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Effects of Cobalt Loading on the Properties of Alumina-Supported Cobalt Oxide

Recently Arnoldy and Moulijn (*1*) used a combination of TPR and XRD techniques to study the variation with precalcination temperature of the properties of a reduced 9.1% CoO/Al_2O_3 catalyst. In their report, cobalt oxides in four kinds of chemical environments, i.e., Co_3O_4 (reduced around 600 K), a Co^{3+} phase on the surface (around 740 K), a Co^{2+} phase on the surface (around 875 K), and a $CoAl_2O_4$ spinel structure (around 1160 K) were distinguished from the TPR study (Table 1). The relative amount of these four phases on the catalysts depended on the temperature of calcination pretreatment. A series of alumina-supported catalysts with various cobalt loadings has been prepared in our laboratory in order to investigate the effect of the metal loading on the relative concentration of the four species described by Arnoldy and Moulijn. The temperature of calcination treatment of the catalysts prepared was fixed at 773 K. Our intention was to confirm the possible existence of Co_3O_4 crystallites after the calcination treatment. DRS, XRD, and EPR spectroscopies were coupled to a TPR technique to probe the reduction of these species by the hydrogen.

Co/Al_2O_3 catalysts with cobalt loading from 0.1 to 16% were prepared by the incipient wetness method by use of $Co(NO_3)_2 \cdot 6H_2O$ (Merck GR) and Al_2O_3 (Merck, with a surface area of 160 m^2/g) as starting materials. After drying overnight in a 393 K oven, prepared catalysts were calcined for 2 hr in 773 K and stored. The color of the obtained catalysts varied from pale blue to black as the cobalt content was increased.

Figure 1 shows a series of TPR spectra obtained from the prepared catalysts. According to the reduction behavior observed, these catalysts may be classified into three groups: (1) For samples of low Co loading (0.1 and 0.3%), the reduction occurred only after the system temperature was raised over 850 K. This reduction lasted to temperatures higher than 1270 K. (2) In addition to the continuous hydrogen consumption at $T > 850$ K, appreciable reduction was noted in the temperature range between 500 and 900 K at Co loadings >1%. At least two reduction peaks, i.e., 620 and 870 K, were identified from samples with Co loadings of 1, 3, and 8%. (3) When the cobalt loading was further increased to 16%, two shoulders (located at 510 and 550 K) were additionally observed in the TPR. Formation of Co_3O_4 crystallites on the 16% catalyst was suggested on comparing the TPR spectrum from a standard sample of cobalt oxide.

DRS is a useful technique for acquiring information on the chemical species in the top layers of solid samples. Figure 2 shows the variation of the DRS spectrum with co-

TABLE 1

A Comparison of the Assignment of Cobalt Species on Co/Al_2O_3 Catalysts

Cobalt species	TPR reduction temperature (K)	
	Arnoldy and Moulijn	This work
Bulk Co_3O_4	550–630 (increased with calcination temperature)	550
Overlayer Co^{3+}	740	630
Overlayer Co^{2+}	875	870
Spinel	1110–1230	>850

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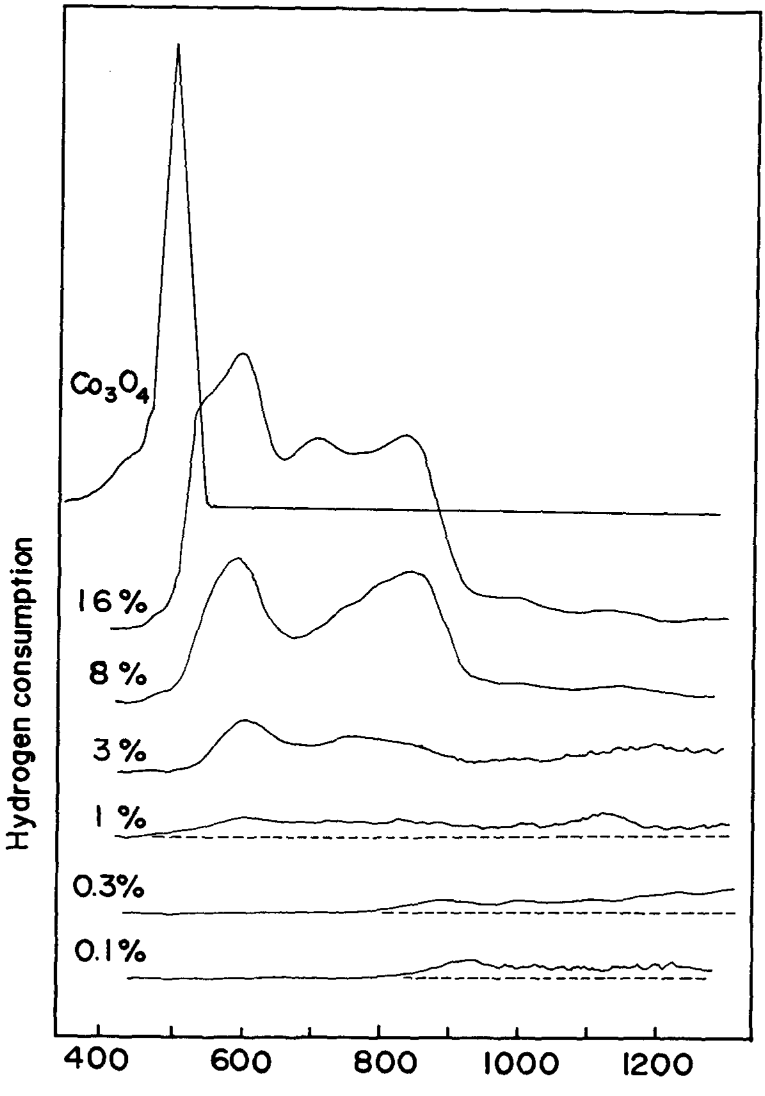

FIG. 1. Variation of TPR spectra with the Co loading (indicated on each spectrum) of the catalysts. The top spectrum was obtained from a sample of 0.02 g Co_2O_3 for comparison.

balt loading. An absorption triplet at 550, 580, and 620 nm was observed for the 0.3% Co/Al_2O_3. This triplet has been established in the literature for the spinel structure of Co–Al oxides (*2*). A conversion of cobalt oxides on this sample into this structure through diffusions of cobalt oxides during the calcination is therefore suggested. The triplet peak was replaced by two separate peaks (at 400 and 700 nm) as the cobalt loading in the catalyst was increased to 1 and 3%. The surplus cobalt oxides on these samples obviously deposited over the spinel structure as overlayer phases. These two DRS peaks have been found and assigned in the literature (*3*) as the absorption by bulk Co_3O_4. However, comparison with a DRS spectra from a standard Co_3O_4 sam-

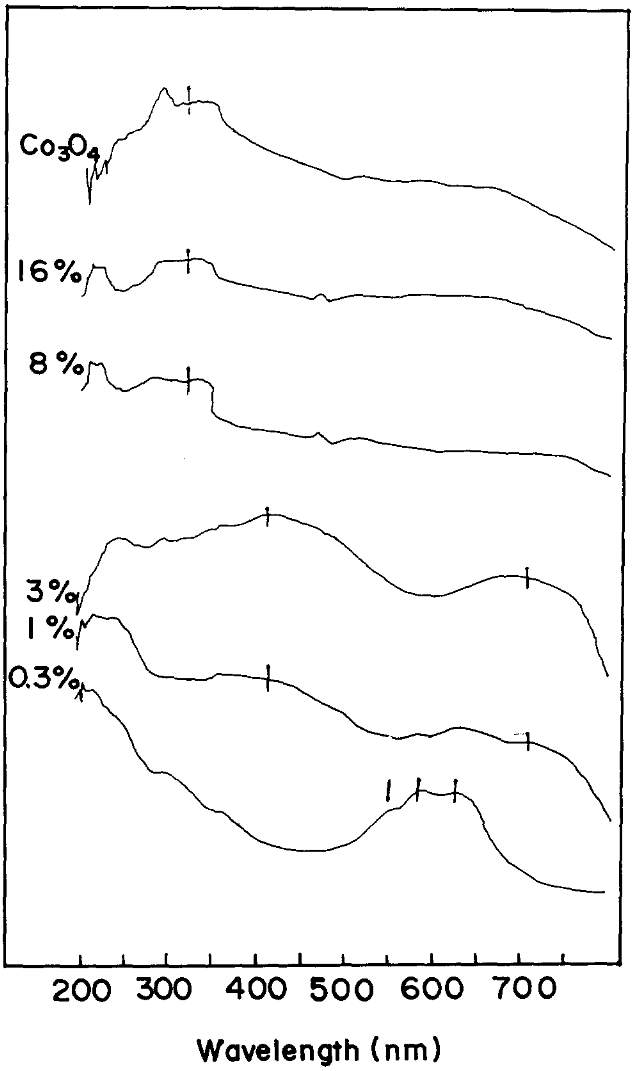

FIG. 2. DRS spectra obtained from Co/Al_2O_3 catalysts with various cobalt loadings.

ple (top of Fig. 2) shows that these two peaks do not come from well-ordered Co_3O_4 crystallites; rather, a distorted overlayer structure of that species is indicated. The distortion of this overlayer may be caused by a "polarization effect" of alumina described by Arnoldy and Moulijn (*1*) or by a contamination with the alumina support during the calcination. Figure 2 also suggests that layers of ordered Co_3O_4 structure were indeed deposited on the distorted overlayer as the cobalt loading was further increased above 8%.

The existence of Co_3O_4 crystallites on samples with the Co loading higher than 8% was confirmed with subsequent XRD experiments (Fig. 3). The formation of these crystallites on the samples of high Co loading suggested that ordered oxide crystallites could be formed only from oxide layers unperturbed by the alumina. It is worthwhile to note that these crystallites do

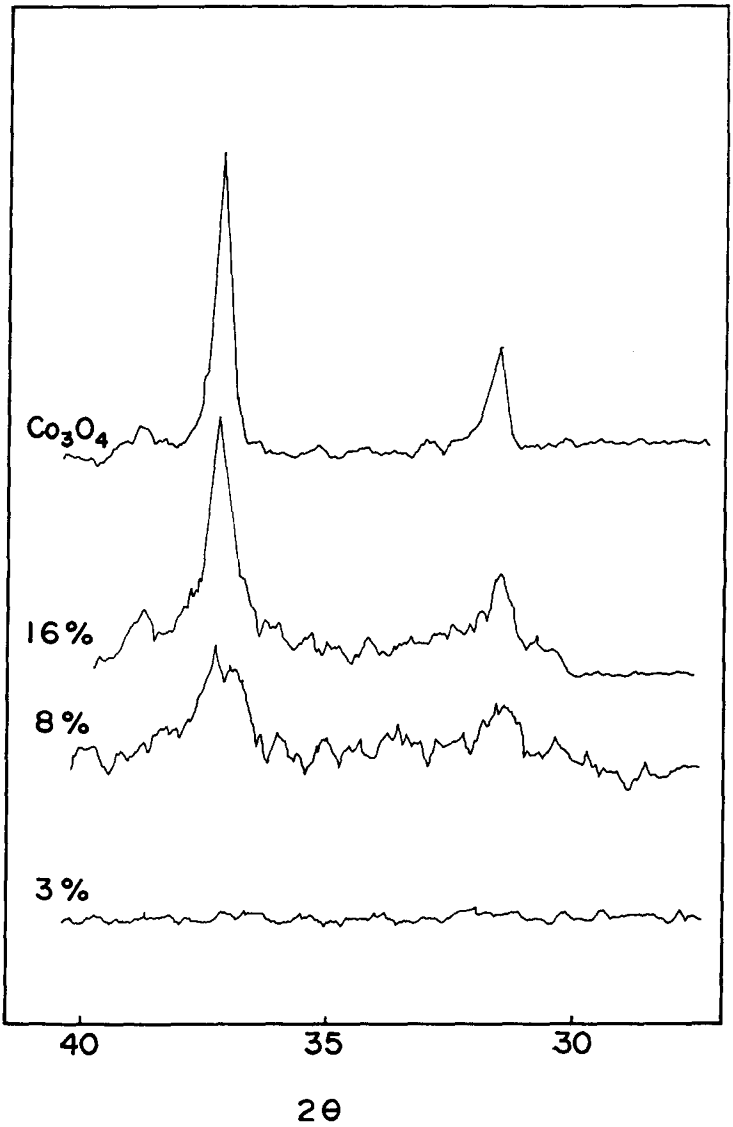

FIG. 3. Variation of XRD spectra with cobalt loadings.

not exist on catalysts with cobalt loading less than 8%.

The experimental results from TPR, DRS, and XRD therefore confirmed that cobalt oxides on Co/Al_2O_3 catalysts may have three structures, i.e., spinels of Co–Al oxide, overlayers of amorphous oxide, and Co_3O_4 crystallites, depending on the location of the oxides. The amorphous structure had at least two TPR peaks (at 600 and 870 K, and probably a third peak at 740 K). Each peak should indicate one kind of cobalt ion in the overlayer. An EPR experiment was therefore designed to investigate the detectable Co species during catalyst reductions. Figure 4 summarizes the observed EPR results from the 1% catalyst after reduction at different temperatures. No significant signal other than some minor noises from impurities on the alumina was

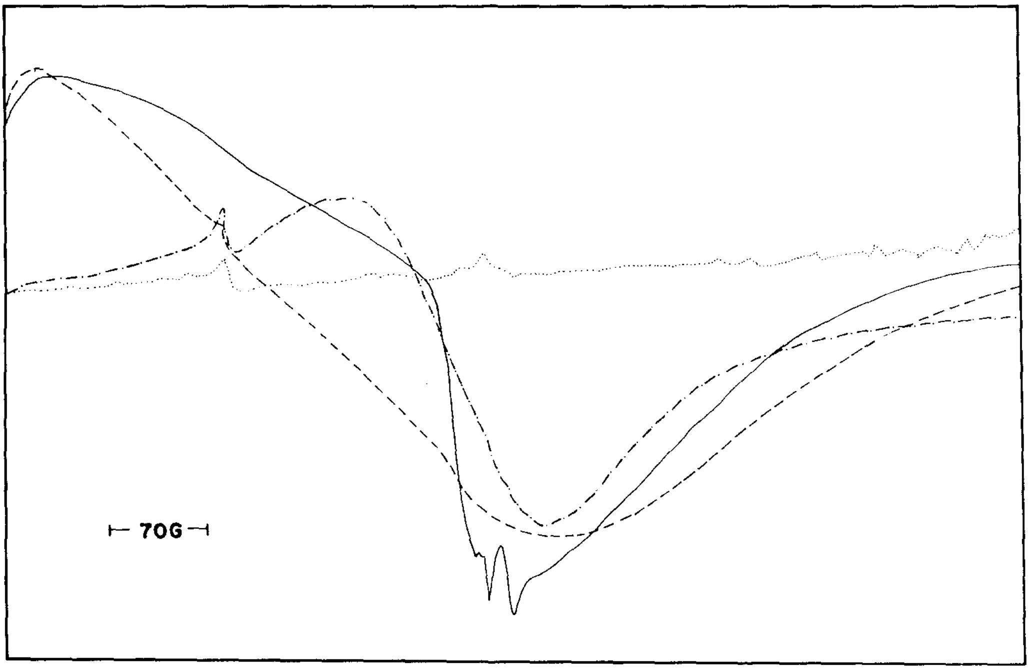

FIG. 4. Variation of EPR spectra with reduction temperatures (dotted line, 570 K; dotted dash, 620 K; dash line, 790 K; solid line, 820 K). The 1% Co/Al_2O_3 was used for the measurement.

observed after a reduction to 570 K. A Co^{3+} peak at $g = 2.9$ (8) and a peak from reduced metal, however, were noted in the EPR spectrum as the reduction temperature was increased to 620 K. The TPR peak around 620 K is therefore assigned as the reduction of a Co^{3+} species in the amorphous overlayers to metal. As the reduction temperature was increased to 790 K, the Co^{3+} peak disappeared. A Co^{2+} peak ($g = 15$) (8) was generated as its replacement. Both the Co^{2+} and the metal peaks were increased as the reduction temperature was further increased to 870 K. Thus the TPR peak around 875 K was assigned to the reduction of the Co^{2+} species in the amorphous overlayer.

Arnoldy and Moulijn elucidated the structure of Co/Al_2O_3 from the observed variation of the reduction phenomena with the calcination temperature (from 380 to 1290 K). The loading of CoO in their study was held at 9.1% (or the loading of Co was 7.2%). Their experiments gave detailed information on the diffusion of cobalt oxides into Al_2O_3 during calcination. In the present study the temperature of the precalcination treatment was held at 773 K and the loading of cobalt was changed from 0.1 to 16%. Our experiments had an advantage of studying the layer structures of cobalt oxides deposited on the support. Table 1 lists a comparison of the assignment of the TPR peak observed for the Co/Al_2O_3 catalysts by these two studies. We agree with the proposal of Arnoldy and Moulijn that there are three cobalt structures, i.e., spinel of Co–Al oxides, amorphous overlayer of cobalt oxides, and crystallites with structure similar to bulk Co_3O_4, on the catalyst. However, the assignment of TPR peak positions to these structures involves some controversies. The main difference is on the peak position of bulk Co_3O_4 in the TPR spectra.

The amount of cobalt oxides migrating into the top layers of the alumina depended on the calcination temperature. With higher calcination temperature, a larger fraction of cobalt oxides converted into the spinel structure, and a smaller fraction remained on the overlayer to form the bulk Co_3O_4 structure. Bulk cobalt oxide was barely detectable in our 8% catalyst calcined at 873 K. It can be imagined that bulk cobalt oxide can only exist on the 7.1% catalysts calcined at low calcination temperature (with a TPR peak at 550 K). As the calcination temperature was increased, the intensity of this peak was gradually decreased and merged into the reduction peak (at 630 K) of Co^{3+} in the amorphous layer.

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HUAN-CHIEN TUNG
CHUIN-TIH YEH

Institute of Chemistry
National Tsinghua University
Hsinchu, Taiwan
Republic of China

CHENG-TSUNG HONG

Refining and Manufacturing Center
Chinese Petroleum Corporation
Chia-Yi, Taiwan
Republic of China

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