. Such a phenomenon is probable in the case of cobalt oxide supported on kieselguhr, which could account for the low degree of reduction. However, an increase in the extent of reduction of

cobalt oxide (75%) in the presence of 5.7 wt% of ThO₂ is observed. The presence of ThO₂ (promoter) can thus cause the increase in the extent of reduction by interaction with the support or by restricting the migration of the support over the active phase. Thus there appears yet another function of the promoters normally added to industrial catalysts. It is therefore clear that the surface properties of the silica-containing catalyst could be altered due to this migration. For example, silicon-containing adlayer has been found to poison Pt surfaces used for methane or CO oxidation reaction (11).

3.2. Effect of Kieselguhr and Thoria on Cobalt FT Catalysts: XPS Studies

XPS studies were made on freshly reduced catalysts A and B (without prior heating in oxygen) using AlK _{α} radiation at room temperature and the typical spectra are shown in Figs. 1 to 3.

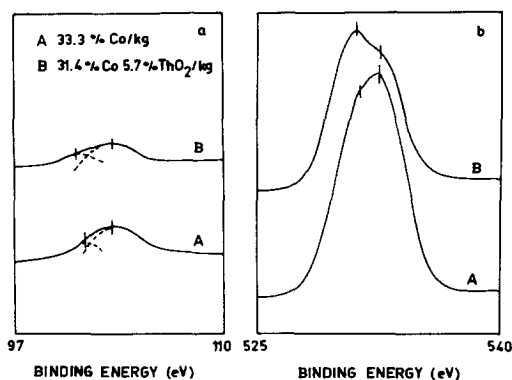


FIG. 1. X-Ray photoelectron spectra of (a) silicon-2p and (b) oxygen-1s in catalysts A and B.

The surface concentration of kieselguhr as deduced from the intensity of Si_{2p} peak (Fig. 1A) is greater in catalyst A than in B. The O_{1s} peak (Fig. 1B) is a doublet for both the catalysts indicating that CoO is also present. In addition the $\text{Co}_{2p_{3/2}}$ to $\text{Co}_{2p_{1/2}}$ peak separation is found to be ~ 15.5 eV for catalyst A (Fig. 2) and it is ~ 15.0 eV for catalyst B which are characteristic values of CoO and cobalt, respectively. The deduction that catalyst A contains a considerable amount of cobalt oxide is in agreement with the low percentage reduction value (39%) observed. However, in catalyst B only a small amount of CoO is

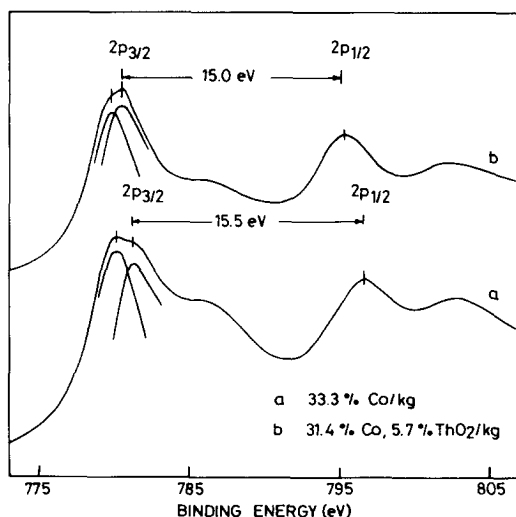


FIG. 2. X-Ray photoelectron spectra of cobalt in catalysts A and B.

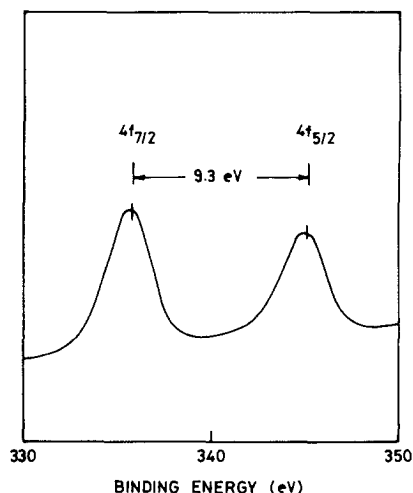


FIG. 3. X-Ray photoelectron spectrum of thorium in catalyst B.

present which accounts for the higher percentage reduction value (75%). The intensity of the O_{1s} peak at 530.6 eV (CoO) for catalyst A is lower as compared to the O_{1s} peak at 532.5 eV (SiO_2). The intensity of the O_{1s} peak at 530.8 eV for catalyst B is higher than that of the 532.4-eV peak indicating the segregation of ThO_2 on the surface. Further, the presence of ThO_2 on the surface has been characterized by $\text{Th}_{4f_{7/2}}$ and $\text{Th}_{4f_{5/2}}$ peaks (Fig. 3) with energy separation of 9.3 eV. Due to the surface segregation of ThO_2 , the concentration of kieselguhr on the surface is decreased as revealed by the intensities of Si_{2p} and O_{1s} (532.4 eV) peaks. In the system containing ThO_2 , a higher percentage reduction of cobalt oxide is also observed. This supports the postulate that thoria (promoter) restricts the migration of kieselguhr (support) over the surface and prevents the encapsulation of cobalt oxide.

Formation of SiO_2 adlayer due to its migration over metallic/metal oxide phase can occur under FT reaction conditions since water is formed as one of the products. Such process could lead to the deactivation of the catalysts. Probably the catalytic promoters, which normally prolongs the life of the catalysts, are functioning by preventing support-adlayer formation over active phase.

TABLE 2
Values of Uptake of Hydrogen and Carbon Monoxide, Extent of Reduction, Dispersion, and Average Crystallite Size for Kieselguhr-Supported Cobalt Catalysts

Catalyst	Total maximum H ₂ uptake (μmol/g)	H ₂ uptake at room temperature (μmol/g)	CO uptake at room temperature (μmol/g)	Percentage reduction	Percentage dispersion	Average crystallite diameter (nm)	H/Co	CO/Co
3% Co/KG ^a	17.9	0.6	4.0	60.2	11.7	8.2	0.034	0.111
10% Co/KG	38.5	6.1	32.1	41.0	11.1	8.7	0.158	0.417
15% Co/KG	47.9	15.3	63.8	47.6	7.9	12.2	0.319	0.666
20% Co/KG	53.7	27.2	77.0	48.0	6.6	14.5	0.507	0.718
25% Co/KG	65.0	46.9	107.1	50.5	6.1	15.9	0.722	0.824
33.3% Co/KG	75.8	70.4	126.0	39.0	6.8	14.0	0.929	0.831

^a KG = kieselguhr.

3.3. Physicochemical Characterization of Kieselguhr-Supported Cobalt Catalysts

Hydrogen chemisorption results and the derived parameters are summarized in Table 2. The H/Co and CO/Co values calculated from the room-temperature adsorption of H₂ and CO, respectively, per accessible cobalt atom at the surface are found to increase regularly with increase in cobalt loadings. Similarly, metal crystallite size calculated from the total H₂ uptake measurements also increases with cobalt loadings (Fig. 4).

The extent of reduction of cobalt oxide in the presence of kieselguhr is found to be ~50% indicating that the cobalt oxide is encapsulated by the support. This encapsulation could have occurred as a result of migration of the support in the reducing atmosphere. Though there is no direct experimental proof for the migration of the support species in the present study, the

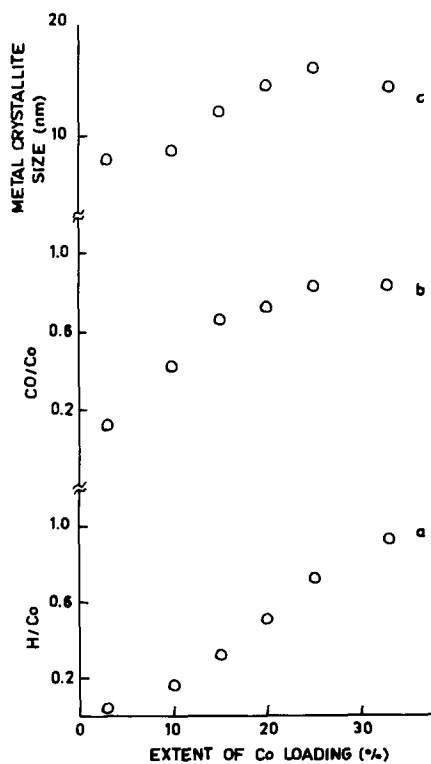


FIG. 4. Variation of H/Co, CO/Co, and metal crystallite size with extent of cobalt loadings on kieselguhr.

literature reports strongly favor this postulate.

The encapsulation phenomenon depends mainly on the mobility of the support species and in turn on factors like hydrogen flow rate, temperature and time of reduction, the partial pressure of H_2 , and water produced and the percentage of metal oxide loadings. It is therefore understandable that the precise control of these parameters at the same instant may not be feasible and this would account for the differences in the percentage reduction values observed experimentally. The observed extents of reduction do not vary systematically with the extent of metal loadings (Table 2).

The H/Co ratio calculated for room-temperature hydrogen adsorption per accessible cobalt atom decreases with the extent of cobalt loadings. A similar trend is also observed for the CO/Co ratio indicating that at low loadings of cobalt, a greater extent of cobalt atoms do not participate in adsorption. Zowtiak and Bartholomew (3) have deduced the activated nature of hydrogen adsorption from the observation that the values of activation energies for hydrogen adsorption on cobalt surfaces supported on silica or alumina increase with decrease in metal loadings. It should be noted that the interaction of silica (kieselguhr) with metals is considered to be weak (1), especially in the form in which the present catalysts are prepared. Though the percentage reduction and percentage dispersion values are al-

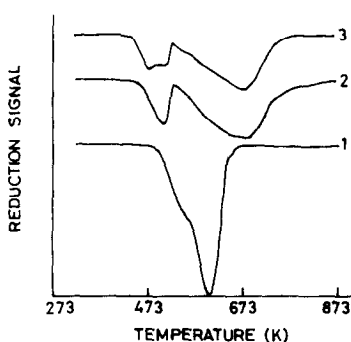


FIG. 5. TPR traces of (1) pure Co_3O_4 , (2) Co_3O_4 in 33.3% Co/kieselguhr, and (3) Co_3O_4 in 31.4% Co, 5.7% ThO_2 /kieselguhr.

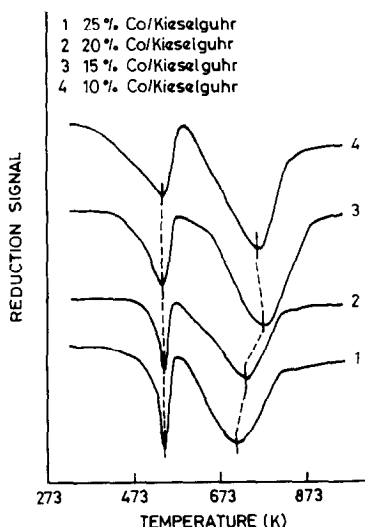
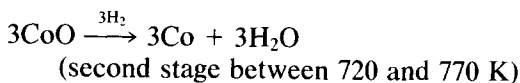
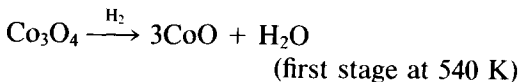


FIG. 6. TPR traces of Co_3O_4 in a series of kieselguhr-supported cobalt samples.

most comparable, the decrease in H/Co and CO/Co values with decrease in cobalt loadings indicates the possible interactions between (i) cobalt metal and kieselguhr support and/or (ii) cobalt and the unreduced cobalt oxide present beneath the surface. However, the H/Co or CO/Co ratio shows no clear-cut dependence on the amount of unreduced cobalt oxide indicating the absence of electronic interactions between cobalt and unreduced cobalt oxide. Though the interaction between cobalt and kieselguhr could be weak, the existence of this interaction is revealed at low cobalt loadings.

The TPR profiles obtained for pure Co_3O_4 and for Co_3O_4 in catalysts A and B, 10, 15, 20, and 25% Co are shown in Figs. 5 and 6. The reduction of cobalt oxide takes place in two stages and the temperature maximum of the second stage of reduction is found to increase with decrease in cobalt loadings (Fig. 6). It is also observed that the ratio of the signal intensities of first and second stage reductions is 1/3 for all the samples. The X-ray diffraction pattern taken for the samples before and after the first stage of reduction indicates that cobalt is present as Co_3O_4 and CoO, respectively. Hence, the reduction scheme can be written as



Though the reduction of pure Co_3O_4 does not give rise to two well-defined signals, probably as a result of overlap between the two stages of reduction, the signal due to second stage of reduction for kieselguhr-supported samples is well discernable and shifts to higher temperatures with decrease in metal loadings while the signal due to first stage of reduction remains constant at 540 K. This indicates that kieselguhr has the tendency to stabilize CoO. Silica has been shown to stabilize Fe^{2+} during the reduction of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ (12). This stabilization of Co^{2+} and consequent resistance to reduction in these samples cannot be accounted in terms of current concepts like Stong Oxide–Oxide Interaction (SOOI). Lund and Dumesic (13) have proposed this concept from the observations made on iron oxide supported on silica wherein they utilized Mössbauer spectroscopy evidence to deduce the incorporation of Si^{4+} ions in the tetrahedral sites of Fe_3O_4 spinel lattice. This type of substitution may not be possible once CoO is formed. The exact nature of this interaction is not clear at present. If such an interaction were to be present, one would observe retardation in the extent of the rate of reduction. Probably the promoters normally incorporated in most of these supported catalysts alter this oxide–oxide interaction favorably so as to facilitate the easy reduction of the active metal oxide.

CONCLUSIONS

Presence of kieselguhr and thoria as support and promoter has definite effect on the physical and chemical nature of cobalt FT catalysts as revealed by gas adsorption, XPS, and TPR studies.

1. Encapsulation of cobalt oxide particles by kieselguhr occurs during reduction by hydrogen at higher temperatures. This phenomenon is the result of the migration of

kieselguhr promoted by the experimental conditions, and this accounts for the decrease in the extent of reduction. However, in the presence of thoria the extent of reduction is higher due to the hindered migration of kieselguhr. This indicates that the function of promoter in this case is the prevention of migration of the support (kieselguhr) over the active phase. This is further evidenced from XPS measurements that ThO_2 is preferentially segregated on the surface of the reduced catalyst.

2. The adsorption stoichiometry of hydrogen and CO per accessible cobalt atom decreases in cobalt loadings, which is attributed to the existence of cobalt–kieselguhr interaction along with the physical changes in the catalyst systems.

3. The reduction of Co_3O_4 occurs in two stages through the formation of CoO which is stabilized by kieselguhr.

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