

Preparation of Cobalt Oxide Catalysts and Their Activity for CO Oxidation at Low Concentration

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A thermogravimetric study of the decomposition of cobalt salts together with surface area measurements (of Co_3O_4) indicated the best choice of starting compound and optimum decomposition temperatures for the preparation of high-area Co_3O_4 powder catalysts. A standard method is proposed for the preparation of such Co_3O_4 catalysts with an area of $\sim 150 \text{ m}^2/\text{g}$, via decomposition in air of a carbonate obtained from cobaltous acetate and sodium carbonate solutions. Catalyst activity was assessed in terms of CO oxidation at very low concentration (50 ppm in oxygen) and high space velocity with regard to possible environmental application. Unsintered and sintered Co_3O_4 powders were characterized by pore size distribution measurements and external particle surfaces were examined by scanning electron microscopy. The different activities of Co_3O_4 catalysts prepared by decomposition of the carbonate, nitrate, hydroxide and oxalate are discussed. The relationship between catalyst activity and surface areas of sintered Co_3O_4 catalysts is discussed in terms of the limitation of reaction rates by pore diffusion. The preparation and performance of various practical forms of Co_3O_4 catalyst are described, including sintered pellets and Co_3O_4 supported on silica granules or preformed alumina spheres. Oxidized cobalt turnings also provide an active catalyst.

INTRODUCTION

It is well established that cobalt oxide (Co_3O_4) is a very effective catalyst for the oxidation of carbon monoxide (1) and the total oxidation of methane (2, 3) and other hydrocarbons (4, 5). It has also been found that the rate of heterogeneous decomposition of nitric oxide (6) is three or four orders of magnitude greater (at 500°C) over unsupported Co_3O_4 compared with other catalysts tested. Consequently when base metal oxides are considered as possible catalysts for environmental applications, cobalt oxide is often among those tested. In the present work, the preparation of cobalt oxide catalysts was studied with respect to the development of both high surface area materials, extending a previous report (7), and sintered or supported

forms relevant to the above use. Hence, catalysts were assessed in terms of their ability to oxidize very low concentrations (50 ppm) of carbon monoxide in oxygen at realistic space velocities. The internal pore structure of some catalysts was investigated by low temperature nitrogen adsorption/desorption and the external surface texture by scanning electron microscopy. These measurements assisted in the discussion of the reaction rates where limited by pore diffusion under the test conditions used.

EXPERIMENTAL METHODS

Information on catalyst preparation is an integral part of the Results and Discussion section but details of starting materials are recorded here. The useful

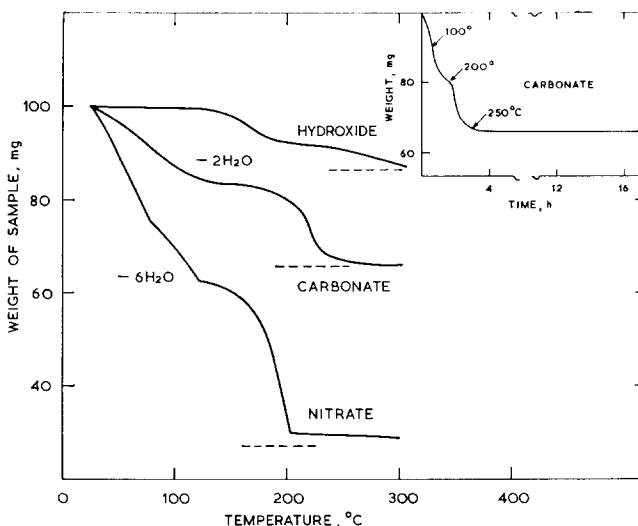


FIG. 1. Thermal decomposition in air of cobaltous nitrate hexahydrate, cobaltous hydroxide and the basic carbonate used to prepare the Co_3O_4 catalyst, designated WSL/100 (see text). Expected weights after Co_3O_4 formation. (---) Inset: Carbonate decomposition at constant temperature, 250°C .

cobalt salts were AnalaR-grade nitrate and laboratory reagent-grade oxalate, acetate and basic carbonate (Hopkin and Williams). The catalyst designated WSL/100 was prepared by decomposition of the carbonate precipitated from solutions of cobaltous acetate and sodium carbonate (AnalaR-grade). As an indication of impurity levels, the following were found when this Co_3O_4 catalyst was analyzed by flame emission spectroscopy and X-ray fluorescence: Na, 0.04%; Ni, $\sim 0.1\%$; Cu, 0.05%; Zn, 0.02%; Fe, Mn, $< 0.01\%$. Catalyst supports used were: silicas, Davison grades 12 and 70 and Porasil "A" (Waters Associates, manufactured by Pechiney-Saint-Gobain) and alumina, type H151 (Alcoa). Cobalt foil (Johnson Matthey, grade 1), 0.25 mm thick, and turnings from a cobalt rod (Materials Research) were oxidized as described below.

The decomposition of cobalt salts was investigated using a Mettler thermo-analyzer; a typical heating rate, in air, was $0.5^\circ\text{C}/\text{min}$. Pore size distributions in prepared catalysts were derived from low-temperature nitrogen adsorption/desorp-

tion isotherms; separate surface area determinations were often made by the BET method. Scanning electron micrographs showed the surface features of catalyst particles; the samples were coated with a Au-Pd alloy film to make them conducting before they were examined at magnifications up to $11,000\times$.

For the measurement of CO oxidation rates, a weighed quantity of catalyst was retained between glass wool plugs in a tubular glass reactor and thermocouples were placed at the ends of the catalyst bed. Nitrogen containing 0.2% CO (British Oxygen) was added to oxygen to produce a concentration of 50 ppm CO (by volume) at the required space velocity. (One set of catalysts was also tested with 1% CO in oxygen.) Carbon monoxide concentrations before and after the catalytic reactor were measured continuously with two infrared analyzers; carbon dioxide formation was also checked in some experiments. The following procedure gave reproducible observations of catalyst activity. The carbon monoxide + oxygen mixture was passed at a rate of 1 liter/min through

the reactor and the temperature was increased until approximately 100% conversion was attained. Then the reactor was cooled to room temperature or until no reaction was observed. Gas flows were adjusted to the required space velocity and the CO oxidation rate was measured following each stepwise increase in temperature.

RESULTS AND DISCUSSION

UNSUPPORTED HIGH-AREA Co_3O_4 CATALYSTS

A survey of preparative methods shows that laboratory Co_3O_4 catalysts are usually prepared by decomposing the nitrate at 400°C or higher temperatures, resulting in surface areas of only a few square meters per gram. To discover if lower decomposition temperatures could be used, thereby increasing the surface area of the catalyst produced, various cobalt compounds were examined in a Mettler thermo-analyzer (Fig. 1). Cobaltous nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ lost water of crystallization in three stages and decomposition was appreciable at temperatures as low as 150°C. X-Ray diffraction confirmed that Co_3O_4 formation was complete after 24 hr. The surface areas developed (Table 1) by decomposing the nitrate at 150 or 250°C were 50 and 32 m^2/g Co_3O_4 , respectively, but further work (see below) indicated the retention of surface nitrogen oxides.

Thermal analysis also showed that the acetate and oxalate could be decomposed at 200 and 250°C, respectively, whereas temperatures in excess of 400°C were required to decompose cobaltous chloride and cobalt hexammine chloride (Table 1). However, the hydroxide and carbonate decomposed readily (Fig. 1) and seemed more promising as starting compounds with respect to the surface area which could be developed in the Co_3O_4 formed.

Cobaltous hydroxide (prepared by pre-

TABLE 1
Thermal Decomposition and Surface Areas

Cobalt compound	Decomposition temp (°C)	Surface area ^a of Co_3O_4 (m^2/g)
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	150	50
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	250	32
$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	200	—
$\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	250	53
$\text{Co}(\text{OH})_2$	150	49–202
$\text{Co}(\text{OH})_2$	200	25
$\text{Co}(\text{OH})_2$	250	20
$2\text{CoCO}_3 \cdot \text{Co}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	250	100–160
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	400+	—
$\text{Co}(\text{NH}_3)_6\text{Cl}_3$	400+	—

^a After heating for 24 hr.

cipitation from cobaltous acetate with ammonium hydroxide and vacuum-dried at 60°C was decomposed at 150, 200 and 250°C and yielded Co_3O_4 samples (as identified by X-ray diffraction) with surface areas of 146, 25 and 20 m^2/g , respectively. The surface area appeared to vary widely with the nature and strength of the solutions used in hydroxide precipitation (from 49 to 202 m^2/g for Co_3O_4 prepared at 150°C) but temperature control could be critical in view of the sensitivity of surface area to decomposition temperature. The surface area of Co_3O_4 produced by decomposing "cobalt carbonate" (at 250°C) varied in the range 100–160 m^2/g according to the method used to precipitate the carbonate. In general, higher-area Co_3O_4 samples were obtained from cobaltous acetate solutions compared with cobaltous nitrate solutions and by adding sodium or ammonium carbonate to the acetate solutions rather than the reverse procedure.

On the basis of the above work, a standard method is proposed for preparing high-area Co_3O_4 catalysts via decomposition of the carbonate rather than the hydroxide because a less critical decomposition temperature can be employed. Sodium car-

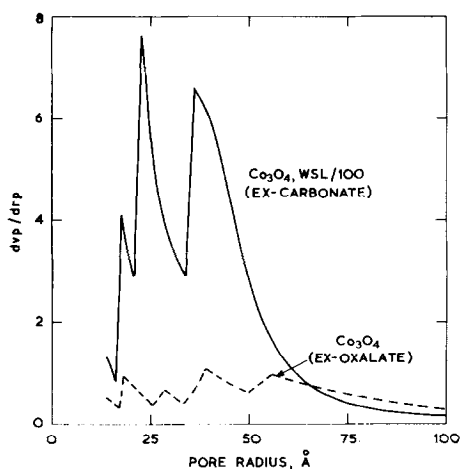


FIG. 2. Pore size distributions in Co_3O_4 catalysts prepared by decomposition of the basic carbonate (WSL/100) or oxalate. Ordinate shows rate of change in the adsorbate volume with changing pore radius; values are $\text{cm}^3 \text{Å}^{-1} \times \text{constant}$.

bonate solution (150 g in 1.5 liters distilled water) is added to cobaltous acetate solution (240 g in 7.5 liters), the voluminous precipitate is filtered, washed four times with 4-liter quantities of distilled water, dried overnight under vacuum in thin layers at 60°C , ground in an agate mill to pass through a 170 mesh (BSS) sieve and thin layers are decomposed in air at 250°C for 24 hr. (This Co_3O_4 catalyst is designated WSL/100.)

This carbonate decomposed as shown by the thermogram (Fig. 1); the mean weight loss in the temperature range to 250°C from six separate decomposition experiments was 33.4%. The inset shows that the weight remained constant after 4 hr when the carbonate was decomposed at 250°C . The thermogram may be interpreted on the assumption that the "cobalt carbonate" prepared was $2\text{CoCO}_3 \cdot \text{Co}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ for which the calculated weight loss on Co_3O_4 formation is 34.3%.

Confirmation of Co_3O_4 formation, despite the modest preparation temperature, is provided in Table 2, which compares the major X-ray diffraction peaks observed from WSL/100 with the JCPDS powder

diffraction file card (8) for Co_3O_4 with respect to both d -spacing and intensity. The crystallite size in WSL/100 measured from the broadening of the (311) X-ray line profile was 70Å (7 nm).

The surface area of the Co_3O_4 , designated WSL/100 was $144 \text{m}^2/\text{g}$. Figure 2 shows the pore size distribution of this Co_3O_4 , derived from low-temperature nitrogen adsorption/desorption measurements (9) and for Co_3O_4 ($53 \text{m}^2/\text{g}$) obtained by oxalate decomposition, as a comparison. The high surface area of WSL/100 (by separate BET determination) was largely associated with 20–50 Å pores; the total pore volume was 0.325ml/g .

CO Oxidation

Figure 3 compares the activity (oxidation of 50 ppm CO) of unsupported Co_3O_4 catalysts prepared, as discussed above, by the decomposition of the carbonate, oxalate, hydroxide, and nitrate. In this comparison similar weights (0.2 g) and particle sizes (<300 mesh BSS) were used in a 9 mm diam reactor with a fixed flow rate of $60,000 \text{cm}^3/\text{hr}$ but as a consequence of variation in bulk density of the catalysts, the space velocities were $\sim 300,000 \text{hr}^{-1}$ for Co_3O_4 prepared from the carbonate and $\sim 200,000 \text{hr}^{-1}$ for the other catalysts. Cobalt oxide prepared from carbonate was the most active catalyst whereas Co_3O_4 from nitrate was much the least active.

TABLE 2
X-Ray Diffraction Data on Co_3O_4

JCPDS data file			WSL/100 catalyst	
(hkl)	I/I_1	d (Å)	Intensity ranking	d (Å)
311	100	2.438	1	2.424
440	45	1.429	2	1.426
220	40	2.860	3	2.84
511	35	1.556		1.546
400	25	2.021	5	2.015
111	20	4.669	6	4.63

Some indication why Co_3O_4 prepared from nitrate (by decomposition at 150°C) was relatively inactive was gained by further examination of samples in a vacuum microbalance linked to a quadrupole mass spectrometer. Mass spectrometric analysis of the gases evolved above 200°C showed traces of nitrogen oxides which had remained after catalyst preparation. Further, when the Co_3O_4 catalyst from the nitrate was subsequently heated at 450°C to desorb surface nitrogen oxides, the activity for CO oxidation was enhanced (Fig. 3, filled triangles). No such enhancement was found when Co_3O_4 from carbonate or oxalate was heated to 450°C . It is concluded that nitrogen oxides remain on the surface of Co_3O_4 prepared by decomposing the nitrate at only 150°C and inhibit the activity.

As noted above, Co_3O_4 prepared from carbonate was the most active catalyst and some possible reasons might be briefly examined. The surface area ($159\text{ m}^2/\text{g}$) was larger by a factor of three compared with Co_3O_4 from oxalate ($53\text{ m}^2/\text{g}$) and by a factor of nine compared with Co_3O_4

from the hydroxide ($18\text{ m}^2/\text{g}$). However, using a CO concentration of 50 ppm, little of the internal surface can be effective due to pore diffusion limitation except at very low conversions (see discussion in next section). Further in support of this view, the activities of the three Co_3O_4 catalysts are obviously not proportional to their surface areas. It then becomes of interest to examine the *external* surface of the catalyst particles. Figure 4 shows scanning electron micrographs of Co_3O_4 catalysts prepared from oxalate or carbonate. Comparison at both low magnification, $956\times$, (Fig. 4A and B) and at higher magnification, $\sim 9000\times$ (Figure 4C and D) shows the different external surface topography of the two types of Co_3O_4 catalyst. Cobalt oxide prepared from oxalate appears to consist of aggregates of rod-like crystals, whereas Co_3O_4 from carbonate contained apparently large blocks and amorphous material. Cobalt oxide from oxalate gives the impression of possessing a higher *external* surface area than Co_3O_4 from carbonate. If this is correct, then the high activity observed

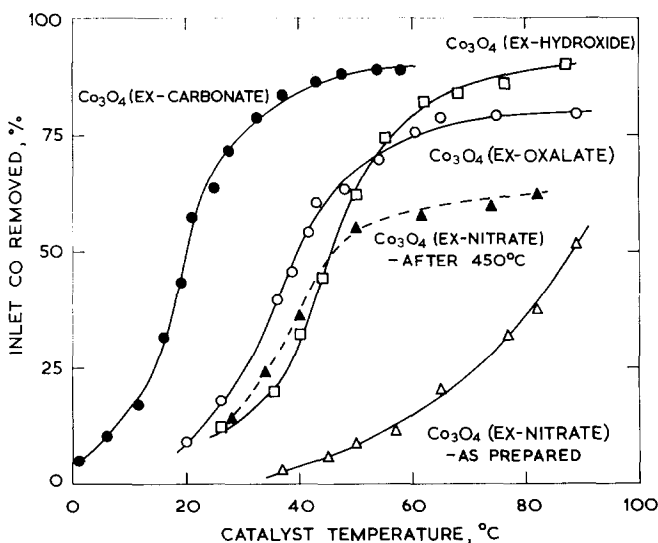


FIG. 3. Oxidation of 50 ppm CO in oxygen (for space velocities, see text) over Co_3O_4 catalysts prepared by decomposition of carbonate, hydroxide, oxalate (at 250°C) or nitrate at 150°C and after heating the latter Co_3O_4 catalyst at 450°C .

TABLE 3
Sintering of Co_3O_4 Prepared from Oxalate

Sintering temp ^a (°C)	Surface area (m ² /g)	Pore vol (ml/g)
Unsintered	57	0.115
300	33	0.080
400	19	0.020
600	5	0.002
700	3	Undetected

^a Maintained for 24 hr.

for Co_3O_4 from carbonate could arise from a greater intrinsic activity.

SINTERED Co_3O_4 CATALYSTS

In this section, the sintering of unsupported Co_3O_4 catalysts is examined, with respect to surface area, pore size and activity for CO oxidation at low concentrations. For the latter study, Co_3O_4 prepared from oxalate, which had a median activity in the unsintered form, was chosen.

Particular preparations of Co_3O_4 obtained by decomposition of carbonate, oxalate or nitrate had surface areas of 158, 50, and 57 m²/g, respectively. After heating in air for 24 hr at 450°C, their respective surface areas were 44, 13, and 13 m²/g while sintering at 800°C further decreased the surface areas to 4, 2, and 2 m²/g. Thus none of the Co_3O_4 catalysts (unsupported and without stabilizing additives) was particularly resistant to sintering but preparation of Co_3O_4 from carbonate again appeared to confer some benefit. The sintering of Co_3O_4 from oxalate was examined in more detail as an adjunct to the study of catalyst activity in relation to sintering.

Figure 5 shows the pore size distribution for Co_3O_4 samples prepared from oxalate

(by decomposition at 250°C) and after further heat treatment for 24 hr at the temperatures indicated. Heating to 300°C removed much of the porosity due to the smaller pores (<50 Å) but larger pores were unaffected and hence the relative decrease in total pore volume (Table 3) was small. At 400°C the collapse of the pore structure was more pronounced and there was a larger reduction in total pore volume. Higher temperatures further decreased the surface area and pore volume (Table 3) until at 600°C (Fig. 5) the pore system had virtually disappeared, and was not detected after sintering at 700°C. It is interesting to note the appearance of the external surface after sintering as viewed in the scanning electron microscope. Samples of Co_3O_4 from oxalate, heated at 700°C, and from carbonate, heated at 800°C (Fig. 4E and F), while retaining something of their characteristic difference, also have now the same granular texture induced by sintering.

CO Oxidation

The activity of the series of Co_3O_4 catalysts (0.4 ml, <300 mesh BSS particles, in a 9 mm diam reactor) prepared from oxalate, with the properties described above, was tested for CO oxidation at concentrations of 50 and 10,000 ppm CO in oxygen. Figure 6 shows that using 50 ppm CO, conversions over unsintered Co_3O_4 and catalysts sintered at 300 and 400°C are almost equal at the higher temperatures despite the threefold variation in surface area (Table 3). Conversion was lower over Co_3O_4 sintered at 600°C and the catalyst sintered at 700°C was much less active. The conversion of 50 ppm CO at 30, 50 and 70°C is plotted as a function of surface area in Fig. 7 which

FIG. 4. Scanning electron micrographs of Co_3O_4 catalysts prepared by decomposition of oxalate: (A) magnification 956 ×; (C) 9520 ×; (E) after sintering at 700°C, 8920 ×; or by carbonate decomposition; (B) 956 ×; (D) 8760 ×; (F) after sintering at 800°C, 9860 ×.

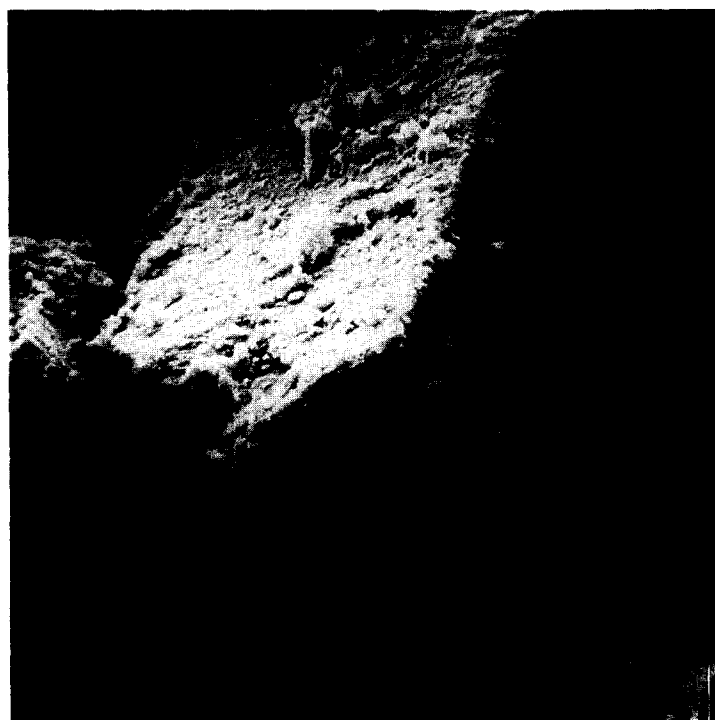
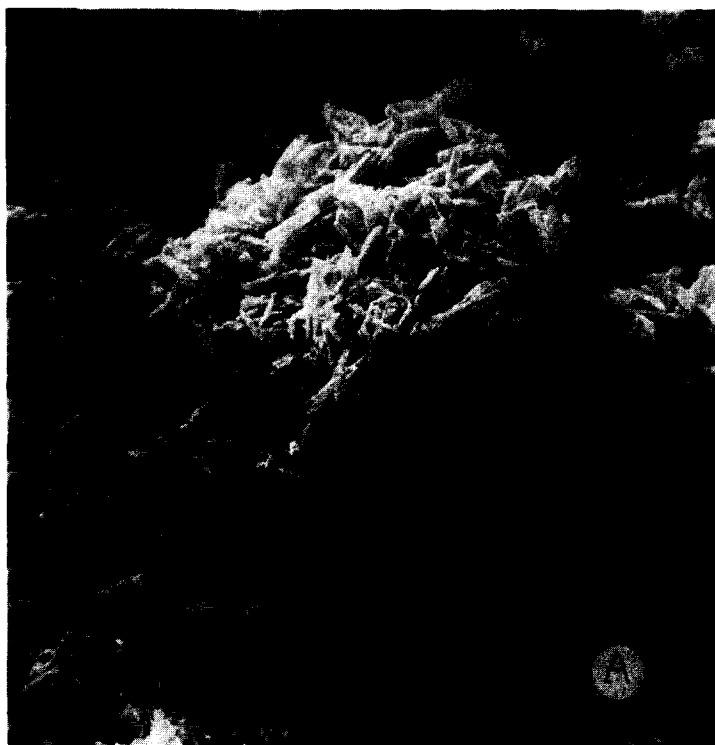


Figure 4

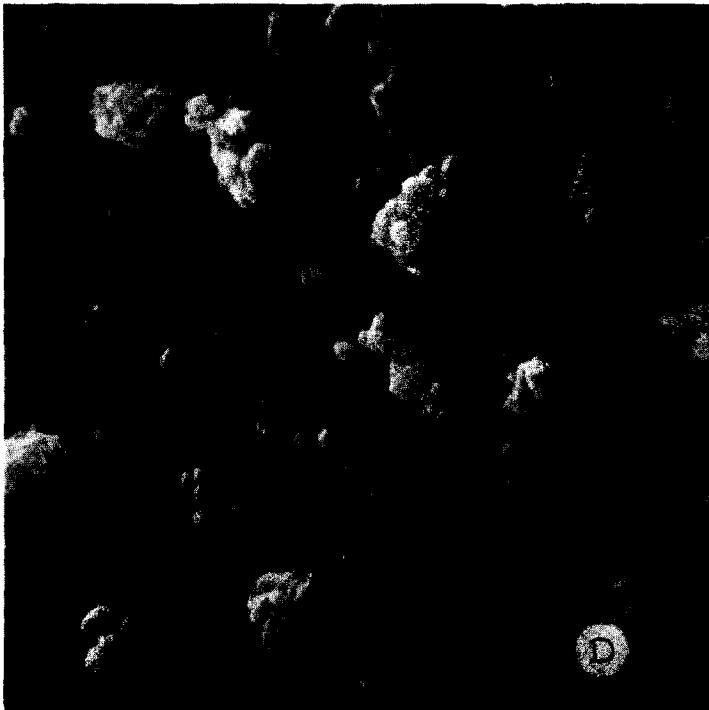


Figure 4 (Continued)

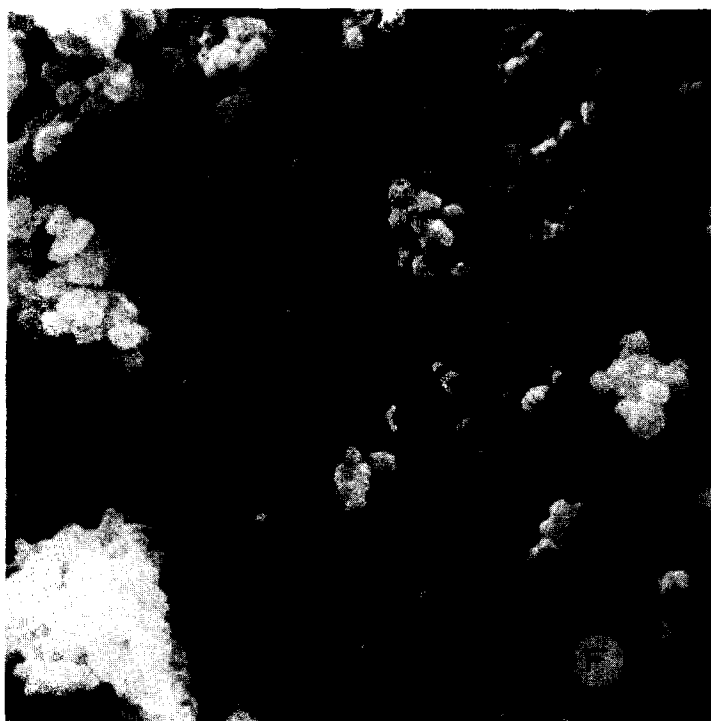
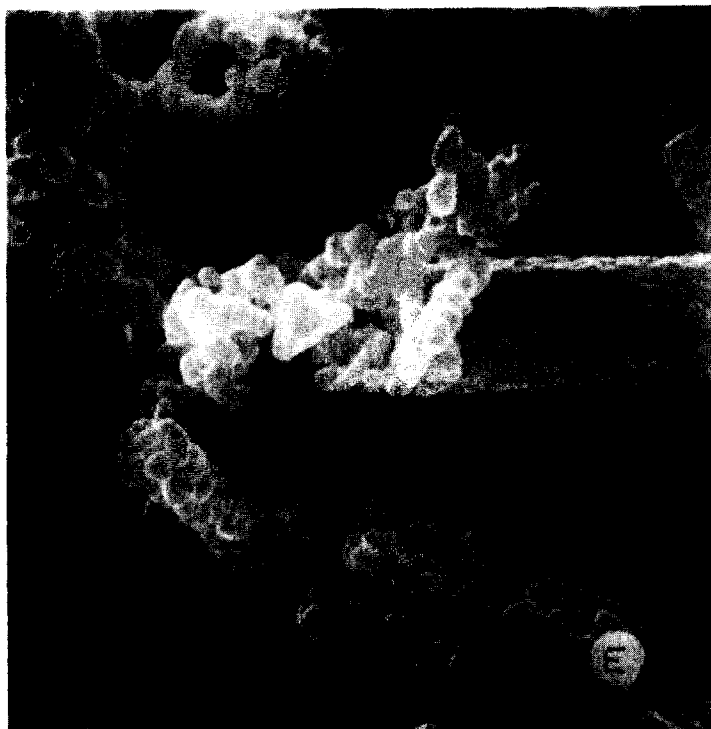


Figure 4 (Continued)

also shows the variation in the conversion of 10,000 ppm (or 1%) CO at 90°C (filled circles).

Using the theoretical treatment given by Wheeler (10) for the limitation of reaction rates by diffusion in porous catalysts, it is instructive to calculate the fraction of the total surface available as a function of CO concentration and percentage conversion. While the calculation must contain assumptions about the pore structure of the catalysts used, it indicates the general trends to be expected when measuring catalyst performance at such low reactant concentrations. The fraction, f , of the total surface available to the reactant is given by Eq. (1). This assumes that CO oxidation over Co_3O_4 is a first order reaction (11).

$$f = \frac{1}{h} \tanh h, \quad (1)$$

where h is a dimensionless quantity related to the reaction parameters in a flow system by:

$$h \tanh h = \left(\frac{a^2}{18D_K} \right) \left(\frac{F_A}{C_A} \right) \times \frac{1}{\rho_B V_g} \log_e \frac{1}{1 - \alpha}. \quad (2)$$

The quantities in Eq. (2) and their values for the unsintered Co_3O_4 catalyst are as follows:

- a average particle diameter, 0.005 cm,
- F_A feed rate, moles/ml catalyst/sec,
- C_A inlet concentration, moles/ml,
- ρ_B bulk density, 0.65 ml/g,
- V_g pore volume, 0.115 ml/g,
- α fraction converted,
- D_K diffusion coefficient for a single pore, cm^2/sec .

The Knudsen diffusion coefficient, D_K , was evaluated from

$$D_K = \frac{2r\bar{c}}{3}, \quad (3)$$

where r , the mean pore radius, is 40 Å and \bar{c} is the average molecular velocity taken as 10^5 cm/sec. Figure 8 shows calculated values of the quantity f as a function of conversion for CO inlet concentrations of 50 to 50,000 ppm.

Figure 8 suggests that only a small fraction of the internal surface is effective for CO oxidation at the 50 ppm level except at very low conversions. Consequently, the points along the plateau of plots in Fig. 7 showing the lack of response of oxidation rate to variation in surface area at high conversions (measured at 50 or 70°C) by Co_3O_4 catalysts, unsintered or sintered at 300 or 400°C can be understood. At low conversions (measured at at 30°C), the oxidation rate shows a response to variation in surface area: the percentage converted doubled when the surface area increased from 20 to ~55 m^2/g . Although f is still small at 15–25% conversion, for a reactant concentration of 50 ppm its rate of change with α is nevertheless significant in this region. When the CO concentration was 10,000 ppm, much of the internal surface should be effective at high conversions and in Fig. 7 the oxidation rate shows a good response to surface area for all the Co_3O_4 catalysts used.

When the internal surface was largely eliminated by sintering at 600°C and, particularly, at 700°C, the CO oxidation reaction must be confined to the external surface region of the catalyst. The continued decrease in surface area (Table 3) can then only be at the expense of this external surface and correspondingly the rates of CO conversion must decline from "plateau" conversions. The external surface area is, of course, much larger than calculated from particle size and the SEM photographs confirm the existence of a highly textured surface. They also provide visual evidence that sintering to 700°C induces changes in the external surface.

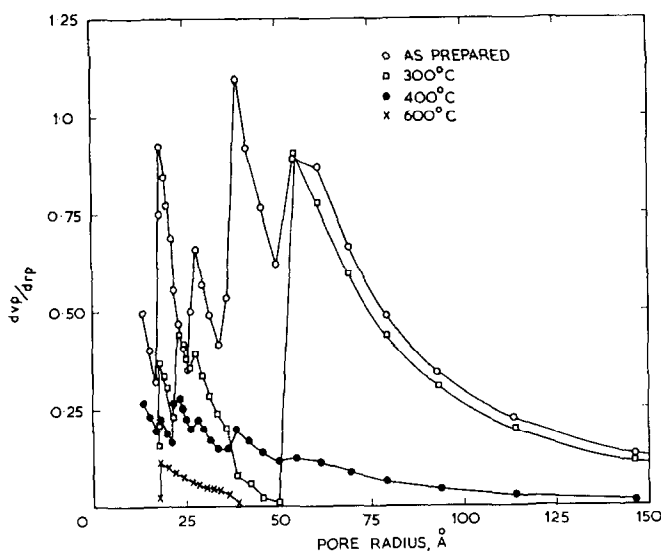


FIG. 5. Pore size distributions in Co_3O_4 catalysts prepared from oxalate or heated further for 24 hr at temperatures indicated. (Ordinate, see caption to Fig. 2.)

Pelleted Co_3O_4

The catalysts discussed above were in the form of fine powders, whereas for many practical purposes, pelleted forms of Co_3O_4 would be more useful. Pellets of cobalt oxide were prepared by compressing (commercial) basic cobaltous carbonate,

which was then decomposed to Co_3O_4 at 250°C in air for 24 hr. Such pellets exhibited good activity but lacked mechanical strength (although less weak than pellets of compressed Co_3O_4). Sintering these Co_3O_4 pellets (formed via the compressed carbonate) at 800°C in air for 24 hr (followed by further heating at 500°C in

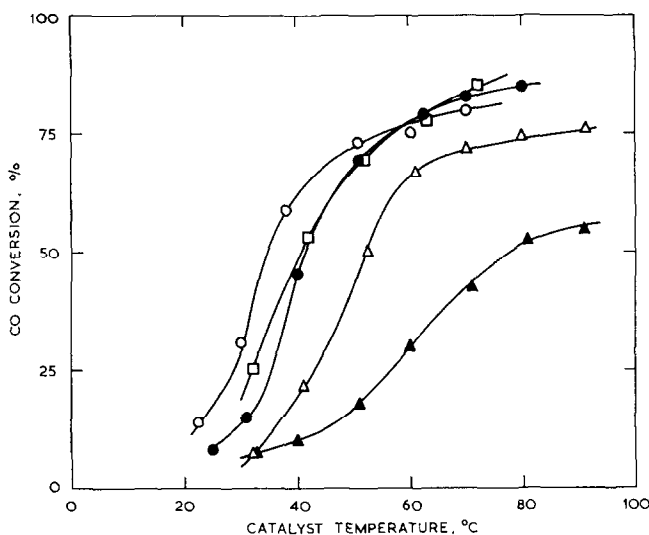


FIG. 6. Oxidation of 50 ppm CO in oxygen (space velocity $150,000 \text{ hr}^{-1}$) over Co_3O_4 catalysts prepared from oxalate: unsintered (O); and sintered for 24 hr at: 300°C (□); 400°C (●); 600°C (△); or 700°C (▲).

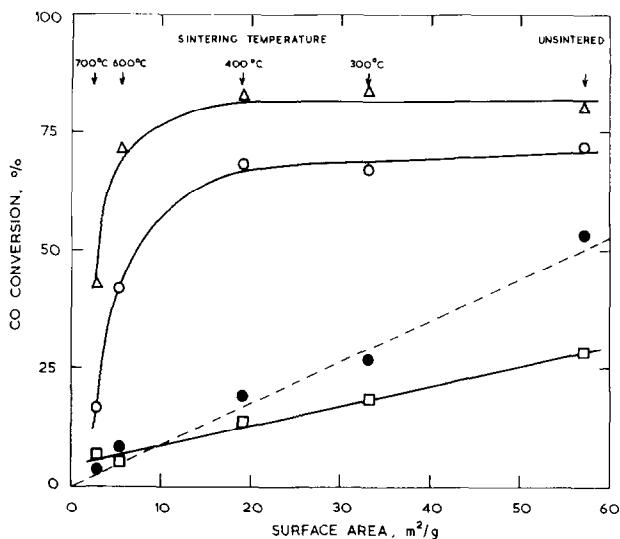


FIG. 7. Variation in the percentage CO converted at 30°C (\square); 50°C (\circ); and 70°C (Δ); (see also caption to Fig. 6) as a function of surface area using 50 ppm CO in oxygen, or at 90°C using 1% CO (\bullet).

air to ensure that traces of CoO were reoxidized) produced a marked increase in their strength. There was an associated decrease in surface area from 109 m²/g for unsintered pellets to 2.4 m²/g (sintered pellets).

Figure 7 indicates that CO oxidation rates fall sharply as the external surface

is decreased by severe heat treatment (800°C) and so the gain in pellet strength was achieved by sacrificing catalyst activity. As expected, a measurable rate of CO oxidation was only observed above ~180°C with a space velocity of 45,000 hr⁻¹, using 10 ml broken pellets, ~0.3 cm size, in a 2.5 cm diam reactor (Fig. 9).

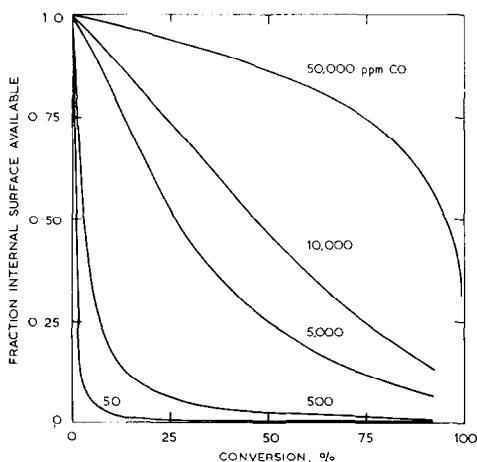


FIG. 8. Calculated values of "fraction of available surface," f , as a function of conversion for CO inlet concentrations indicated (see text for other parameters).

SUPPORTED Co_3O_4 CATALYSTS

Another approach to providing practical catalysts with an adequate surface area and activity is to deposit the active component (in this case Co_3O_4) on a preformed support.

Co_3O_4 -Silica

It was shown previously (12) that the surface area of Co_3O_4 deposited on various silica supports could be determined by selective CO chemisorption. Surface areas up to ~60 m²/g of Co_3O_4 were measured in catalysts prepared by nitrate impregnation of small silica granules followed by decomposition of the nitrate at 150°C. While this surface area compares favorably

with the area of sintered Co_3O_4 pellets ($2.4 \text{ m}^2/\text{g Co}_3\text{O}_4$), activity for CO oxidation when subsequently tested was poor despite the use of small silica granules.

Attempts were also made to prepare Co_3O_4 -silica catalysts by the adsorption method to achieve an even Co_3O_4 distribution because electron micrographs had shown (12) that impregnated catalysts contained clusters of Co_3O_4 crystallites which facilitated sintering. Neither hexammino cobaltic chloride nor chloropentammino cobaltic chloride was found after washing to have adsorbed on Davison grades 12 and 70 silicas to any appreciable extent ($<0.5\%$ Co). Following the adsorption of cobaltous oxalate (in ammonia solution) washing and drying, cobalt contents up to 6.6% (on Porasil "A") were observed but Co_3O_4 was not detected by X-ray diffraction when this catalyst was heated at 450°C in air, and even the characteristic black color was not developed.

Co_3O_4 -Alumina

Alumina spheres (Alcoa H151), 0.3 cm diameter, were impregnated directly with

cobaltous nitrate, oxalate or acetate by saturating them in the appropriate solutions. Additionally, cobalt carbonate was precipitated from cobaltous acetate solution inside the pore structure of the alumina support or freshly precipitated carbonate applied to its surface. The preparations were dried (60°C) and the cobalt salt decomposed to Co_3O_4 at 250°C (except the nitrate, decomposed at 150°C). Catalysts prepared from carbonate were superior to the other preparations, particularly the catalyst made by *in situ* precipitation (Fig. 9). The latter alumina-supported catalyst (which contained 6.7% Co_3O_4) oxidized 95% of the CO (50 ppm in oxygen) at $\sim 100^\circ\text{C}$ and a space velocity of $45,000 \text{ hr}^{-1}$ using 10 ml catalyst in a 2.5 cm diam. reactor. As recorded above, CO oxidation was just observable at $\sim 180^\circ\text{C}$ using sintered Co_3O_4 pellets (of the same size as the Al_2O_3 support) and at the same space velocity, $45,000 \text{ hr}^{-1}$. Thus the alumina-supported Co_3O_4 catalyst was significantly more active than the sintered pellets.

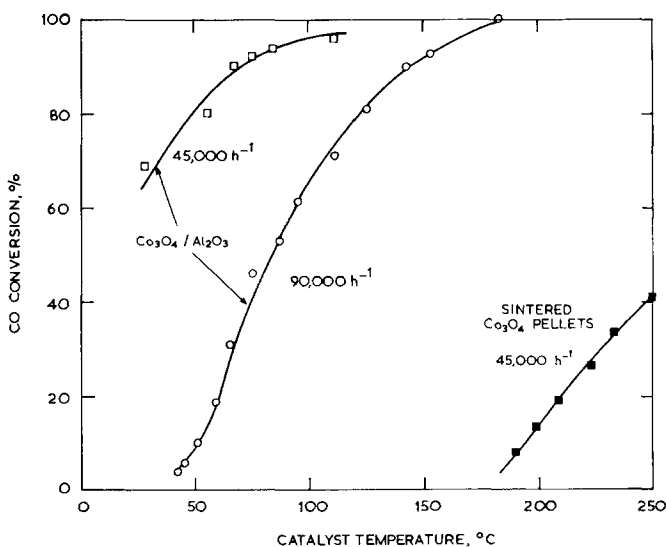


Fig. 9. Oxidation of CO (50 ppm in oxygen) at space velocities indicated using sintered Co_3O_4 pellets or Co_3O_4 supported on alumina spheres.

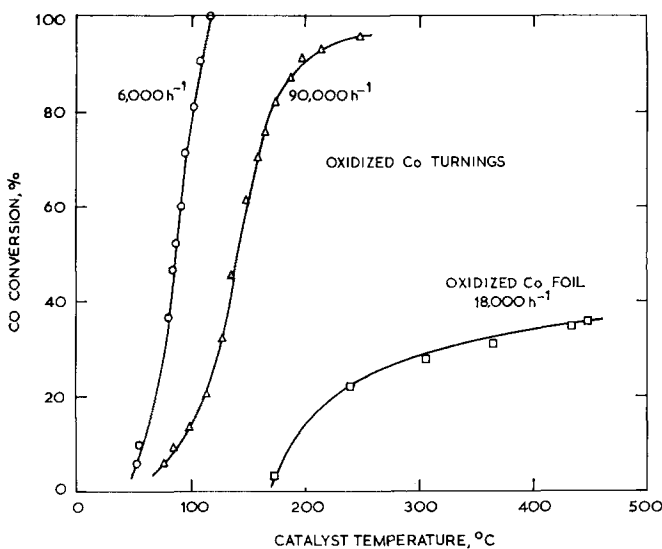


FIG. 10. Oxidation of CO (50 ppm in oxygen) at space velocities indicated using oxidized cobalt foil (\square), or oxidized cobalt turnings (\circ , \triangle).

OXIDIZED COBALT METAL

Catalysts prepared by forming a surface oxide layer on cobalt metal foil might be used advantageously in various configurations where it is necessary to reduce the resistance to gas flow offered by the catalyst charge. While cobalt metal is easily oxidized, the requirement of an adherent layer exposing Co_3O_4 to the gas phase is less easily met.

It was reported (13) that the scale formed in air or oxygen between 300 and 900°C consists of a thin layer of Co_3O_4 on the outside of a CoO layer next to the metal and that the scale is stable to cracking if formed below 600°C or above 750°C. Below 600°C, the thickness of the Co_3O_4 layer relative to total scale thickness is favorable but oxidation rates were found, in the present work, to be slow (1.4% weight gain after 140 hr at 500°C in dry oxygen). Therefore, the foil was oxidized at 1000°C (6.2% weight gain after 10 min), then maintained at 500°C for 16 hr and 300°C for 8 hr to assist the transformation of CoO to Co_3O_4 . The oxide layer produced was shown by X-ray diffraction to

have about equal amounts of CoO and Co_3O_4 .

Although the geometric area of the foil tested was only 40 cm², it exhibited modest activity for CO oxidation (Fig. 10) and suggested that similar catalysts with larger superficial areas might usefully be prepared. Hence turnings were cut from a cobalt rod and oxidized at 1000°C for 30 min and then at 490°C for 16 hr, yielding a catalyst with an area of 0.3 m²/g. The surface area per unit weight of the cobalt oxide layer itself, supported on the cobalt metal, would of course be larger. Figure 10 shows that such catalysts (10 ml charge in a 2.5 cm diam reactor) have an appreciable activity for oxidizing CO at low concentration.

CONCLUSIONS

Various forms of cobalt oxide (Co_3O_4) are very active catalysts for the oxidation of trace amounts of carbon monoxide at near ambient temperatures and high space velocities. If required, Co_3O_4 catalysts with large surface areas can be prepared by avoiding the high decomposition temperatures often employed to decompose the precursor compound. Cobalt oxide cata-

lysts prepared from some carbonate or hydroxide precursors had surface areas of 150 m²/g or more. The provision of practical Co₃O₄ catalysts may require a compromise between improving pellet strength, gas access, sinter-resistance, etc., at the expense of surface area and activity. In this connection, very active catalysts were obtained from some Co₃O₄ preparations on alumina supports (although use at too high temperature is known to lead to interaction between Co₃O₄ and this support). Novel forms of Co₃O₄ catalyst are obtained by oxidizing cobalt metal surfaces.

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