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Measurement of Dispersion in Silica-Supported Cobalt Oxide Catalysts

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Areas of Co_3O_4 in silica-supported cobalt oxide catalysts were measured by selective CO adsorption at 33°C on previously vacuum-outgassed surfaces. Necessary information on the effect of outgassing temperature on CO uptake and also on the CO adsorption per unit area was obtained using unsupported Co_3O_4. An estimate was made of the number of possible adsorption sites and compared with experimental data for CO adsorption at −78°C. Mean crystallite sizes from X-ray line-broadening were used to estimate Co_3O_4 areas in unsupported and silica-supported catalysts. The theoretical X-ray intensity and intensities from sintered samples of both types of catalyst relative to an internal standard are compared and discussed. Conditions under which agreement occurred between Co_3O_4 areas measured by gas adsorption or estimated from X-ray data are reported. Lack of agreement in the more sintered samples was ascribed to crystallite aggregation, occurring in the same temperature range for both catalyst types. This latter feature was shown to be a consequence of the structure of the supported catalysts, which were examined as ultrathin sections by electron microscopy.

INTRODUCTION

Cobalt oxide is one of the most active oxides for catalyzing oxidation reactions, as shown, for example, in the oxidation of hydrocarbons over a series of single-component catalysts (*1*). It has also been shown to head the activity sequence for ethylene oxidation (*2*) where the oxides used were supported on silica or silica–alumina pellets. In the formulation of combustion catalysts based on Co_3O_4, either alumina, or preferably calcium aluminate, supports were used (*3*). It seemed worthwhile, therefore, to develop methods for measuring the surface area of cobalt oxide dispersed on a support as an aid to the development of practical cobalt oxide catalysts.

The surface area of single-component oxide catalysts or the *total* area of supported oxide catalysts can, of course, be measured by the BET method. In order to measure the area of the active component, in this case Co_3O_4, when supported, selective chemisorption on the cobalt oxide is indicated. Chromia areas have been measured in chromia–alumina (*4*) and chromia–silica–alumina catalysts (*5*) by oxygen-chemisorption on the hydrogen-reduced catalysts; a pulsed reduction–reoxidation technique was used with supported bismuth oxide and bismuth molybdate (*6*). It was noted, however, at the outset of the present work that Co_3O_4, when outgassed at moderate temperatures, will adsorb appreciable quantities of carbon monoxide. The selective chemisorption technique described for Co_3O_4–silica catalysts uses this adsorbate, and only a small correction for adsorption on the silica support is required.

Cobalt oxide areas were also calculated from the crystallite sizes measured by X-ray line-broadening; sections cut in an ultramicrotome were examined by electron microscopy. To make use of these techniques, it was necessary to have catalysts where the cobalt oxide existed as definite small crystallites on the support, thereby limiting the exposed area of the active oxide. Nevertheless, it is of interest to discover to what extent and under what conditions agreement can be obtained between surface areas derived from selective chemisorption and from these instrumental techniques.

EXPERIMENTAL METHODS

Materials

Cobalt oxide (Co_3O_4) was prepared by decomposing either Analar cobaltous nitrate or cobaltous oxalate. In order to prepare catalysts with a high surface area it is desirable to find the minimum decomposition temperature, and a special study was made of the thermal decomposition of cobalt salts using a Mettler thermoanalyzer. It was found that cobaltous nitrate could apparently be completely decomposed by heating in air at 150°C for 24 hr, and this was confirmed by X-ray diffraction analysis. Cobaltous oxalate was decomposed by heating at 250°C for 24 hr.

Supported Co_3O_4 catalysts were prepared by impregnation or adsorption of the nitrate or oxalate on silica supports, followed by decomposition at the temperatures specified above. The silica supports used were Davison, grade 70, or Porasil E (Waters Associates Ltd, manufactured by Pechiney-Saint-Gobain), with measured surface areas of 296 and 24 m^2/g, respectively. An example of catalyst preparation by impregnation, yielding $\sim$10% Co_3O_4 on the support, is as follows. Molar cobaltous nitrate solution, 85 ml, was diluted with an equal volume of water and 50 g Davison 70 silica were added; the slurry was dried initially over a water bath and then in a vacuum oven at 100°C for 18 hr. The catalyst was transferred to a drying oven at 100°C, the temperature was raised slowly to 150°C and was maintained at 150°C for 24 hr. A similar procedure might be followed using cobaltous oxalate dissolved in 0.88 Analar ammonia, and the catalyst containing 11.5% Co_3O_4 on Porasil E was made by this method. Cobaltous oxalate from this solution adsorbs readily on the silica support, and an adsorption-type catalyst can also be prepared, the latter being filtered and washed before drying. However, the catalyst containing 5.7% Co_3O_4 on Davison 70 was left unwashed and is, therefore, classified as an adsorption–impregnation type, because oxalate solution would be left in the pores and subsequently dried out there.

Measurements

A glass volumetric apparatus incorporating greaseless stopcocks was used for the measurements of CO adsorption. Pressures were measured with miniature Pirani gauges, operated at constant filament temperature, with self-balancing control units. The catalyst sample, $\sim$0.5 g, was outgassed ("vacuum," $< 10^{-3}$ Torr) typically at 450°C for 16 hr (but other temperatures, specified below, were also used) before CO adsorption, usually at 33°C. Carbon monoxide, "spectroscopically pure" (British Oxygen Co. Ltd) was supplied from break-seal Pyrex vessels. The adsorbed volumes are reported per gram of *discharged* catalyst. The BET areas of the catalysts were measured by the flow method of Nelson and Eggertsen (7), using nitrogen (cross-section area 15.8 Å) as the adsorbate. Samples were outgassed in a stream of helium at 150°C for 90 min.

Crystallite sizes were measured by X-ray line-broadening (Cu$K\alpha$ radiation) using a Philips diffractometer, comprising a PW 1130 generator, a PW 1050/25 goniometer fitted with a curved crystal focusing monochromator, and a krypton proportional counter with rate meter/chart recorder presentation of the results. Diffraction intensities were obtained from the areas of the peaks; usually a ratio of intensities was required, where the catalyst sample had been mixed in known proportion with NaF by hand-grinding in a boron carbide crucible.

Catalysts, prepared as thin sections, were also examined in the electron microscope (rated best-line resolution, 4.5 Å). The catalyst sample was set in the end of a block of Araldite resin, and thin sections were cut in an ultramicrotome.

RESULTS AND DISCUSSION

Selective CO Chemisorption

Two preliminary requirements are information on the effect of outgassing on the subsequent uptake of carbon monoxide and a correlation between the volume of CO per gram of *unsupported* Co_3O_4 and the BET surface area.

Figure 1 shows the results of various outgassing treatments on the shape of the CO adsorption isotherms for unsupported cobalt oxides prepared from the nitrate or oxalate. Outgassing the catalysts at temperatures above those used when calcining the starting materials causes some sintering, and after each CO adsorption measurement the BET area was measured, so that CO uptakes could be expressed as the volume adsorbed per square meter of surface. Catalysts prepared from the nitrate (closed symbols) are discussed first. A very mild outgassing treatment (150°C for 16 hr) is clearly insufficient to prepare the surface for CO adsorption (at 33°C). Outgassing at 250°C for 16 hr increased the uptake of CO but the isotherm does not show any change in shape indicative of the quantity corresponding to saturation coverage. A further increase in outgassing temperature to 350°C provided a satisfactory isotherm for cobalt oxide samples prepared from the nitrate, and the uptake (~0.16 ml CO/m^2 surface) was not increased by outgassing at 450°C. In contrast, the CO uptake on samples prepared from the oxalate (open symbols) was substantially less after outgassing at 350°C, and an outgassing temperature of 450°C was required to give an equivalent CO uptake.

Figure 2 shows the volume of CO adsorbed at 33°C on samples of Co_3O_4 (prepared from nitrate or oxalate) with a range of surface areas obtained by calcining at temperatures above the decomposition temperatures. Before CO adsorption, the samples were outgassed at 450°C on the basis of the information given above. The volume of CO adsorbed is a linear function of the BET area, and each square meter of Co_3O_4 surface adsorbed 0.16 ml CO at 33°C. It would seem that this quantity does not represent full coverage (as discussed below), and from an adsorption isotherm obtained at −78°C the "coverage" was 0.252 ml CO/m^2. However, CO adsorption on the silica supports used was very small at 33°C, and this temperature appeared to be a suitable choice for selective chemisorption of CO on Co_3O_4 supported on silica. Examples of CO adsorption isotherms for Co_3O_4–silica catalysts at 33°C are shown in Fig. 3; CO adsorption on the

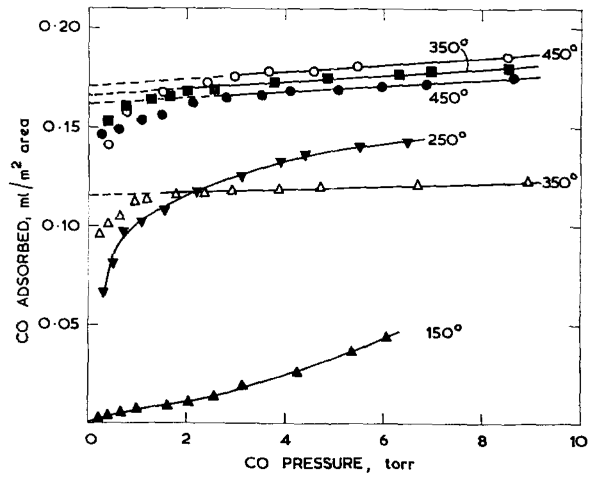

FIG. 1. CO adsorption (at 33°C) per m^2 Co_3O_4, prepared by decomposition of cobaltous nitrate (solid symbols) or cobaltous oxalate (open symbols) and outgassed at temperatures indicated for 16 hr.

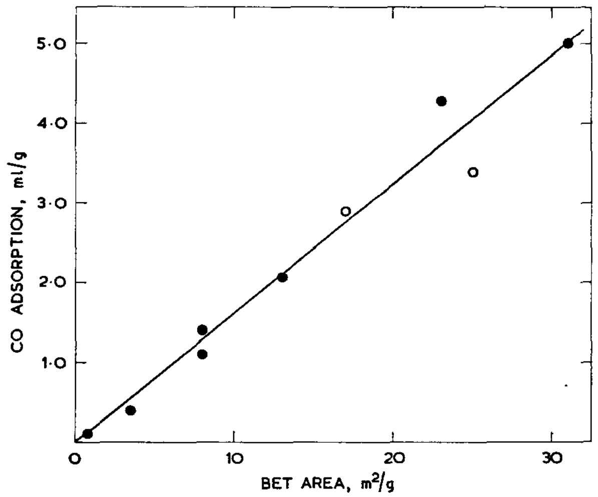

FIG. 2. CO adsorption (ml/g) at 33°C on unsupported Co_3O_4 prepared from nitrate (●) or oxalate (○) calcined at different temperatures, and outgassed at 450°C for 16 hr as a function of BET area (m^2/g).

silica used in catalyst preparation is also shown for comparison.

It is of interest to compare the quantity of CO adsorbed (on unsupported Co_3O_4 of known BET area) with the estimated number of possible adsorption sites, although some of the assumptions which have to be made are rather arbitrary. In a recent publication (*8*) the difficulty of evaluating the effect of the discontinuity represented by the surface on the energy of the crystal was noted, and factors tending to cause a distribution among cation sites different from that in the bulk spinel were discussed. Cossee (*9*) inferred, from magnetic measurements, that Co_3O_4 possesses the normal spinel structure $A[B_2]O_4$, with the Co^{2+} ions occupying the tetrahedral (or A sites) and the Co^{3+} ions the octahedral or B sites. It was assumed for present purposes that only the low index planes, (100), (110) and (111), are exposed and that the surface terminated at the maximum numbers of anions. Cations in the plane of the surface or exposed through interstices in the close-packed oxygen layer may constitute pos-

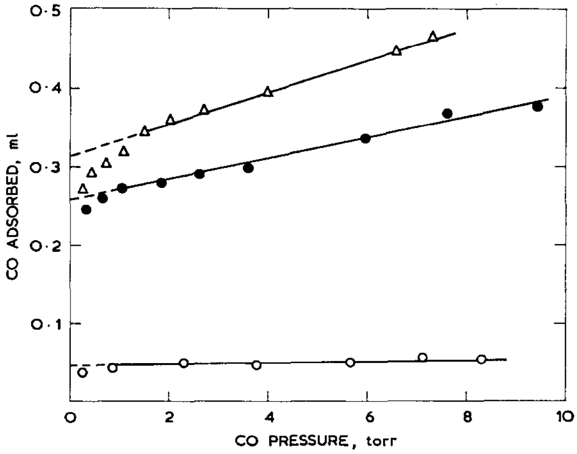

FIG. 3. CO adsorption isotherms at 33°C for silica-supported catalysts; 5.7% Co_3O_4, 0.467 g (△); 10.2% Co_3O_4, 0.474 g (●); Davison 70 silica support, 0.94 g (○).

sible sites. Representations of the (100) and (110) planes are given by Cimino and Schiavello (*8*), and Ref. (*10*) may also be consulted with respect to the (111) plane.

The mean numbers of sites are 3.7×10^{14}, 7.4×10^{14} and $14.8 \times 10^{14}/\text{cm}^2$ for cations in tetrahedral and octahedral positions and for the oxygen anions, respectively. The CO uptake at −78°C was 6.8×10^{14} molecules/cm². Recently, weak infrared bands observed for CO adsorption at high coverages on unreduced nickel oxide (11) were assigned to CO species attached to both nickel ions of nickel oxide lattices and lattice oxygen ions. Similar bands were found with samples of cobalt (oxide ?) and analogous assignments were made. In these circumstances it is not possible at present to make obvious correlations between number and type of sites and number of adsorbed CO molecules.

Crystallite Size Measurements

The mean crystallite size D was derived from X-ray line-broadening, using the Scherrer equation and the classical value of the Scherrer constant, $K = 0.90$, correcting for instrumental broadening using Warren's expression (*12*). It is proposed to calculate the surface area of Co_3O_4 from crystallite size measurements by assuming that Co_3O_4 is present as crystallites of cubic shape having one face contacting the support. Thus:

$$\text{area } (\text{m}^2/\text{g } Co_3O_4) = 5 \times 10^4/\rho D,$$

where the density of Co_3O_4, $\rho = 6.07$. The same relation was used for unsupported Co_3O_4 to compensate for crystallite contact preventing gas access. Hence, surface areas from crystallite size measurements can be compared (next section) with surface areas of Co_3O_4 determined by selective CO adsorption (for supported catalysts) or by the BET method (for unsupported catalysts).

When comparisons of surface areas from selective chemisorption and from X-ray line-broadening are made, using supported *metal* catalysts, large discrepancies may be found if no allowance is made for "X-ray amorphous" material not included in the mean crystallite size value. It seemed advisable, therefore, to apply the method used previously with supported metal catalysts (*13*) to estimate the fraction of the cobalt oxide contributing to the mean size determination. In principle, this fraction can be found by comparing the intensity of radiation scattered from the "unknown" sample with that from a standard sample where all the cobalt oxide might be detectable as a consequence of extensive sintering. The comparison was made using an *internal* standard for reasons given previously (*13*); in the present work NaF was chosen because it gave a strong (200) reflection, close to, but not seriously overlapping with, the strongest (311) reflection of Co_3O_4. The catalyst sample to be examined was mixed in a known proportion with NaF, and the intensity ratio α determined, where

$$\alpha = \frac{\text{area } Co_3O_4 \text{ (311)}}{\text{area NaF (200)}}.$$

The observed value of α was adjusted to a reference system containing equal weight of Co_3O_4 and NaF. Then, if the value of α is known for a standard catalyst where all the Co_3O_4 is detectable by X-ray diffraction (this value is designated α_s) adjusted to the same reference system, the detectable fraction in the "unknown" catalyst sample can be obtained. The theoretical calculation of α_s and its experimental determination are discussed below.

The theoretical value of α can be calculated from the expression:

$$\alpha = \frac{I_1}{I_2} = \frac{p_1 F_1{}^2 \phi_1(\theta_1) G_1 V_2 M_2}{p_2 F_2{}^2 \phi_2(\theta_2) G_2 V_1 M_1},$$

where p is the multiplicity factor; $\phi(\theta)$ is the combined Lorentz polarization factor; G is the mass of the component in the mixture; and V and M are the volume and molecular weight of the unit cells, respectively. The calculation of the structure factor F involves *inter alia* the anion parameter u, which required special determination for Co_3O_4 in the present work and is reported elsewhere (*14*). The exact relation of the anion lattice to the cation positions is described by the anion parameter, and

$u = 0.375$ in the ideal structure where planes of A-site cations are exactly halfway between planes of B-site cations and the anions. The determined value (*14*) was $u = 0.392$ so that, for the reference system $G_1 = G_2$, the theoretical value for α_s (where all the Co_3O_4 is detectable) is 1.26.

Figure 4 shows values of crystallite size D and intensity ratio α for two series of catalysts, unsupported Co_3O_4 and 10% Co_3O_4 supported on Davison 70 silica. Values of α and D are plotted as a function of sintering temperature, which is either the temperature for decomposing nitrate (150°C) or oxalate (250°C), or represents extra heat treatment (in air) at higher temperatures. The values of α and D observed could depend on various parameters in addition to the steady calcination temperature (e.g., rate of temperature run-up, thickness of the layer), producing scattered points if not strictly controlled. However, apart from a value of α (half-filled circle) and D (bisected circle) at 450°C, where a different furnace was used, smooth plots were obtained. Crystallite growth (values of D) is marked for unsupported Co_3O_4 compared with the supported catalysts. Eventually, at the highest calcination temperature, 1000°C, the supported catalyst showed evidence of cobalt silicate formation.

The variation of the intensity ratio α with sintering temperature (Fig. 4) is of particular interest. The initial increase in α with sintering temperature might be caused by the growth of highly dispersed Co_3O_4 not previously contributing to the area of the diffraction peak. The plot of α versus sintering temperature reaches a maximum at ~400–500°C, passing close to the theoretical value of $\alpha = 1.26$. At first sight, it might seem that α should remain at the maximum value, although the calcination temperature has been increased, but it is understood, from previous experience with palladium black and palladium–charcoal catalysts (*13*), that α can be diminished by X-ray absorption effects. Aggregation of crystallites into large clusters and the growth of large crystallites lead to differential intensity losses and a decrease in observed values of α. It is noticeable that supported Co_3O_4, where there is little crystallite growth with increasing calcination temperature, is subject to relatively little decrease in α below the expected plateau value compared with unsupported Co_3O_4.

Comparison of Adsorption and X-Ray Data

From the above discussion, it would seem that catalysts outgassed or calcined below

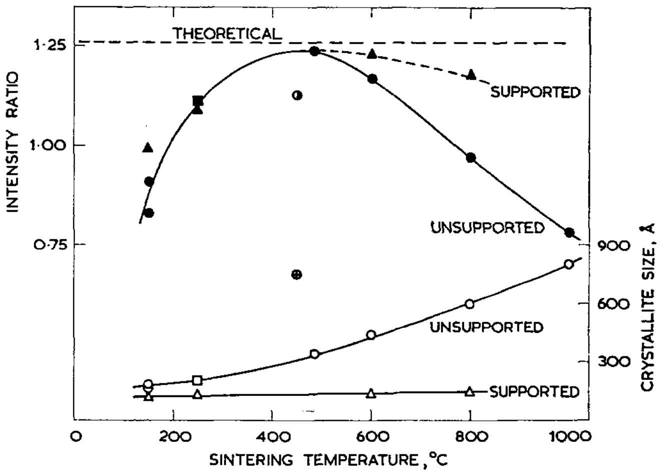

FIG. 4. Effect of sintering temperature on the X-ray intensity ratio (solid symbols) and on the crystallite size (open symbols) for unsupported Co_3O_4 prepared from cobaltous nitrate (circles) or oxalate (squares) and for a 10% Co_3O_4–silica catalyst (triangles); other symbols, see text.

(say) 450°C with α well below 1.26, may contain highly dispersed Co_3O_4 not included in the crystallite size (D) determination by X-ray line-broadening, and therefore a correction should be made to the Co_3O_4 areas calculated from values of D. It was found, however, that Co_3O_4 areas in *unsupported* catalysts (BET areas) subjected to pretreatment temperatures up to 450°C agreed satisfactorily with areas calculated from D, *without making a correction for highly dispersed* Co_3O_4. Table 1 shows that this observation applies to samples of unsupported Co_3O_4 prepared from the nitrate and pretreated at temperatures from 150 to 450°C (5 results) or from the oxalate (4 results).

Values of the intensity ratio α below 1.26 in catalysts pretreated below $\sim$450°C could alternatively arise from poorly crystallized Co_3O_4. Provided that such material has a mean particle size approximately equal to the crystallite size measured by X-ray line-broadening, then Co_3O_4 areas calculated from D and by the BET method would be in agreement.

Sintering of the crystallites into aggregates at higher temperatures inhibits access of gas to the crystallite surfaces, which become interfaces between contacting crystallites. Areas of Co_3O_4 calculated from D, and also measured by the BET method, for samples heated in air at 485–1000°C and cooled to room temperature in air exhibit increasing disagreement. Accompanying this divergence of surface areas (columns 6 and 7, Table 1, nitrate preparations), the value of α eventually decreases because, as pointed out above, it is also sensitive to crystallite aggregation.

It is of interest, then, to see if agreement can be obtained between Co_3O_4 areas in supported catalysts determined by CO chemisorption and areas calculated from crystallite size. In particular, where α is less than 1.26 is it necessary to apply a correction to the area calculated from D, or is the situation like that found for unsupported Co_3O_4? Table 2 shows the comparison of Co_3O_4 areas (columns 5 and 7) for series of silica-supported Co_3O_4; the total catalyst (BET) area is also given in column 6. Any correction to the Co_3O_4 area calculated from crystallite size D will increase the calculated area and, once again, agreement with the Co_3O_4 area derived

TABLE 1

UNSUPPORTED COBALT OXIDE

Preparation	Calcination temp for 24 hr (°C)	Outgassing[a] temp for 16 hr (°C)	X-ray diffraction			BET area (m²/g)
			D (Å)	α	Calcd area (m²/g)	
Nitrate 150°C; 24 hr	—	150[b]	180	0.91	46	50
	—	300	200	0.96	41	46
	—	350	225	0.96	37	41[c]
	—	450	235	0.95	35	31
	450	300	750	1.13	11	13
	485	450	340	1.24	24	13
	600	450	435	1.17	19	8
	800	450	595	0.97	14	4
	1000	450	800	0.78	10	1
Oxalate 250°C; 24 hr	—	150[b]	200	1.11	41	53
	—	300	310	1.17	27	34
	—	450	255	1.08	32	25
	—	450	485	1.08	17	17

[a] Before CO chemisorption, subsequently outgassed at 150°C before BET area, except [b].

[b] Before measuring BET area only; outgassing for 1.5 hr.

[c] From CO chemisorption.

TABLE 2

Cobalt Oxide on Silica Catalysts

Catalyst	Pretreatment[a] (°C)	X-ray diffraction			Total area (BET method) (m²/g catalyst)	Area (from CO adsorption) of Co_3O_4 (m²/g Co_3O_4)
		D (Å)	α	Calcd area of Co_3O_4 (m²/g Co_3O_4)		
10.2% Co_3O_4/Davison 70	—	120	0.99	69	265	—
(nitrate impregnation)	Vac 300	150	0.98	55	250	59
	Vac 350	150	1.02	55	250	49
	Vac 450	120	1.08	69	265	31
	Air 500; Vac 450	155	1.16	53	260	2
	Air 600; Vac 450	135	1.23	61	140	2
	Air 800; Vac 450	140	1.18	59	135	4
	Air 1000	Silicate detected			—	—
11.3% Co_3O_4/Porasil E	—	185	0.96	45	—	—
(nitrate impregnation)	Vac 300	180	0.91	46	—	52
	Vac 350	185	1.01	45	—	43
	Vac 450	175	1.20	47	—	36
	Vac 450	200	0.95	41	—	31
	Air 500; Vac 450	240	1.03	34	—	<1
11.5% Co_3O_4/Porasil E	—	125	0.67	66	—	—
(oxalate impregnation)	Vac 450	185	0.83	45	—	30
5.7% Co_3O_4/Davison 70 (oxalate adsorption)	Vac 450	135	0.46	61	—	64

[a] Vacuum outgassing for 16 hr; heated in air for 24 hr.

from CO adsorption measurement requires α to be ignored.

Reasonable agreement between columns 5 (X-ray area) and 7 (CO adsorption area) occurs for ~10% Co_3O_4 deposited by nitrate impregnation on Davison 70 silica, with vacuum outgassing at 300 or 350°C. (The information on CO uptake per square meter from Fig. 2 was used although it refers to vacuum outgassing at 450°C, as Fig. 1 indicates that CO uptakes per unit area on samples prepared from the nitrate are similar if outgassed at 350°C, and probably 300°C.) When samples of this catalyst preparation were outgassed at 450°C in vacuum, or heated in air at 500°C and above, before outgassing (results nos. 4–7 in Table 2), the agreement was lost.

Similarly, for a series of ~11% Co_3O_4 catalysts, deposited on Porasil E, again by nitrate impregnation, agreement is reasonable between X-ray and CO adsorption areas, after outgassing at 300 or 350°C, but falls away after outgassing at 450°C, and is lost after heating in air at 500°C.

Catalysts prepared from the oxalate also showed poor agreement when outgassed at 450°C, if entirely an impregnation technique was used in the preparation, but good agreement (final result in Table 2) if prepared by the adsorption–impregnation method (see Experimental Methods section).

In summary, agreement was found between Co_3O_4 areas in silica-supported catalysts calculated from crystallite size and measured by CO chemisorption, provided that (a) no correction for X-ray amorphous material (α less than 1.26) was made, and (b) the pretreatment temperature did not exceed 350°C for impregnated-type catalysts, or 450°C for the adsorption–impregnation type. Hence, agreement between "X-ray" and "adsorption" areas is found for both unsupported Co_3O_4 and silica-supported Co_3O_4 under very similar conditions.

It is believed that this result arises from the structure of silica-supported Co_3O_4 catalysts, as discussed in the next section.

Structure of Co_3O_4–Silica Catalysts

It was proposed that pretreatment temperatures above 450°C cause crystallite aggregation in *unsupported* catalysts, and that "X-ray" and "adsorption" areas disagree because gas cannot reach the individual crystallite surfaces. The same explanation is advanced for the disagreement observed after pretreatment above 350–450°C applied to Co_3O_4–silica catalysts. Electron micrographs suggest that Co_3O_4 is deposited on the silica support (after impregnation with cobaltous nitrate and calcination), as clumps of crystallites. Figure 5 shows evenly distributed dark patches of Co_3O_4 on the lighter silica support, and at higher magnifications some structure within the dark patches can be distinguished. An approximate size distribution for these patches of Co_3O_4 is as follows: 20% < 750 Å; 75% in the range 750–1000 Å; 5% > 1000 Å. The mean crystallite size measured by X-ray line-broadening, was 120 Å. This comparison supports the somewhat subjective visual impression that Co_3O_4 is present on the support as clumps of smaller crystallites. If the forces between the Co_3O_4 crystallites and the silica support are weak, the Co_3O_4 crystallites will aggregate, on heating, with very much the same response as that shown by *unsupported* Co_3O_4 crystallites. It would follow that Co_3O_4 areas calculated from crystallite size or measured by gas adsortpion would agree or disagree over much the same temperature ranges for both unsupported and silica-supported Co_3O_4.

When the divergence between X-ray areas and adsorption areas occurs, it is largely due to a sharp decrease in the adsorption area. For example, in supported Co_3O_4 the crystallite size is not changed by increasing severity of heat treatment, reflecting the "anchorage" of the crystallites to the support. Figure 6 shows that the loss of area on sintering occurred in a very similar way, with a sharp fall at ~450°C, for both unsupported Co_3O_4 (the BET area) and silica-supported Co_3O_4 (the CO adsorption area). This sharp decrease in area is not thought to be due to the collapse of the silica support pore structure, happening coincidentally at 450°C, because as column 6 in Table 2 shows, the 10% Co_3O_4–

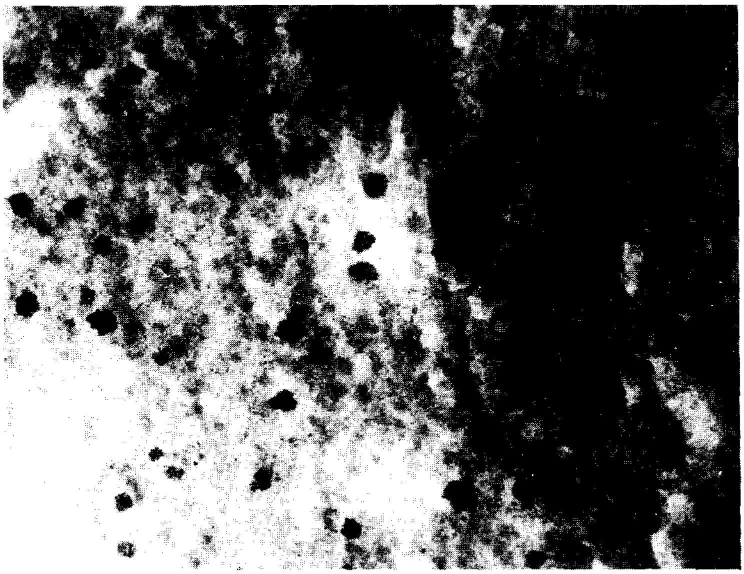

FIG. 5. Electron micrograph from ultramicrotome section of 10% Co_3O_4–silica catalyst showing dark patches of Co_3O_4 on the lighter silica support; magnification 30,000×.

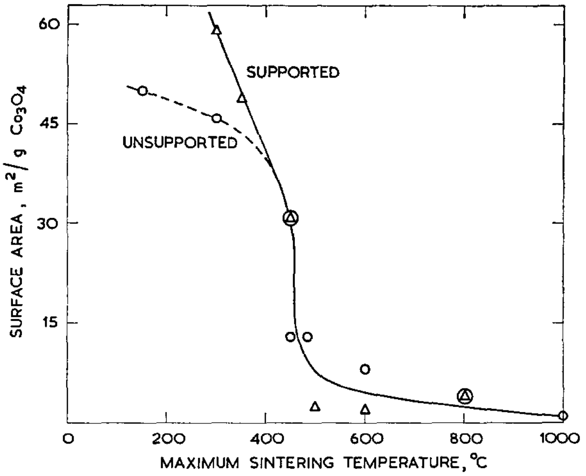

FIG. 6. Surface area (BET method) of unsupported Co_3O_4 (○) and the Co_3O_4 area (CO adsorption method) in a 10% Co_3O_4–silica catalyst (△) as a function of maximum temperature during heat treatment (in air) or vacuum outgassing. Areas expressed per gram of Co_3O_4 in both cases.

silica catalyst retained its *total* area unchanged up to 600°C.

CONCLUSIONS

Carbon monoxide can be selectively adsorbed at 33°C on Co_3O_4 which has been prepared as a silica-supported catalyst, thus providing a method for measuring the area of the catalytically active component (Co_3O_4) of the catalyst. The catalyst requires prior vacuum outgassing at 350 or 450°C, depending on whether cobaltous nitrate or oxalate was used in the preparation. These temperatures are close to the limiting temperatures above which crystallite aggregation occurs in both supported and unsupported Co_3O_4, causing a sharp loss in area. Below the limiting temperature, Co_3O_4 areas calculated from crystallite size determined by X-ray line broadening agree with Co_3O_4 areas measured by gas adsorption. Therefore, Co_3O_4 areas in "as prepared" silica-supported catalysts (i.e., not subjected to temperatures above those used in their preparation) with maximum Co_3O_4 dispersion, may be determined by the X-ray method. Depending on the nature of the active oxide dispersion, X-ray line-broadening might be applied to other supported oxide systems, or in conditions where the selective gas adsorption method is inappropriate for area measurement, with due regard to the limitations imposed by crystallite aggregation.

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