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Preparation and Characterization of Dispersed "Cobalt Oxide" Supported on γ-Al_2O_3

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Samples of "cobalt oxide" supported on γ-Al_2O_3 were prepared from a variety of precursors. The samples were characterized by X-ray analysis, temperature-programmed reduction, and measurement of magnetic susceptibility. Their properties were compared with those of bulk Co_3O_4 and $CoAl_2O_4$ and the observed differences were related to the method of preparation.

Introduction

The nature of cobalt catalysts supported on γ-Al_2O_3 has been the subject of many investigations (*1–17*). Most of these studies were concerned with the role of cobalt in hydrocracking processes and tried to provide an understanding of hydrodesulfurization of fossil fuels. During the final heat treatment in the preparation of these catalysts, cobalt ions diffuse into the γ-Al_2O_3 structure and can occupy octahedral or tetrahedral sites. In most studies (*1–17*) it was reported that a dispersed "δ-phase" predominates when the cobalt loading is less than 2%. This phase consists of Co(II) ions and shows many of the chemical features of bulk $CoAl_2O_4$. This phase contains "nonreducible" cobalt. A second β-phase occurs at higher cobalt loading and consists of Co_3O_4 crystallites which can be reduced easily.

In almost all of the above studies, the precursor used to prepare the γ-Al_2O_3-supported cobalt samples was an aqueous solution of cobalt nitrate. However, the literature does not include any systematic study of the influences of the precursor compound or the pH of the precursor solution on the dispersion of cobalt on γ-Al_2O_3.

In the present study, various precursors are used to prepare γ-Al_2O_3 samples containing "cobalt oxide." Each precursor is dissolved in an aqueous solution at a known pH. X-ray analysis, temperature-programmed reduction studies, and magnetic susceptibility measurements are used to characterize the composition and properties of each supported cobalt oxide sample.

Experimental

Preparation of samples. Bulk Co_3O_4 was prepared by the decomposition of $Co(NO_3)_2 \cdot 6H_2O$ (Mallinckrodt) at 450°C for 24 hr. $CoAl_2O_4$ was synthesized by dissolving appropriate weights of $Co(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (Allied Chemical) in water and evaporating to dryness, followed by careful decomposition of the product at 450°C. The resulting mixed oxides were heated in air at 950°C for 24 hr. CoO was prepared by heating $CoCO_3$ (Allied Chemi-

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TABLE I

PRECURSORS AND pH USED TO IMPREGNATE THE SUPPORT γ-Al_2O_3 WITH 11.29 WT% COBALT[a]

Precursor used	Acid to adjust pH	pH of solution
Acetate	HAC	2.7
Acetate	HAC	5.6
Acetylacetonate	HAC	1.9
Citrate	Citric acid	1.9
Nitrate	HNO_3	2.7
Nitrate	HNO_3	5.6

[a] Weight percent cobalt defined as 100 × wt(Co)/[wt(Co) + wt(Al_2O_3)].

cal) at 1000°C in an argon atmosphere for 24 hr. The γ-Al_2O_3 was prepared by heating boehmite at 500°C in air for 24 hr. Boehmite (γ-AlOOH) was prepared hydrothermally according to the procedure of A. B. Kiss (*18*).

Samples of cobalt oxide containing 11.29 wt% cobalt supported on γ-Al_2O_3 were prepared from various cobalt precursors, namely cobalt acetate, cobalt nitrate, cobalt citrate, and cobalt acetylacetonate. The latter two compounds were prepared in this laboratory. Analyses for the actual compositions of $Co(NO_3)_2 \cdot 6H_2O$ and $Co(C_2H_3O_2)_2 \cdot 4H_2O$ were performed by heating representative samples in air to 500°C and obtaining the weight loss. Corrected values reduced the compositions of cobalt dispersed on γ-Al_2O_3 samples from a nominal 11.38 wt% cobalt to 11.29 wt%. The products Co_3O_4, CoO, and $CoAl_2O_4$ were confirmed by X-ray analysis, temperature-programmed reduction, and magnetic susceptibility measurements; the phase γ-Al_2O_3 was confirmed by X-ray diffraction analysis. An aqueous solution of each cobalt precursor was prepared and the pH was adjusted with acid. The acid was usually chosen to have the same anion as the precursor (see Table I). γ-Al_2O_3 was impregnated with the precursor solution, dried on a hot plate, and then heated in a drying oven at 230°C for 24 hr. The final heat treatment was carried out at 450°C for 24 hr.

Characterization of samples. X-ray powder diffraction analyses of the samples were obtained using a Philips diffractometer and monochromatic high intensity Cu$K\alpha_1$ radiation (λ = 1.5405 Å). The diffraction patterns were taken in the range of $12° < 2\theta < 72°$ with a scan rate of 1° 2θ/min and a chart speed of 30 in./hr.

Magnetic susceptibility was measured with a Faraday balance at a field strength of 10.4 kOe from liquid nitrogen temperature to 700 K. Honda–Owens (field dependency) measurements (susceptibility vs $1/H$) were also made at room temperature and liquid nitrogen temperature, and all magnetic susceptibility data were corrected for core diamagnetism.

Temperature-programmed reduction (TPR) measurements were taken using a Cahn system 113 thermal balance. The samples impregnated on γ-Al_2O_3 were preheated in air at 400°C for 4 hr to remove most of the residual water before reduction. However, to correct for all of the residual water, a sample of γ-Al_2O_3 was heated in dry air to 950°C and its weight loss was used to correct the initial sample weights. This correction amounted to approximately one third of the total weight loss of a fully reduced sample of γ-Al_2O_3 impregnated with 11.29 wt% cobalt. The samples were cooled down to room temperature and were then heated at 60°C/hr from room temperature to 950°C in a purified Ar/H_2 (85/15) atmosphere; the rate of gas flow was 60 ml/min. The samples were maintained at 950°C for 4 hr in order to ensure constant weight. Two samples, i.e., $CoAl_2O_4$ and the cobalt oxide, dispersed on γ-Al_2O_3, which was prepared from a cobalt acetate precursor at pH 2.7, were heated in pure hydrogen at 950°C until ~99% of the cobalt was reduced to cobalt metal.

Results and Discussion

The bulk standard, Co_3O_4, was prepared by the decomposition of $Co(NO_3)_2 \cdot 6H_2O$ at 450°C in air for 24 hr. X-ray diffraction anal-

TABLE II

TEMPERATURE PROGRAMMED REDUCTION DATA FOR 11.29 wt% COBALT[a] FOR VARIOUS PRECURSORS SUPPORTED ON γ-Al_2O_3

	Weight loss (%)		
Samples	320°C Ar/H_2	950°C Ar/H_2	950°C Pure H_2
$CoAl_2O_4$	0	8.37	8.92[b]
Acetate			
pH 2.7	0.03	2.72	2.91[c]
pH 5.6	0.55	2.76	
Acetylacetonate			
pH 1.9	0.03	2.67	
Citrate			
pH 1.9	0.06	2.69	
Nitrate			
pH 2.7	0.97	2.69	
pH 5.6	0.97	2.69	

[a] Weight percent cobalt defined as 100 × wt(Co)/[wt(Co) + wt(Al_2O_3)].

[b] 98.7% of the value calculated for complete reduction.

[c] 98% of the value calculated for complete reduction.

TABLE III

PHASES FORMED BY 11.29 wt% COBALT[a] FROM VARIOUS PRECURSORS DISPERSED AND DECOMPOSED ON γ-Al_2O_3

Precursor samples	Temperature of decomposition (°C)	Phases
Acetate		
pH 2.7	450	γ-Al_2O_3
pH 5.6	450	Co_3O_4 + γ-Al_2O_3
Acetylacetonate		
pH 1.9 (in HAC)	450	γ-Al_2O_3
Citrate		
pH 1.9	450	γ-Al_2O_3
Nitrate		
pH 2.7	450	Co_3O_4 + γ-Al_2O_3
pH 5.6	450	Co_3O_4 + γ-Al_2O_3

[a] Weight percent cobalt defined as 100 × wt(Co)/[wt(Co) + wt(Al_2O_3)].

ysis of the product confirmed the presence of Co_3O_4. Temperature-programmed reduction of the product was carried out under an atmosphere of $Ar/H_2(85/15)$ from room temperature to 950°C. For the standard Co_3O_4 sample, reduction commenced at 220°C and was complete at 320°C. The observed weight loss of 26.6% is consistent with a calculated value of 26.5 wt% for the reduction of Co_3O_4 to cobalt metal. These results are in agreement with those previously reported in the literature (*19*).

However, bulk $CoAl_2O_4$ showed no appreciable reduction in an $Ar/H_2(85/15)$ atmosphere when heated up to 320°C. The product was then heated from 320°C to 950°C and maintained in the reducing atmosphere at 950°C for a total of 4 hr in order to achieve constant weight. The observed weight loss of 8.37% corresponds to 92.5% of the calculated value for the reducible cobalt present. Reduction of $CoAl_2O_4$ in a pure hydrogen atmosphere at 950°C resulted in the reduction of 98.7% of the total reducible cobalt (see Table II), because of the greater reducing power of pure hydrogen compared with that of $Ar/H_2(85/15)$.

X-ray analysis of the reduction products formed from bulk $CoAl_2O_4$, which had been reduced at a maximum temperature of 950°C, indicated the presence of metallic cubic cobalt, and α-Al_2O_3. These results are consistent with the temperature-programmed reduction data given in Table II.

The sample of "cobalt oxide" supported on γ-Al_2O_3, prepared from the cobalt nitrate precursor at pH 2.7, contained 11.29 wt% of cobalt. This sample when formed at 450°C was identified by X-ray analysis as Co_3O_4 + γ-Al_2O_3 (see Table III). Magnetic susceptibility data (Table IV) confirmed the presence of the oxide Co_3O_4. This sample was reduced in an atmosphere of $Ar/H_2(85/15)$ and at 320°C the observed weight loss of 0.97% corresponds to the calculated value for the reduction of all the Co(III) to Co(II) (Table II). There was no evidence of free cobalt metal in the product. From magnetic susceptibility measurements of the product reduced at 320°C, the moment of the cobalt, namely 4.2 BM, corresponded to the value for Co(II) in a tetrahedral environment (*20*).

TABLE IV

MAGNETIC SUSCEPTIBILITY DATA FOR 11.29 wt% COBALT[a] FROM VARIOUS PRECURSORS SUPPORTED ON γ-Al_2O_3

Samples	μ(BM)/mol Co	θ (K)
Co_3O_4	2.8	−112
$CoAl_2O_4$	4.2	−94
Acetate precursor		
pH 2.7	4.2	−45
pH 5.6	3.7	−47
Acetylacetonate precursor		
pH 1.9	4.2	−38
Citrate precursor		
pH 1.9	3.9	−44
Nitrate precursor		
pH 2.7	2.9	−69
pH 5.6	2.9	−66

[a] Weight percent cobalt defined as 100 × wt(Co)/[wt(Co) + wt(Al_2O_3)].

From Table II it can be seen that the additional weight loss between 320 and 950°C was 2.69% which is 91% of the value calculated for the complete reduction of all the cobalt(II). The cobalt reduced in this temperature range is referred to as "fixed cobalt(II) in a tetrahedral oxide environment." This cobalt species is similar to the cobalt(II) in $CoAl_2O_4$ in its property toward reduction.

The sample of cobalt oxide supported on γ-Al_2O_3 prepared from the nitrate precursor at pH 5.6 showed little change from that prepared at pH 2.7. Undoubtedly, the formation of a considerable quantity of Co_3O_4 is a result of the partial oxidation of Co(II) by the nitrate ion, particularly during decomposition of the nitrate precursor.

For the samples prepared from cobalt acetate as a precursor at pH 2.7, the TPR results shown in Table II indicate that most of the cobalt oxide is fixed and only a small quantity of Co_3O_4 is present in the final product. The X-ray results confirmed these observations. When the pH of the cobalt acetate was raised to 5.6, there was an observed increase in the Co_3O_4 content and a corresponding reduction in the amount of initial "fixed cobalt."

The magnetic susceptibility measurements are summarized in Table IV. The sus-

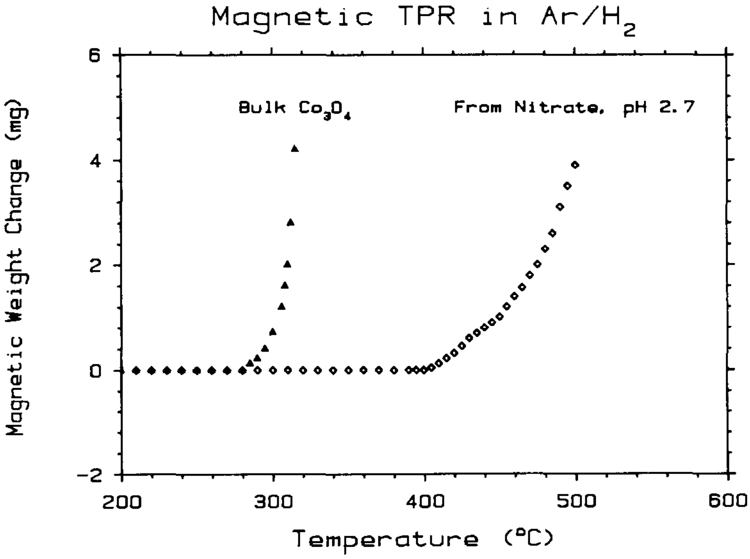

FIG. 1. Variation of weight with application of a magnetic field as a function of temperature for supported "cobalt oxide" prepared from a cobalt nitrate precursor compared with bulk Co_3O_4.

ceptibilities for bulk samples of Co_3O_4 and $CoAl_2O_4$ were determined to be 2.8 BM/mol Co and 4.2 BM/mol Co, respectively. The values for μ, given in Table IV, for the products obtained from the decomposition of the acetate, acetylacetonate, and citrate precursors are consistent with the relative quantity of fixed cobalt present in the samples as obtained by TRP studies (Table II).

For the products obtained from the nitrate precursor there appears to be a discrepancy between the susceptibility data and the TPR results. The μ values indicate that almost all of the cobalt is present as Co_3O_4, whereas the TPR results show the apparent formation of a large amount of fixed cobalt oxide during the initial stage of the reduction process. Figure 1 characterizes the reduction of bulk Co_3O_4 and 11.29 wt% cobalt on γ-Al_2O_3 (from the nitrate precursor at pH 2.7) in an oscillating magnetic field. The observed change in weight, therefore, measures the relative quantity of metallic cobalt formed during the reduction process. It can be seen that whereas bulk Co_3O_4 reduces immediately to cobalt metal at 290°C, the supported samples produce no metallic cobalt until 420°C. This indicates that the initial stage of the reduction process involves the reduction of cobalt(III) to cobalt(II), which behaves then as tetrahedral cobalt in an oxide environment. Hence, for all of the supported cobalt samples reduced between 220 and 320°C, the reduction process can be represented as a change of Co(III) to Co(II).

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