

On the Existence of Two Phases of Cobalt Oxide on a Zirconia Support

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Received May 12, 1975

Catalysts of varying concentrations of cobalt oxide on ZrO_2 supports were prepared by impregnation and calcination to 600°C. In very dilute catalysts the cobalt oxide consists of a two-dimensional dispersed "δ-phase" of as yet undetermined stoichiometry. At higher concentrations, a saturated δ-phase is in equilibrium with bulk or "β-phase" particles. The latter appear to be Co_3O_4 spinel particles. The saturated δ-phase has about 4.8×10^{18} Co atoms per m^2 , i.e., about 60% of the estimated concentration of surface cobalt atoms on polycrystalline Co_3O_4 . Further heating to 800°C causes Ostwald ripening of the β-phase particles, presumably by surface diffusion via the δ-phase. This suggests very poor wetting of the support by the β-phase. Diffusion couples of Co_3O_4 -porous ZrO_2 , held at 850°C for many days, also illustrate the establishment of the δ-phase. Byproducts of this experiment are the estimated values of 0.22 wt% for the solubility, and 10^{-17} - 10^{-16} cm^2/sec for the volume diffusion coefficient of cobalt (as an undetermined oxide) in monoclinic zirconia at 850°C.

INTRODUCTION

Hogan (1) and, more recently, Zechina *et al.* (2) found a two-dimensional phase in the system chromic oxide-silica. Up to 57% of the surface OH groups in silica, observed by ir absorption, could be replaced by surface chromate or dichromate groups. Further addition of chromic oxide beyond this point presumably resulted in the formation of three-dimensional particles. O'Reilly and MacIver (3) studied the system chromia/ γ -alumina by EPR. They found two EPR lines, one of which was assigned to a highly dispersed, or "δ-phase," and the other to a bulk-like, or "β-phase." Tomlinson *et al.* (4) adopted the same terminology in their description of the system cobalt oxide/ γ -alumina, which they investigated by magnetic susceptibility measurements. Both O'Reilly and MacIver and Tomlinson *et al.* found their δ-phases to be most prevalent in dilute catalysts

and to tend to disappear again in more concentrated catalysts.

In some earlier work, one of us (5) investigated cobalt oxide catalysts supported by monoclinic zirconia, with a view to their possible application as automobile exhaust emission catalysts. The methods of investigation were catalytic activity in the combustion of ethylene, nitric oxide chemisorption, and the linewidth of the Co_3O_4 (311) X-ray diffraction line, the only one not obliterated by zirconia lines. From these linewidths, a mean particle size, hence a likely surface area of the three-dimensional Co_3O_4 spinel particles could be deduced. This area correlated reasonably well with the measured catalytic activity, compared to that of pure Co_3O_4 . On the other hand, the NO chemisorption measurements suggested cobalt oxide areas which were many times larger, by as much as a factor of 10, or more.

This observation applied not only to samples prepared by impregnation methods but also to mechanical mixtures of Co_3O_4 and ZrO_2 that were subsequently heated to 700°C for 16 hr. This suggested a large-area δ -phase, accounting for most of the NO chemisorption but of low catalytic activity in equilibrium with a β -phase of more modest area, accounting for most of the catalytic activity. The latter is assumed to be essentially pure Co_3O_4 spinel, on the basis of the single observable diffraction line and on the basis of its high catalytic activity.

It was then found that very dilute samples of cobalt oxide on zirconia, prepared by impregnation and calcination to 600 or 800°C , and presumably containing only a dilute δ -phase, had a very low catalytic activity. Per cobalt atom, the specific activity for the combustion of ethylene was about 100 times lower than that of pure Co_3O_4 , assuming the latter has about 8×10^{18} surface cobalt atoms per m^2 . More surprisingly, these dilute samples chemisorbed nitric oxide copiously, to the extent of several moles of NO per mole of Co in the samples. This multiple NO chemisorption on very dilute samples has since been confirmed and has also been found for the case of dilute nickel oxide-zirconia samples (6). The present paper again confirms this phenomenon and measures the decline of the adsorption multiplicity with increasing concentration of the δ -phase.

Another pertinent prior experiment was carried out by Y. Y. Yao (7). A small amount of low surface area Co_3O_4 was mechanically mixed with ZrO_2 , such that the ratio of surface areas was 1:1500, respectively. This mixture was tested for catalytic activity in the combustion of carbon monoxide and retested several times after increasingly hot heat treatments. The catalytic activity increased with increasing heat treatments, until it appeared to saturate after a $\frac{1}{2}$ -hr treatments at 950°C (the

zirconia had been pretreated at 1000°C). At this time, the catalytic activity had increased by a factor of 10 over that of the initial mixture. Analyzed according to our point of view, saturated δ -phase had finally formed over all of the zirconia surface by surface diffusion from the β -phase. Since the δ -phase should have an area at least 1500 times as large as that of the original β -phase, yet the activity increased by only a factor of 10, it follows that the activity for this test reaction, per square meter, is at least 150 times higher on the β -phase than on the δ -phase.

The present work was undertaken for the purpose of repeating the earlier qualitative experiments under more controlled conditions, using purer materials, and for the purpose of a quantitative determination of the concentration of the saturated δ -phase. The following qualifications should be noted: (1) It seems reasonable to suppose that the saturation concentration of the δ -phase varies from one (hkl) face of the substrate to another. Our value is a polycrystalline average, which can be expected to vary somewhat, depending on the preparation of the substrate. (2) Purity, likewise, is a potentially important factor. Some impurities may well compete with cobalt oxide for adsorption on the zirconia substrate. (3) Equilibration requires that temperatures have been reached where appreciable diffusion of catalyst over substrate can take place. A few hours at 600°C seems sufficient in the case of impregnated cobalt oxide-zirconia catalysts. The β -phase, incidentally, is never in equilibrium, relative to coarsening, i.e., "Ostwald ripening." The need for moderately high temperatures, to establish the δ -phase, can be a problem in systems where catalyst and substrate are mutually soluble. This does not appear to be the case in the system under discussion (8-10), at least not until very high temperatures are reached (11).

EXPERIMENTAL

Zirconia was made by decomposition of zirconium nitrate (Johnson Matthey, Spec-pure grade) at 300°C, followed by calcination at 800°C for 6 hr. This resulted in a BET area of about 11 m²/g. For the impregnation with cobalt oxide, a measured amount of Co(NO₃)₂ solution was added to the dried and weighed ZrO₂. The solids were then dried slowly in a desiccator under vacuum and then calcined at 600°C for 6 hr. The nitric oxide was purified by several freezing evaporation cycles, retaining two-thirds of the middle fraction for the chemisorption experiments (12). Research grade CO and ultrapure grade Ar (Matheson Co.) were used without further purification.

The volumetric measurements for BET area and NO and CO chemisorption measurements were performed in a conventional constant volume adsorption apparatus equipped with a precision pressure gauge containing a fused quartz Bourdon capsule, with a pressure range of 0–1000 Torr (Texas Instruments Model 145). Adsorbents were initially degassed under vacuum (10⁻⁶ Torr) at 400°C for 3 hr. Argon was the adsorbate used for the BET total area measurements. NO and CO chemisorption isotherms were taken at 25°C.

The catalytic test reaction consisted of the oxidation of ethylene in an excess of oxygen. The inlet concentrations were 0.194 and 1.2%, by volume, respectively, the diluent being helium. The reactor was a U-shaped quartz tube in a vertical furnace. The down flow section of the U acted as a preheater for the gas mixture. The catalyst was loosely packed between quartz wool plugs in the upflow section of the U. The inside diameter of the U tubes varied from 3 to 4 mm. The quantity of catalyst used varied from 0.015 to 0.1 g. Flow rates were varied in order to keep the percentage of ethylene burnup below

30%, if possible. In the most concentrated, hence active, samples this was not quite possible. The compositions of the inlet and outlet gases were monitored by a continuous sampling, on-stream mass spectrometer. At the initial temperature of 400°C it took several hours to reach a true steady state. The temperature was then lowered to 350°C, and another measurement of the percentage of conversion was made immediately.

For a macroscopic diffusion experiment, thin disks of monoclinic zirconia were prepared by adding 0.3% polyvinylbutyral binder to small-particle size (about 50 Å) monoclinic ZrO₂, pressing in a steel die, and calcining at 805°C for 68 hr. The small-particle ZrO₂ was derived from two sources: (1) by boiling the Johnson Matthey Spec-pure "zirconium nitrate" overnight and (2) by precipitating zirconyl nitrate, of indifferent purity, with ammonia, filtering the resulting amorphous hydrated oxide, and converting it to the monoclinic form by hydrothermal digestion at 250°C in an autoclave for 2 hr. Material 2 led to greenish-tinted disks with a higher BET area than the pure white ones (6.11 vs 2.2 m²/g). All disks had dimensions of approximately 0.6-cm diameter × 0.018-cm thickness. They were vacuum coated on one flat side with about 5 × 10⁻⁵ cm of cobalt metal. They were then placed into an air furnace, at 850°C, for various periods up to 2 weeks. It is assumed that the cobalt quickly oxidized to Co₃O₄, some of which then diffused into the porous zirconia to form a saturated δ-phase. After the 850°C treatment the disks were broken, and cobalt concentration profiles were determined by microprobing across the broken cross section (see Fig. 1). Counts were taken at 5-μm intervals, using a fully focussed spot of a 20-kV, 100-nA beam in an ARL EMX probe. Standards for the probe were made by aqueous impregnation methods.

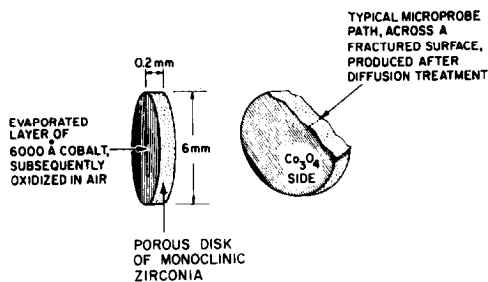


FIG. 1. Illustration of the diffusion couple experiment.

The X-ray diffraction work was carried out on a computer-controlled Norelco powder diffractometer with a diffracted-beam, graphite monochromator, using a fine-focus copper tube. Step scanning over the Co_3O_4 (311) line was carried out at intervals of 0.05°C in 2θ , using counting times of 400 sec for the weakest (most dilute) samples and 100 sec for the stronger reflections. The low-angle tail of the Co_3O_4 (311) line suffers from interference from the nearby, weak ZrO_2 ($10\bar{2}$) line. A correction was carried out by subtracting the high-angle tail of the ZrO_2 ($10\bar{2}$) line, obtained from a sample which contained no Co_3O_4 β -phase (see, e.g., Fig. 2). The normalization factor for this subtraction was obtained by comparing intensities at a nearby angle where there is no diffraction line. For the purpose of estimating the mean particle size, the width at half

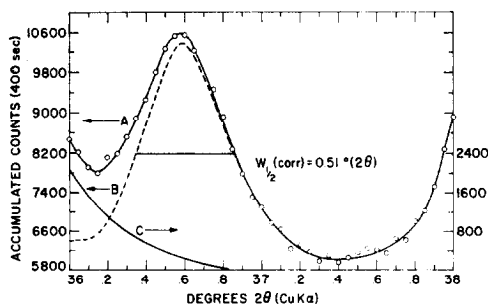


FIG. 2. Example of X-ray diffraction line (311) of Co_3O_4 , obtained by 400-sec counts (sample 4-149A; 0.015 g Co/g ZrO_2); showing subtractive correction for the tail of the nearby, weak ZrO_2 ($10\bar{2}$) line.

height of the corrected curve was deconvoluted from instrumental broadening by using the upper curve of Fig. 9-9 of Klug and Alexander (13) and the formula for particle size broadening given in that reference.

For the purpose of estimating the relative percentage of β -phase in several samples, the corrected (311) line was integrated from its intensity maximum to the adjacent high-angle minimum. The resulting area was then normalized by the integrated intensity of a nearby zirconia line, automatically obtained by a scanning integration, with background subtraction, on the diffractometer.

RESULTS AND DISCUSSION

A. Chemisorption

Typical NO and CO adsorption isotherms, at 25°C , on one of the Co_3O_4 - ZrO_2 samples are shown in Figs. 3a and b, respectively. In both figures, curve A gives the total uptake; curve C the uptake on a surface degassed at 25°C after the first adsorption; and curve B the difference between curves A and C. Each point was measured after the elapsed time of 1 hr. Curves B and C are considered to be, respectively, the irreversible and reversible parts of the total coverage. The irreversible parts of the CO and NO chemisorption

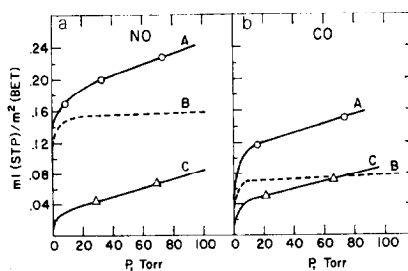


FIG. 3. Example illustrating the NO (a) and CO (b) chemisorption method; for the $4.62\text{-}\mu\text{mol}/\text{m}^2$ sample of Table 1; A, total chemisorption; C, reversible portion (readsorbed after outgassing); and B, the difference, taken to be the irreversible portion.

TABLE 1
NO and CO Uptake on Co₃O₄-ZrO₂ Catalysts^a

| <i>C</i> , Co ion concentration (μmol/m ² (BET)) | <i>q</i> ₁ , NO uptake (μmol/m ² (BET)) | <i>q</i> ₂ , CO uptake (μmol/m ² (BET)) | <i>q</i> ₁ / <i>C</i> | <i>q</i> ₂ / <i>C</i> |
|---|---|---|----------------------------------|----------------------------------|
| 0.518 | 2.27 | 0.62 | 4.38 | 1.20 |
| 0.926 | 3.75 | 0.98 | 4.05 | 1.06 |
| 1.885 | 4.92 | 1.70 | 2.61 | 0.90 |
| 4.62 | 7.04 | 3.30 | 1.55 | 0.71 |
| 14.62 | 8.34 | 5.40 | 0.57 | 0.37 |
| 29.1 | 8.71 | 5.98 | 0.30 | 0.21 |
| 44.3 | 9.33 | 6.70 | 0.21 | 0.15 |

^a BET areas of all samples are close to 11 m²/g.

^b Irreversible uptake at 60 Torr and 25°C.

data on a series of samples are given in Table 1 and plotted in Fig. 4. Use of the irreversible portion only had two advantages: (1) It was found to be relatively independent of pressure, and (2) it was found to be essentially zero for the zirconia substrate.

The results in Table 1 show that the increase in the amount of NO (*q*₁) and CO (*q*₂) chemisorption, at constant temperature and pressure, is much slower than the corresponding increase in the concentration of cobalt on the substrate surface. In a plot of the logarithm of *q*₁ and *q*₂ vs the logarithm of the cobalt ion surface concentration, *C* (Fig. 4), each curve breaks up into two approximately linear

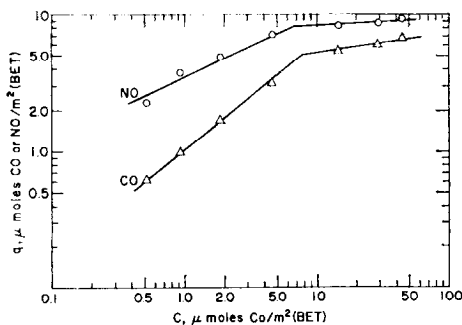


Fig. 4. Log-log plot of chemisorption results, from Table 1.

TABLE 2
Values of *n* and *k* in the Chemisorption of NO and CO on the δ-Phase of Cobalt Oxide^a

| | NO | CO |
|----------|------|------|
| <i>n</i> | 0.45 | 0.78 |
| <i>k</i> | 3.5 | 1.02 |

^a *n* and *k* from the equation $q = kC^n$ where *q* = micromoles of adsorbed gas/square meter (BET) and *C* = micromoles of cobalt/square meter (BET); all values for 25°C.

sections. The straight-line sections corresponding to the samples of lower cobalt content are interpreted by us as being due to the δ-phase. Once this is saturated, any additional cobalt is assumed to form β-phase particles, with only a portion of their atoms at the surface, hence less chemisorption per mole of cobalt. The straight-line segments of the log-log plots can be expressed by the empirical equation

$$q = kC^n, \quad (1)$$

where *k* and *n* are constants, at constant temperature and pressure. Table 2 gives the values of *k* and *n*, for both CO and NO chemisorption, for the δ-phase branches of the curves.

An interesting effect can be seen from column 4 of Table 1. In the most dilute sample (in cobalt content), over four molecules of NO are adsorbed for each atom of cobalt. As the cobalt concentration increases, this multiplicity factor decreases, until it is only slightly greater than unity at the intersection, interpreted by us as the saturated δ-phase. The multiple adsorption of NO has been seen before (6) for dilute samples of both cobalt oxide and nickel oxide on zirconia. It has not been investigated in detail. By contrast, the multiplicity for CO-sorption decreases from 1.2 for the most dilute sample to 0.67 at the intersection point, where the δ-phase is saturated.

We shall now carry out a typical calculation to demonstrate from present data the near inevitability of the existence of a δ -phase. Consider, for instance, the 29.1- $\mu\text{mol Co}/\text{m}^2$ (BET) sample of Table 1. Assume for a moment that there is only a β -phase. Dividing the NO uptake of 8.71 $\mu\text{mol}/\text{m}^2$ by 7.3, the number of micromoles per square meter of irreversibly adsorbed NO on bulk Co_3O_4 (14), we obtain 1.19 $\text{m}^2 \text{Co}_3\text{O}_4/\text{m}^2$ (BET) for this sample. Assume the last number is unity, to within experimental uncertainties. The substrate area therefore has to be assumed to be totally covered by β -phase. At 29.1 $\mu\text{mol}/\text{m}^2$, using the bulk density of 6 g/cm^3 , this calculates to a mean thickness of 3.9 Å of Co_3O_4 spread out over all the substrate area. Such a thin layer should be X-ray invisible. Actually, however, this sample has a well-developed, strong Co_3O_4 (311) line, whose width corresponds to a mean particle diameter of 670 Å. We must now figuratively scrape away much of the 3.9 Å layer to produce enough volume for the large, X-ray visible particles, leaving a very thin (NO-adsorbing) layer, i.e., the δ -phase.

B. Catalysis

The results of the catalysis experiments are summarized in Fig. 5. The abscissa is

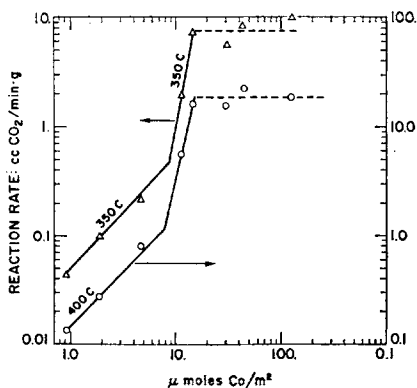


FIG. 5. Catalytic activities at 350 and 400°C. Reaction rates in cubic centimeters STP of CO_2 per minute per gram of catalyst; inlet concentrations: 0.194% C_2H_4 , 1.2% O_2 , in He.

in micromoles of cobalt per square meter of zirconia area. The ordinate gives the rate of CO_2 production, in cubic centimeters STP per minute per gram of catalyst. In order to get reproducible steady-state values, it was necessary to go to relatively high temperatures. At lower temperatures, some very slow changes in the condition of the catalyst surfaces take place. The disadvantage of the higher temperatures is that they result in high specific activities. This, in turn, leads to two types of experimental inaccuracies: (1) possibly excessive adiabatic temperature rise in the catalyst bed, beyond the measured furnace temperature, leading to apparent reaction rates that are too high; (2) gas diffusion and pore diffusion limited reactions, leading to apparent rates that are too low. In the case of our most active samples, increasing the gas flow rates to the highest feasible values always caused an increase in the apparent reaction rates. This is a clear indication that errors due to gas diffusion limitations overshadowed errors due to adiabatic temperature rise, for this reason: With increasing flow rate, the percentage of ethylene burnup goes down, and that is what determines the maximum possible temperature rise. The reaction rate is proportional to the product of flow rate and percentage of burnup, and this product increased with increasing flow rate and decreasing percentage of burnup.¹ The reaction rates of Fig. 5 can therefore be regarded as lower limits, when the rates are high (in the β -phase region).

On the log-log curves of Fig. 5, a break in slope occurs at about 8.5 μmol , or 4.9×10^{18} atoms of cobalt, per square meter of substrate. We again interpret this break as the point at which the δ -phase is saturated and the β -phase nucleates. Over most of the δ -phase range, the lines in Fig. 5 have an approximately

¹ Kinetic mass action effects would also cause a slight shift in this direction but not enough to account for our observations.

45° slope, suggesting that the activity per surface cobalt atom in the δ -phase happens to be relatively independent of the cobalt concentration, for the test reaction chosen here. Once the β -phase nucleates, the activity vs concentration curve assumes a steeper slope, because of the very much higher catalytic activity of this phase. This is true in spite of the fact that, for each incremental amount of cobalt added at this stage, only a fraction becomes surface atoms. The uppermost, approximately horizontal portions of the curves probably represent activities that are severely limited by gas phase mass transfer processes.

The 14.62- $\mu\text{mol}/\text{m}^2$ sample already had a visible Co₃O₄ (311) X-ray diffraction line. For the 29.1- $\mu\text{mol}/\text{m}^2$ sample, this line was quite strong, and its width suggests a mean particle diameter of 671 Å for the β -phase. This yields an X-ray area of 14.9 m²/g for the β -phase in this sample, by the usual approximations. From the intersection point of the 400°C data of Fig. 5, we estimate that about 8 $\mu\text{mol}/\text{m}^2$ was used to form the δ -phase, leaving 21.1 $\mu\text{mol}/\text{m}^2$ to form β -phase particles. This corresponds to 1.69 mg of Co₃O₄, hence 0.0252 m² of X-ray area (all values are taken per square meter of substrate area). Since Co₃O₄ has about 13.3 μmol of surface cobalt per m² (from crystallographic estimates and from chemisorption data), we arrive at a value of 0.336 surface μmol of cobalt in the β -phase, compared to the 8 μmol in the δ -phase. Again, from the intersection point in Fig. 5, we estimate that out of a total activity of 15.3 units for this sample, 1.16 units can be ascribed to the saturated δ -phase, the remainder to the β -phase. These numbers lead to the ratio of 290 for the activity of a surface cobalt atom in the β -phase relative to one in the δ -phase. This ratio could well be inaccurate by a factor of two or three, but it is certainly a large ratio, as already pointed out in the Introduction.

C. X-Ray Diffraction Results

The ratio of the integrated intensity of the (311) X-ray diffraction line of Co₃O₄ to that of the (11 $\bar{1}$) line of ZrO₂ versus the weight ratio of cobalt to zirconia is plotted for three samples in Fig. 6. The three samples had approximately the same BET area of 11.1 m²/g. Under these conditions one would expect the x -intercept to correspond to the saturated δ -phase, without any β -phase. The three points do not form a good straight line. The least-squares line through the three points meets the x -axis at a weight ratio of 0.00646 g Co/g ZrO₂. That amounts to 9.87 μmol , or 5.95×10^{18} atoms, per m². This value is considerably larger than the one obtained from the chemisorption experiments, which are considered to yield the most precise value of the concentration of the saturated δ -phase, of the various experimental approaches used in this work. It is not easy to detect a phase boundary by the appearance of an X-ray diffraction line because X-ray diffraction is not very sensitive to phases present in small-volume percentages. This difficulty is further aggravated in the present case where the particles are expected to become smaller as the amount of β -phase becomes small. As the line becomes weaker, it also broadens more, making it more difficult to separate

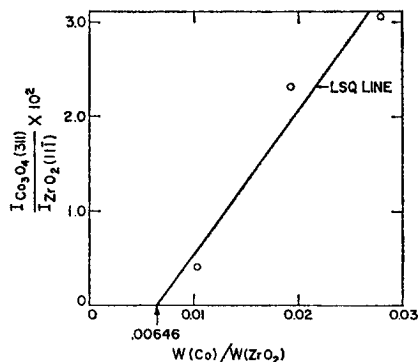


FIG. 6. X-ray diffraction (integrated) intensity ratio of Co₃O₄ (311) to ZrO₂ (11 $\bar{1}$) vs Co/ZrO₂ weight ratio, for three samples.

it from background. On the other hand, the most concentrated of the three samples probably has too low an integrated intensity due to microabsorption effects.

The experiment on Ostwald ripening of the β -phase is summarized in Table 3. These two samples are not part of the series used for the chemisorption and catalysis experiments. The starting materials were the same, but the impregnation with cobalt nitrate solution was carried out in a slightly different manner, which led to somewhat smaller β -phase particle sizes after a 600°C, 16-hr calcination. The zirconia substrate also had been pretreated in a slightly different manner and then calcined for 16 hr at 850°C, prior to the cobalt impregnation. Its BET surface area was 12 m²/g. After the 600°C calcination, the mean particle diameter of the β -phase was determined from the width of the Co₃O₄ (311) diffraction line. The samples were then calcined for 16 hr at 800°C (always in air), and the width of the (311) diffraction line was again measured. The narrowing was very appreciable, as shown by Table 3.

Some transmission electron microscopy has been carried out in the past on the cobalt oxide-zirconia system, although none was carried out on the present samples. The zirconia generally looks like a

rock pile, with slightly elongated, somewhat faceted rocks. The majority of pores would appear to us to consist of interstices between the "rocks" and to have dimensions of the order of but probably smaller than the rocks. In other words, we would expect an abundance of interstices in the range of 500 Å or less in the two samples discussed above. The fact that the majority of Co₃O₄ particles coarsen to much larger dimensions, even in the relatively dilute sample, suggests an absence of capillarity, i.e., poor degree of wetting. After forming a surprisingly concentrated δ -phase, the remaining cobalt oxide agglomerates into a β -phase which does not seem to wet the δ -phase at all.

D. Diffusion Experiment

The results of the microprobe analysis of two macroscopic diffusion couples are shown in Figs. 7 and 8. The two samples were treated at 850°C for 308 and 218 hr, respectively. The substrates had specific surface areas of 2.2 and 6.11 m²/g, respectively. The ordinates are in weight percentage of cobalt (as metal), the abscissas in micrometers of distance from the cobalt oxide-zirconia interface. A curve of the

| Sample | Wt% cobalt ^a | Particle size ^b (Å) after | |
|--------|-------------------------|---|--------------------|
| | | 600°C ^c | 800°C ^c |
| 4-149A | 1.5 | 270 | 2190 |
| 4-149B | 4.0 | 327 | 1590 |

^a g Co/(g Co + g ZrO₂) × 100; ignoring oxidized state of the Co.

^b From width at half height of Co₃O₄ (311) X-ray diffraction line; see text.

^c Highest temperature reached, in air, for 16 hr.

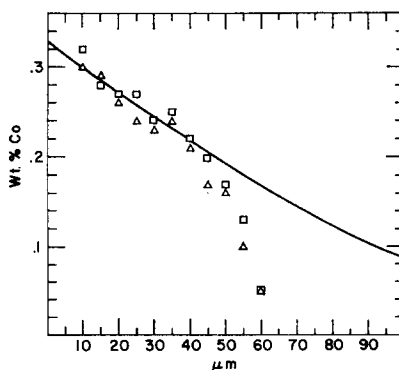


Fig. 7. Cobalt concentration profile in a disk of 2.2 m²/g porous monoclinic ZrO₂ vs distance from Co₃O₄-ZrO₂ interface; after 308 hr at 850°C; (Δ) and (□) represent microprobe traverses across two different paths.

type $C = C_0 [1 - \theta(KX)]$ has been fitted to some of the points, those which are relatively close to the boundary. C_0 is the concentration of cobalt on the zirconia side of the boundary and is also the expected concentration throughout the zirconia at infinite time. $\theta(KX)$ is the error integral. This formula would hold in the case of true volume diffusion, assuming a concentration-independent diffusion coefficient. Actually, we are dealing here with surface diffusion along an interior, porous surface. Thus, K is related to a pseudo-diffusion length, which has no simple physical interpretation in this case. At larger X values, the experimental points fall sharply below the curve, suggesting that the surface diffusion rate decreases with decreasing cobalt concentration. A possible explanation is that the vanguard of cobalt atoms, at low concentrations, tend to be trapped at special surface sites or on high index planes. This phenomenon is almost always encountered in the chemisorption, and even in the physical adsorption, of gases on a surface.

The C_0 values divided by the specific surface area of the substrates, were expected to yield the desired saturation concentrations of the δ -phase. This calculation leads to 25 and 14.3 $\mu\text{mol}/\text{m}^2$, respectively, for the samples with the 2.2 and 6.11 m^2/g substrates. Besides being unequal, these values are also appreciably too high, compared to the range of 7–8 $\mu\text{mol}/\text{m}^2$ for the saturated δ -phase, deduced from the chemisorption and catalysis experiments. The pellet diffusion results suggest that the implied assumption of zero volume solubility of cobalt oxide in zirconia is not quite accurate. If, on the contrary, we assume that the zirconia grains near the cobalt oxide interface have had enough time, at 850°C, to reach saturation volume solubility as well as a saturated δ -phase, two simultaneous linear equations will give the values of both the volume solubility

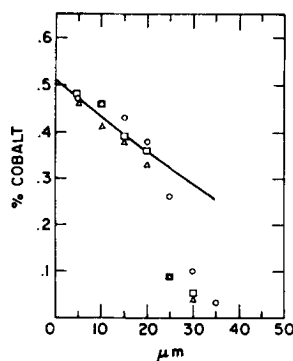


FIG. 8. Cobalt concentration profile vs distance from interface; on a 6.11- m^2/g porous, monoclinic ZrO_2 disk, after 218 hr at 850°C; different point markings represent microprobe traverses along different paths.

and the δ -phase saturation concentration, as follows.

$$\begin{aligned} 2.2x + y &= 0.00325 \\ 6.11x + y &= 0.00514, \end{aligned} \quad (2)$$

where x is the saturation concentration of the δ -phase in grams of Co per square meter of zirconia, and y is the volume solubility, grams of Co per gram of ZrO_2 . The coefficients of x are the measured specific surface areas. The values on the right side of the equations are taken from the ordinate intercepts of Figs. 7 and 8. The solution gives $x = 4.83 \times 10^{-4}$ g Co/ m^2 ZrO_2 , or 8.2 $\mu\text{mol}/\text{m}^2$ for the saturated δ -phase, and $y = 0.0022$ g Co/g ZrO_2 for the volume solubility of cobalt (calculated as metallic cobalt, but, no doubt, in the form of an oxide) at 850°C. The value for the saturation concentration of the δ -phase, obtained from this analysis, is pleasingly close to the values obtained from the chemisorption and catalysis experiments. The assumption that volume saturation had been reached near the Co_3O_4 - ZrO_2 interface requires diffusion coefficients of cobalt oxide in zirconia, at 850°C, of the order of 10^{-17} – 10^{-16} cm^2/sec . This estimate is based on ZrO_2 particle dimensions of 0.4 μm and a diffusion time of 308 hr.

Some additional microprobe data, not shown here, for a $6.11\text{-m}^2/\text{g}$ disk held at 850°C for only 5 days, showed a C_0 value of only $0.46\text{ wt}\%$, as opposed to the $0.514\text{ wt}\%$ (see above) for a similar disk held at 850°C for 9 days. This suggests that 5 days were insufficient to produce full volume saturation of cobalt oxide in the zirconia grains nearest the $\text{Co}_3\text{O}_4\text{-ZrO}_2$ interface. It follows that the estimated volume diffusion coefficient, at 850°C , of about $10^{-17}\text{-}10^{-16}\text{ cm}^2/\text{sec}$, is approximately correct, i.e., it is not just a minimum value.

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