

Interaction of Ozone with Nickel Ions Adsorbed on Alumina

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Received February 7, 1974; revised December 13, 1976

Nickel ions adsorbed on alumina react strongly with surface oxygen species. Electron donation from the alumina facilitates oxidation of the nickel by ozone, producing an active oxide which is brown at low concentrations and black at high concentrations. The variation in color is attributed to a particle size effect.

At very high concentrations, the interaction of nickel ions with alumina is reduced because the nickel compound used for impregnation crystallizes at the surface. Exposure of these samples to ozone does not produce the active oxide.

INTRODUCTION

The extensive use of alumina as a catalyst and catalyst support has prompted many investigations of its surface structure and properties. Several workers have shown that the surface is heterogeneous for adsorption and catalysis (1-4). The model proposed by Peri (1) gives an insight into the nature of the various sites at the surface. Transition metal ions adsorbed on alumina may interact specifically with certain groups of these sites. The behavior of the supported metal ion will, therefore, be influenced by the heterogeneity of the alumina surface, and consequently may lead to variations in catalytic activity of the supported metal, as has been noted for nickel on various supports (5).

We report here a selective reaction of ozone with nickel ions adsorbed on alumina. There is scant modern information on the reaction of ozone with inorganic compounds. Solutions of cobalt ion give a precipitate of cobalt hydroxide on treatment with ozone (6). The ozonides of the alkali (7, 8) and alkaline earth (9) metals have been reported. These compounds, containing the O_3^- ion, are colored red to

brown, and tend to be unstable at room temperature. In general, however, the action of ozone is to raise the oxidation state of the metal. The chemistry of the nickel-oxygen-water system is very complex. A number of oxide-hydroxides of Ni(III) and Ni(IV) are known, and can exist in various modifications (10), e.g., α , β , or γ -NiO(OH), $Ni_3O_2(OH)_4$. A nickel compound containing "active" oxygen, formed by reaction of sodium hypochlorite on nickel solutions, is frequently used as an oxidizing agent in organic synthesis (11).

EXPERIMENTAL METHODS

Nickel-aluminas of various concentrations were prepared by impregnation of alumina with a solution of nickel sulfate. The mixture was boiled for 5 min and then the nickel-alumina was washed once to remove excess nickel sulfate, and dried at 100°C. To form the product, samples were exposed to a stream of ozone-oxygen, produced by electrical discharge. After a certain time, which varied with the concentration of nickel on the alumina, a black compound was generally formed. At low concentrations however, the compound

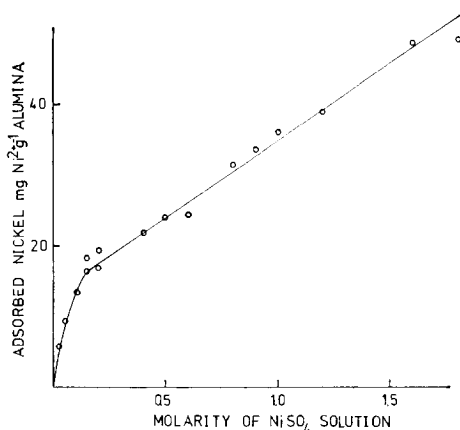


FIG. 1. Partition curve of nickel sulfate between the solution and the chromatography alumina

was brown. The compounds could be decomposed by heating or by reaction with hydrogen peroxide (see below).

The nickel content of the nickel-aluminas before ozone treatment was determined by flushing the nickel off the alumina with dilute acid, and measuring the nickel concentration by atomic absorption spectroscopy.

BET areas of the samples were obtained with a Perkin-Elmer Sorptometer.

The materials were (i) chromatography grade alumina (May and Baker), BET area $190 \text{ m}^2 \text{ g}^{-1}$; (ii) γ -alumina (12) containing very little sodium, activated at 600°C , BET area $180 \text{ m}^2 \text{ g}^{-1}$; and (iii) S. L. R. grade nickel sulfate (Fisons).

RESULTS

Chromatography Alumina as Support

Figure 1 shows the variation in amount of nickel ion adsorbed on the chromatography alumina as the concentration of the nickel sulfate solution is increased. The curve can be divided into two distinct regions. The partition ratio of adsorbed Ni^{2+} to aqueous Ni^{2+} , which is initially high, decreases by a factor of six at approximately $13\text{--}15 \text{ mg Ni}^{2+} \text{ g}^{-1}$ alumina. A limited amount of nickel ion can therefore interact strongly with the surface. The nickel ions could not be flushed off the

alumina by washing, but were displaced by dilute acid.

Stability of Active Oxide

The time required to produce the active oxide, on passage of ozone over the sample, depended on the amount of moisture in the sample, the partial pressure of ozone, and the adsorbed Ni^{2+} content. Samples dried for 24 hr or longer gave reproducible results. The ozone partial pressure was not readily controllable. The various samples were therefore placed in a number of small boats, in a tube, and exposed to the ozone simultaneously. As the intensity of blackness increased over an appreciable time, the "end-point" was imprecise, and the observation was to a large extent subjective. The ozone treatment times are therefore only semiquantitative. However, the general features, which are shown in Fig. 2, are reproducible. For adsorbed Ni^{2+} contents of $<15 \text{ mg g}^{-1}$, the reaction was fast; above this concentration the reaction was slower, and above 40 mg g^{-1} the rate of reaction decreased very rapidly. Nickel sulfate itself, in the anhydrous or hydrated form, showed no change on exposure to ozone for long times (overnight). The "break" at $15 \text{ mg Ni}^{2+} \text{ g}^{-1}$ alumina in the formation time curve (Fig. 2) corresponds to the concentration of adsorbed Ni^{2+} at which the partition ratio alters markedly in Fig. 1. Therefore, the greater the proportion of strongly bound Ni^{2+} , the shorter the reaction time, and at high concentrations of adsorbed Ni^{2+} ($44 \text{ mg g}^{-1} \equiv 2.4 \times 10^{14} \text{ Ni}^{2+} \text{ cm}^{-2}$) when the alumina surface must be almost completely covered with nickel sulfate, the active oxide is only produced with difficulty, if at all.

At concentrations $<6 \text{ mg Ni}^{2+} \text{ g}^{-1}$ alumina ($\equiv 0.05 \text{ M}$ impregnating solution) the active oxide was brown. Both brown and black active oxides decomposed to a white material on heating. The times taken for the active oxides to change color at a fixed temperature, 70°C , are shown in Fig. 2.

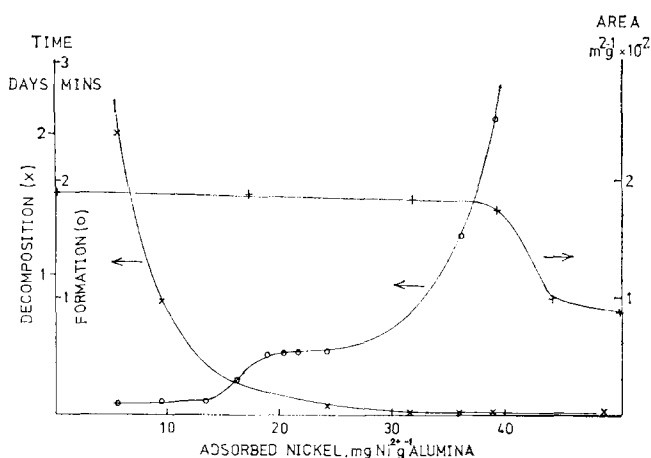


FIG. 2. Formation time and decomposition time of supported active oxides, and area of corresponding samples, as a function of the amount of nickel ion adsorbed on chromatography alumina.

Above $\sim 15 \text{ mg Ni}^{2+} \text{ g}^{-1}$ alumina, the stability of the active oxide decreases considerably. Therefore, the ease of formation is related to the stability. The decomposed active oxide could be regenerated with more ozone.

The BET areas of the nickel-aluminas are shown in Fig. 2. The specific area decreases sharply at concentrations $> 40 \text{ mg g}^{-1}$. This suggests that the pores in the alumina are being blocked by nickel sulfate and the alumina surface is probably saturated. The concentration at which the area starts to decrease corresponds with that at which the active oxide becomes very difficult to produce (Fig. 2).

Active Oxygen Content

The active oxides could be decomposed to the green nickel-alumina by treatment with hydrogen peroxide. The amount of active oxygen was estimated by reacting samples with excess hydrogen peroxide and back titrating an aliquot of the supernatant liquid with permanganate. Alumina itself adsorbs ozone which reacts with peroxide. The samples were therefore left overnight after ozone treatment to allow as much excess ozone as possible to decompose.

Blank runs with alumina alone showed that the adsorbed ozone accounted for no more than 10–15% of the maximum titer found. Figure 3 shows the amount of hydrogen peroxide required to decompose the active oxide plotted against the amount of adsorbed Ni^{2+} . The results are sufficiently reproducible to show that two maxima are obtained, one at $\sim 15 \text{ mg Ni}^{2+} \text{ g}^{-1}$, which coincides with the region at which the partition ratio, formation time and decomposition time show marked changes (Figs. 1 and 2), and one at $\sim 32 \text{ mg Ni}^{2+} \text{ g}^{-1}$.

γ -Alumina as Support

The nickel/ γ -alumina behaved similarly to the nickel/chromatography alumina, forming both brown and black active oxides on treatment with ozone. The brown oxide was only evident on γ -alumina impregnated with very low concentration nickel solutions, $< 0.005 \text{ M}$.

Figure 4 shows the active oxygen content of γ -alumina samples impregnated with various nickel solutions and treated with ozone. The amount of active oxide decreases at high nickel concentrations similarly to the results for the chromatography alumina. However, in contrast, there is

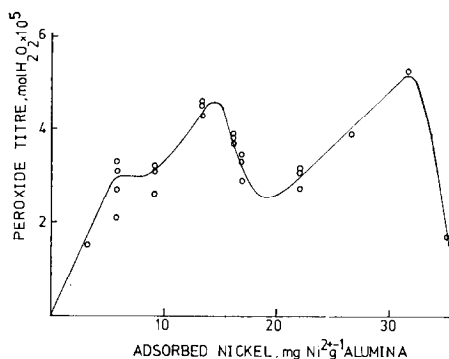


FIG. 3. Amount of hydrogen peroxide required to decompose the active oxide as a function of the amount of nickel ion adsorbed on chromatography alumina.

little variation in active oxide content with nickel concentration for samples prepared from solutions $\leq 0.2 M$.

Though the nickel salts which may be used for impregnation, e.g., sulfate, nitrate, chloride, do not react themselves to produce the active oxide, we found that the above reactions could be simulated with a gel of nickel hydroxide. When ozone was passed through the gel, a black compound was formed which reverted to nickel hydroxide on treatment with hydrogen peroxide. Quantitative experiments showed that 1 mole of H_2O_2 reacts with 2 g atom of nickel ion.

DISCUSSION

It has been known for over 100 years that nickel salts in alkaline solution are readily oxidized (13). The active oxide (11) used now in organic preparations is generally produced from nickel solutions and sodium hypochlorite. As shown above, ozone and nickel hydroxide gel also react to give a black active oxide. This suggests that the action of alumina in the nickel-alumina-ozone reaction is similar to that of the base in the above examples. Adsorbed base (Na) is not necessary, however, as the sodium free γ -alumina gave the active oxide on treatment with nickel solutions and then ozone.

The electron donor properties of γ -alumina have been investigated by Flockhart *et al.* (14). They showed by ESR that adsorbed TCNE forms radical anions of maximum concentration approximately 10^{12} cm^{-2} . The active oxygen atom concentration of our nickel/ γ -alumina is $6 \times 10^{12} \text{ cm}^{-2}$. The surface composition of our alumina will differ from that of Flockhart *et al.*, as after the preliminary activation at 600°C , the alumina was treated with aqueous nickel solution and then reactivated at 100°C . A high concentration of surface hydroxyls will therefore be present.

Figure 1 shows the partition curve of nickel on the chromatography alumina, and a similar curve for γ -alumina has been reported (15). The above results for the formation and decomposition times of the active oxide show a relationship between the stability of the active oxide and the relative amount of strongly adsorbed nickel ion. Studies of cobalt ions adsorbed on silica (16) suggest that strongly adsorbed transition metal ions incorporate the surface hydroxyls, as possibly O^{2-} ions, in their coordination sphere. The nickel/alumina surface complex is therefore similar to aqueous nickel hydroxide gel in having basic groups in close proximity to the metal ion. The high-valent nickel formed by treatment with an oxidizing agent is therefore stabilized by electron donation from surface oxygen species.

The reactivity curves for both nickel aluminas (Figs. 3 and 4) can be divided

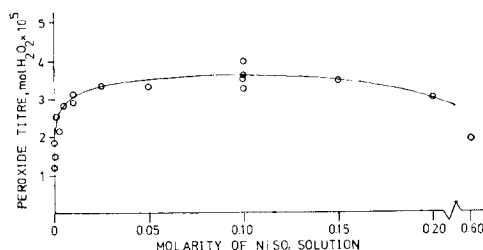


FIG. 4. Amount of hydrogen peroxide required to decompose the active oxide on γ -alumina as a function of the concentration of impregnating solution.

into three regions: (a) high concentrations where the reactivity falls, (b) medium concentrations with a high reactivity where the active oxide is black, and (c) low concentrations where the active oxide is brown.

a. At high concentrations of nickel sulfate solution, the parent compound is retained at the surface and eventually blocks the pores of the adsorbent. The area of the adsorbent therefore decreases at this stage (Fig. 2). Nickel sulfate itself does not react with ozone and so the activity curves fall.

b. The stoichiometry of the reaction of peroxide with the surface active oxide may be inferred from data for the bulk compounds. A typical bulk active oxide (11) contains 1 g atom oxygen/2.7 g atom nickel. The nickel hydroxide gel-ozone material contained 1 g atom oxygen/2 g atom nickel. The ratio of adsorbed nickel ion to active oxygen atoms for the chromatography alumina are 3.2:1, 5.6:1, and 10.1:1, at concentrations of 5.75, 15, and 31.5 mg nickel g⁻¹ alumina, respectively. Therefore, not all of the adsorbed nickel is reactive and the fraction reactive decreases with concentration.

The reactivity curve (Fig. 3) for the chromatography alumina is complex, possibly because of the effects from sorbed sodium ions.

The nickel/ γ -alumina, in the medium concentration region (Fig. 4) gives an approximately constant active oxygen concentration as the adsorbed nickel concentration is increased. The plateau active oxygen atom concentration is 6×10^{12} cm⁻², which will be related to the electron donor concentration. The stoichiometry of the nickel ion-base interaction is, however, unknown.

c. At low concentrations of impregnating solution (<0.05 M for chromatography alumina and <0.005 M for γ -alumina) the active oxide produced is brown. Though there is an order of magnitude difference in concentration of impregnating solution between the two aluminas, the adsorbed

nickel concentrations will differ less because of the greater affinity of γ -alumina for nickel ions [cf. partition curves, Fig. 1 and in Ref. (15)].

The color of the bulk active oxide depends on the method of preparation. A red solution (17) is formed by passing ozone through a nickel solution containing bicarbonate at 0°C. Cooling keeps the nickel in solution. The red color which develops when ozone is then added is ascribed to a colloidal form of the active oxide. The brown color of the active oxide formed on alumina at low nickel concentrations therefore probably results from a particle size effect, i.e., at high dispersion of adsorbed nickel ions, small particles are obtained. The supported brown oxide is stable at room temperature indefinitely, unlike the colloidal solution.

The interaction of ozone with nickel ions adsorbed on alumina may therefore be interpreted in terms of the basic properties of the alumina and the dispersion of the nickel ion.

ACKNOWLEDGMENT

J. K. G. thanks the Science Research Council for support.

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