

On the Poisoning of Co_3O_4 Catalysts by Alumina and Magnesia

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Alumina-doped and magnesia-doped cobaltous-cobaltic oxide, Co_3O_4 , samples of about 8 and 9 cationic percent dopant concentrations, respectively, were prepared and tested for catalytic activity relative to that of the pure cobalt oxide. They were also analyzed by ion scattering spectrometry (ISS), to look for possible surface enrichment of the dopant. The specific catalytic activity of the Al_2O_3 -doped Co_3O_4 was found to be depressed by a factor of about 4-5, while the MgO -doped Co_3O_4 was poisoned by a factor of about 8. The ISS spectra clearly indicate that the alumina-doped sample has a surface which is highly enriched in aluminum concentration, relative to the bulk. The ISS results for the Mg -doped sample are difficult to interpret, but at least show that the outermost surface layers are impoverished in cobalt, hence they are probably enriched in magnesium.

These experiments were designed to partially test a hypothesis of "poisoning by substrate dissolution," to account for the fact that Al_2O_3 -supported Co_3O_4 has a peculiarly low catalytic activity for the oxidation of CO and hydrocarbons compared to pure Co_3O_4 . Similar, though somewhat less striking results are obtained for MgAl_2O_4 -supported Co_3O_4 . Such supported catalysts are generally made by impregnation with aqueous cobalt nitrate, followed by calcination to about 500-600°C. There is evidence that this temperature is insufficient to produce profound bulk interdiffusion between catalyst and support in the solid state, and that there is a Co_3O_4 phase left. It was therefore theorized that the decomposing cobalt nitrate, a hot, acidic liquid, might dissolve some of the substrate, thus yielding substrate-doped Co_3O_4 similar to the doped samples described above. Our results appear to fall short of explaining the peculiarly low activity of Al_2O_3 -supported Co_3O_4 , but are large enough to possibly explain the performance of the MgAl_2O_4 -supported catalyst.

INTRODUCTION

It has been known for a long time that Co_3O_4 is one of the best base metal catalysts for the total oxidation of hydrocarbons and carbon monoxide (1,2). It is, however, a very sensitive catalyst, easily poisoned by substances such as SO_2 , Na , Cl , Mg and Al . The first of these is probably most serious from the point of view of application to automotive emissions. This paper is concerned with Al and Mg poisoning.

It has generally been found (1-3) that there is a great loss of catalytic activity when cobalt oxide is produced on a high area alumina substrate, relative to the activity of the pure, unsupported catalyst,

even though the latter has a much lower surface area. Comparing mechanically blended $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ with samples of similar composition produced by impregnation with cobalt nitrate, both having been heated to 600°C, Yao (3) found the former to be about two orders of magnitude more active than the latter. Such samples did not change from black to the characteristic blue color of $\text{CoO-Al}_2\text{O}_3$ solid solutions until temperatures in the vicinity of 900°C were reached. This suggests that appreciable solid state interdiffusion had not taken place in the 600°C calcined samples, and thus cannot explain the deactivation. This view is supported by the magnetic measurements of Tomlinson

et al. (4), who deduced the presence of a phase magnetically similar to bulk Co_3O_4 in cobalt-nitrate-impregnated γ -alumina samples calcined to 500°C .

One of us (5) has had somewhat similar experiences with a series of MgAl_2O_4 -supported cobalt oxide catalysts. The support generally had about $70\text{--}80\text{ m}^2/\text{g}$ specific surface area and the catalysts had concentrations in the range of $6\text{--}28\text{ wt}\%$. They were similarly prepared, by impregnation of the support with cobalt nitrate solutions, drying at room temperature, and calcining to 600°C . Per square meter of total BET area, these samples were about 100 times less active than pure Co_3O_4 . It seems unlikely that there was any appreciable interdiffusion between Co_3O_4 and MgAl_2O_4 at 600°C .

We propose the following hypothesis. During the calcination of cobalt nitrate impregnated samples, the decomposing nitrate, a hot, acidic liquid, dissolves some of the substrate. The resulting Co_3O_4 particles will then be doped with Al_2O_3 and/or MgO . It is further conceivable that the surface of the particles might be enriched in the dopant, relative to its volume concentration, according to an equilibrium distribution coefficient, resulting in a high degree of poisoning. Solid state mixing is not believed to occur until temperatures considerably higher than the preparation temperature of 600°C are reached.

This hypothesis is supported by the following additional observation of Yao (3). If, after impregnation with cobalt nitrate, the samples were treated with ammonia vapor, prior to drying and calcination to 600°C , then the resulting catalysts had nearly as much activity as the mechanical mixtures. We interpret this to mean that the cobalt nitrate was converted to a hydroxide by the ammonia, and subsequently calcined without melting, hence, without dissolving any substrate.

In order to test one aspect of the above hypothesis, MgO - and Al_2O_3 -doped

Co_3O_4 , in the $8\text{--}9\text{ mol}\%$ range, were prepared, tested for catalytic activity, relative to that of pure Co_3O_4 , and the surfaces were examined by ion scattering spectrometry (ISS) to determine the surface-to-volume concentration ratio of the dopant.

EXPERIMENTAL METHODS

An alumina-doped sample of Co_3O_4 , containing 8.3 cationic percent Al, was prepared by mixing analyzed nitrate solutions, slowly evaporating to dryness, and heating in air for 16 hr at 800°C . Its BET area was $1.8\text{ m}^2/\text{g}$. A Mg-doped sample, containing 9.3 cationic percent Mg, was prepared in the same manner and had a BET area of $1.05\text{ m}^2/\text{g}$. Particles in the $0.5\text{--}1\text{ mm}$ range were used for the catalytic activity tests. The reactor was a U-shaped silica tube in a vertical tube furnace. The downflow section of the U acted as a preheater for the gas mixture. The catalyst was loosely packed into the 3 mm i.d. upward flow section. Inlet and outlet gases were analyzed on a continuous sampling mass spectrometer. The samples for the ion scattering spectrometer (ISS), 3M Company Model No. 520, consisted of 8 mm diameter pressed discs. These samples were first ground in an agate mortar and pestle, then wet with a small quantity of concentrated cobalt nitrate solution, dried at 125°C , pressed in a steel die at about 30,000 psi, and reheated in air at 600°C for 2 hr. The purpose of the cobalt nitrate salt was to provide some cohesion to the pellets. The salt was unquestionably decomposed to the oxide during the subsequent heat treatment.

RESULTS AND DISCUSSION

The catalytic activities for the oxidation of ethylene, of doped Co_3O_4 , compared to those of pure Co_3O_4 , are summarized in Table 1 for two temperatures, 260 and 300°C . Precision measurements at these temperatures are difficult due to a very slow decay of activity, believed to be due

TABLE 1
SPECIFIC REACTION RATES^a

Sample	260°C	300°C
Co ₃ O ₄	0.66 ^b	2.17
Co ₃ O ₄ (5.4 w/o Al ₂ O ₃)	0.155	0.45
Co ₃ O ₄ (4.9 w/o MgO)	0.106	0.286

^a (ml CO₂/min m²); inlet gas concentration was 0.2% C₂H₄, 1.2% O₂, balance He. Data were taken about 8 min after temperature was reached; i.e., after the first, fast decay due to product poisoning had taken place.

^b Average of four experiments.

to product poisoning, i.e., the slow formation of "surface carbonates" (6,7). When higher temperatures are chosen, this difficulty tends to disappear, but other problems, associated with pore diffusion

limitations, then tend to appear. Roughly speaking, the alumina-doped sample is poisoned by a factor of about 4–5, and the magnesia-doped sample by a factor of about 6–8, relative to pure Co₃O₄. This is enough to explain the performance of MgAl₂O₄-supported cobalt oxide, according to our hypothesis, but is too weak an effect to completely explain the unusually low activity of alumina-supported cobalt oxide, prepared by impregnation with cobalt nitrate. It can, however, be an important contributory effect.

X-Ray diffraction showed the presence of an appreciable quantity of a cubic second phase in the Mg-doped sample. This was probably a solid solution of the type Mg_xCo_(1-x)O, with a NaCl type structure,

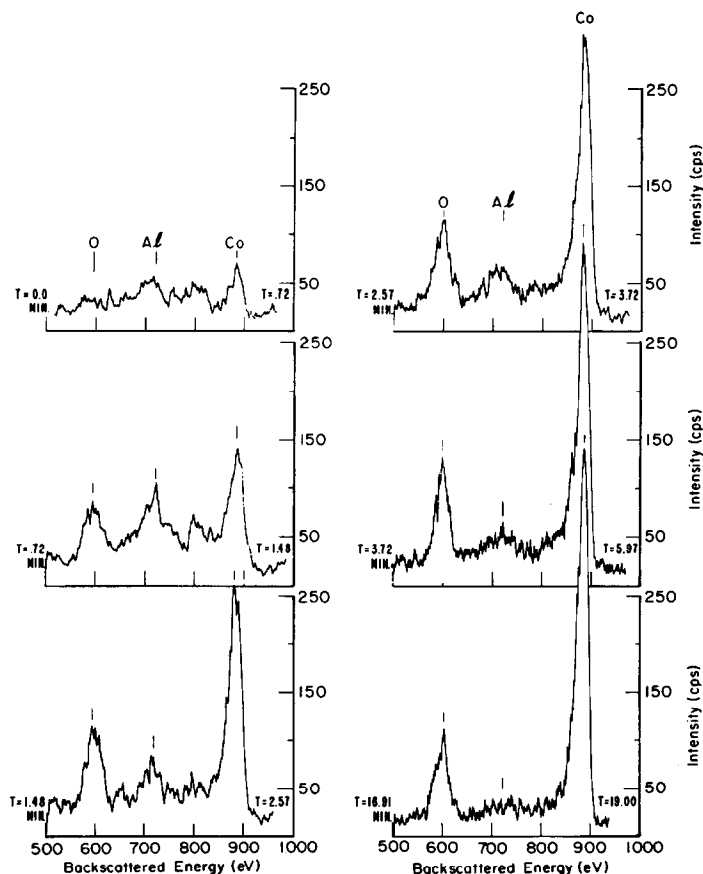


FIG. 1. Series of ISS spectra showing original surface enrichment with aluminum in Al₂O₃-doped Co₃O₄. After approximately 15 min the aluminum peak is no longer detectable.

according to Robins (8) who could detect no solubility of magnesium in the Co_3O_4 spinel phase. The Al-doped sample, on the other hand, showed only a spinel phase. The magnetic measurements of Richardson and Vernon (9) on coprecipitated samples suggest complete miscibility of Al_2O_3 and Co_3O_4 . Thus the Al-doped sample may well have been single phase.

The ISS spectra of Fig. 1 show that there is a greatly enriched concentration of aluminum on the surface of the alumina-doped sample. The ISS (10) is an instrument whose spectrum is sensitive to the outermost atomic layer. The spectra of Fig. 1 were taken using ^4He probe ions at 1000 eV. Scan times of less than 1 min were used for the initial spectra. With increasing time, the helium ion beam gradually erodes the surface by sputtering. This phenomenon allows the examination of the composition of the surface at various depths. The first trace shows a poorly defined spectrum due to adsorbed water and hydrocarbons. This is a common phenome-

non (11). Subsequent traces show oxygen, aluminum, and cobalt peaks. The aluminum peak gradually becomes weaker, until it is no longer detectable, presumably because the steady state concentration is below the sensitivity of the instrument. It follows that the initial surface concentration of aluminum must have been large compared to 8 cation percent. A further estimate is derived from the fact that in pure Al_2O_3 the ISS aluminum:oxygen sensitivity ratio is about 2, for 1000 eV helium 4 ions. Assuming a similar sensitivity ratio in the present case, and comparing the oxygen and aluminum peaks of the second trace in Fig. 1, it would seem that the initial aluminum concentration must have been over 50%. We cannot interpret the results any more quantitatively.

Figure 2 shows typical ISS spectra for the magnesia-doped cobalt oxide sample. Many such traces were taken which confirm reproducibility. After the surfaces of the pellets were used up by sputtering in the ISS apparatus, it was possible to re-

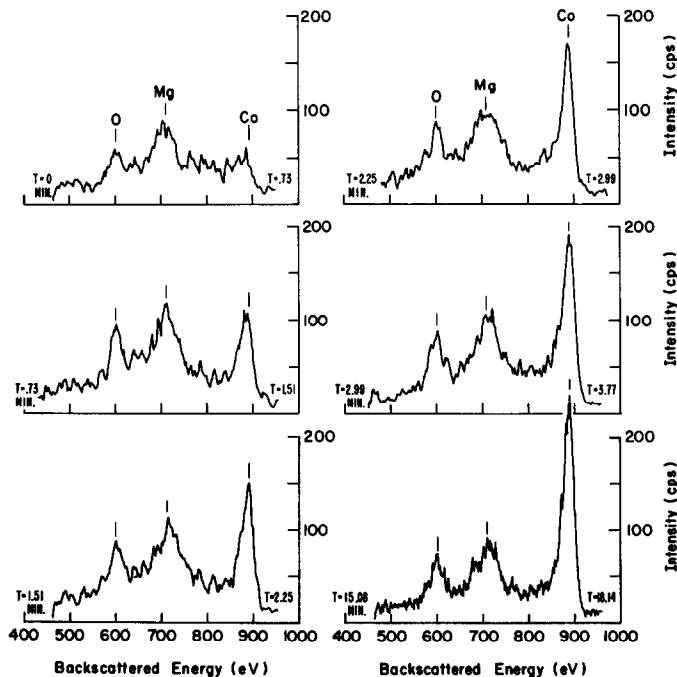


FIG. 2. Series of ISS spectra from MgO -doped Co_3O_4 .

constitute the original surface by reheating the sample at 600°C for a few hours and then obtain a very similar set of ISS traces. (The reconstitution is interpreted as resulting from an equilibrium between the differently composed surface layer and the bulk phases. The layer is thus expected to reestablish itself at a temperature where some diffusion can take place.) The traces of Fig. 2 are substantially different from those of Fig. 1, and more difficult to interpret. The magnesium peak stays virtually constant throughout the experiment. The cobalt peak, on the other hand, rises substantially with time, as in Fig. 1. The following explanation is tentatively suggested: (a) Magnesia is nearly insoluble in Co_3O_4 , hence most of it exists as a separate phase, as already mentioned above. (b) The ISS spectrum is unusually sensitive to Mg in this form. (c) The cobalt oxide phase is initially covered with a thin layer of magnesia (an assumption necessary to explain the catalytic data), but the ISS sensitivity for Mg in this layer is unusually low. ISS spectra have been found to exhibit profound variations in sensitivity occasionally.

A secondary ion mass spectrometer (SIMS) was also used to examine the Mg-doped Co_3O_4 pellet. This is a quadrupole mass analyzer which looks at those sputtered species which come off the surface in ionized form. Figure 3 contains a set of SIMS traces of a Mg-doped Co_3O_4 pellet. These data were reproduced several times. They are qualitatively similar to the ISS traces, in that the Mg signal stays approximately constant, while the Co signal rises with time. There is one quantitative difference, however, which seemed rather shocking. The SIMS traces reached a steady state in about 2 min, while the ISS traces take about 10–13 min. The following is a tentative explanation. Both modes of analysis represent an average of results from many microscopic surfaces, differing

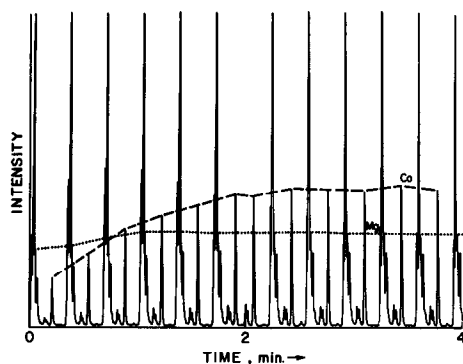


FIG. 3. Series of SIMS spectra from MgO-doped Co_3O_4 . A multiplex system was used which allowed rapid repetition of the cobalt and magnesium portions of the mass spectra. The ^{59}Co peaks are joined by (—), while ^{25}Mg are joined by (· · · ·) to show their change in intensity with time.

in crystallographic orientation, and in geometrical orientation, relative to the incident beam and to the analyzer. If we can assume that the sputtering rates for these different surfaces varies widely, then it follows that the SIMS spectrum, being a spectrum of sputtered ions, will be dominated by those surfaces which sputter fastest.

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