Reduction of Nitric Oxide with Ammonia on Iron Oxide–Titanium Oxide Catalyst

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The reduction of NO with NH_3 on iron oxide–titanium oxide was studied by using a flow reactor between 250 and 450 °C. It was found that NO reacts with NH_3 at a 1:1 mole ratio in the presence of excess O_2 and the reaction is completely inhibited by the absence of O_2. The formation of N_2O, if any, was negligible in all experiments. The experimental data show that the NO–NH_3 reaction in the presence of O_2 is represented by NO + NH_3 + $^1/_4O_2$ = N_2 + $^3/_2H_2O$.

Introduction

It is of practical importance to remove nitrogen oxides (NO_x) in a flue gas from the viewpoint of air pollution control. It has been known that NO_x is selectively reduced by ammonia in the presence of a large excess of oxygen.[1] Several catalysts, for example, V, Mo, and W oxides,[2] platinum metals,[3] CuO,[4] Fe–Cr oxides,[5] Cr_2O_3–Al_2O_3,[6] and zeolite[7] have been known to enhance the NO_x–NH_3 reaction. These catalysts are of limited use in a practical plant, since they are poisoned by SO_x (especially SO_3) which is usually present in an oil- or coal-fired boiler flue gas.[8] We have developed a series of titania-based catalysts which are resistant to the SO_x poisoning. The titania-based catalysts were tested in several pilot plants and found to possess high activity and durability.

Otto et al. proposed a mechanism for the reduction of NO with NH_3 in the absence of O_2 on Pt catalyst[9,10] and CuO catalyst[11] using an isotope-labeling method. The enhancement of the NO–NH_3 reaction by O_2 was observed by Bauerle and Ken Nobe et al.[12-14] and Markvart and Pour.[15] From IR studies Tamaru et al.[16] suggested that the reaction proceeds through the coupling of NO_2-like species with adsorbate NH_4^+ on V_2O_5 catalyst in the presence of O_2. On the other hand, Miyamoto et al.[17] have proposed that the reaction between NO and NH_3 is a reaction between NH_4^+ adsorbed adjacent to $V^{5+}{=}O$ species and a gaseous NO through the Eley–Rideal mechanism.

In view of previous studies, the reaction mechanism between NO and NH_3 has not yet been clarified. In addition the reaction between NO and NH_3 on a titania-based catalyst has not yet been reported. In this paper the reduction of NO with NH_3 on iron oxide–titanium oxide catalyst is presented.

Experimental Section

Catalyst Preparation. The iron oxide–titanium oxide catalyst which contained Fe and Ti at a 1:9 atomic ratio was prepared as follows. Metatitanic acid ($TiO(OH)_2 \cdot nH_2O$) and ferric sulfate were mixed and kneaded thoroughly, dried at 120 °C for 5 h, and calcined at 500 °C for 4 h in air. Then, the calcined powder was molded into a tablet of 6-mm diameter and 6-mm height by a pelletizing machine. Subsequently, the pellets were crushed, a portion of 10–20 mesh being used in the experiments.

Reaction. The reaction of NO with NH_3 was carried out in a conventional flow-type apparatus, illustrated in Figure 1. A vertical 16-mm i.d. quartz tube reactor was heated to 250–450 °C with an electrical furnace. The reactor contained a catalyst bed of 4–8 mL. A gas was passed through the catalyst bed at a rate of 240 mL/h, producing a space velocity of 30 000–60 000 h^{-1}(NTP). A typical test gas contained 300 ppm NO, 360 ppm NH_3, 3% O_2, and the remainder N_2. In several experiments SO_2, CO_2, and H_2O were added to the gas mixture. Water was introduced into the reactor by a pump. The test gas was prepared by mixing gases from cylinders (pure grade) without further purification. The concentration of NO_x was measured by a chemiluminescence analyzer. The concentration of NH_3 was determined by Nessler's method after absorption with boric acid solution.

Results and Discussion

Catalytic Activity in NO–NH_3 Reaction. Catalytic activity of the iron oxide–titanium oxide catalyst in the NO–NH_3 reaction was examined. In Figure 2 the activity, NO conversion, vs. temperature is shown. It is seen that the catalyst possesses high activity over a temperature range of 350–450 °C. When one considers the high space velocity (60 000 h^{-1}) and the low NH_3/NO mole ratio (1.2) employed in the present experiment, the catalyst is extraordinarily active and selective.

Catalytic Activity in NH_3–O_2 Reaction. The catalyst was found to possess activity for the decomposition of NH_3. Therefore the catalytic activity in the NH_3–O_2 reaction was examined. In Figure 3 NH_3 conversion vs. temperature is shown. It is seen that substantial NH_3 decomposition occurred above 300 °C. The main reaction is represented by eq 1. The formation of NO was negligible over a temperature range of 265–425 °C. The yield of NO was

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \qquad (1)$$

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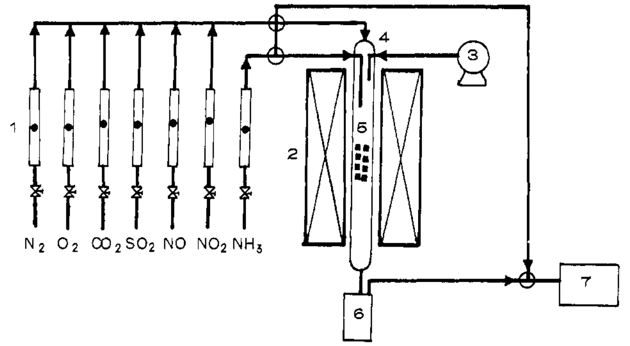

Figure 1. Schematic diagram of experimental apparatus: (1) flow meter, (2) electric furnace, (3) water pump, (4) reactor, (5) catalyst, (6) ammonia trap, (7) NO_x analyzer.

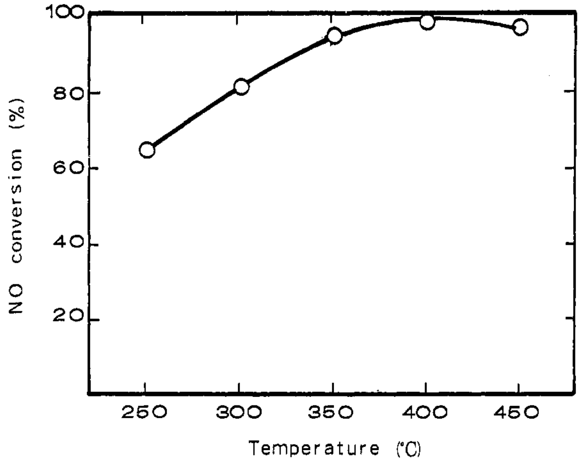

Figure 2. Catalytic activity of Fe_2O_3-TiO_2 catalyst in NO-NH_3 reaction. Gas composition: NO, 200 ppm; NH_3, 240 ppm; SO_2, 500 ppm; O_2, 3%; CO_2, 12%; H_2O, 12%; N_2, balance. Space velocity: 60 000 h^{-1}.

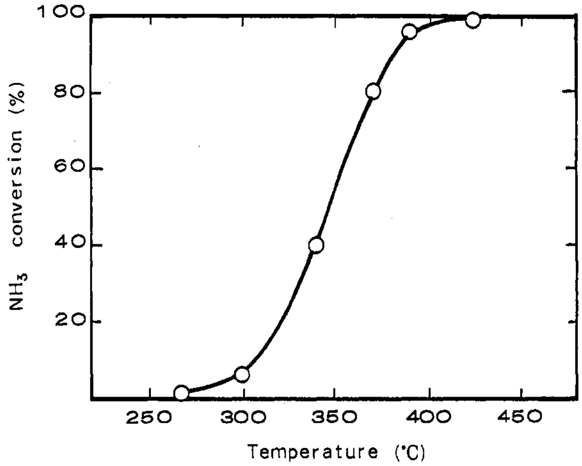

Figure 3. Catalytic activity of Fe_2O_3-TiO_2 catalyst in NH_3-O_2 reaction. Gas composition: NH_3, 250 ppm; O_2, 3%; N_2, balance. Space velocity: 30 000 h^{-1}.

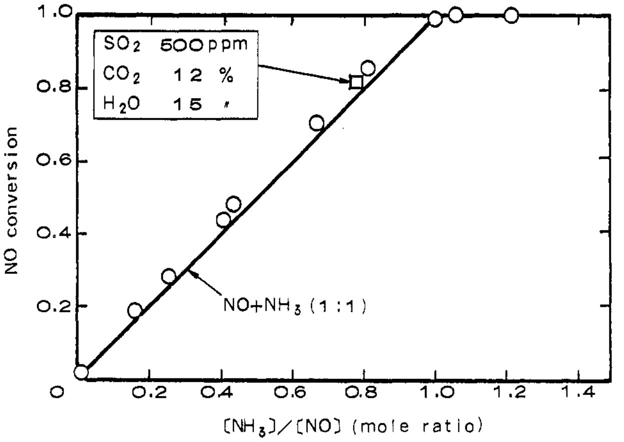

Figure 4. NO conversion as a function of (NH_3)/(NO) ratio. Gas composition: NO, 300 ppm; NH_3, 0–370 ppm; O_2, 3%; N_2 balance. Temperature: 350 °C. Space velocity: 30 000 h^{-1}.

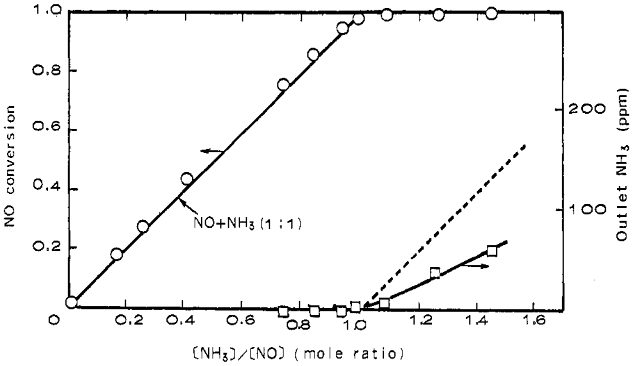

Figure 5. NO conversion and outlet NH_3 as a function of (NH_3)/(NO) ratio. Gas composition: NO, 300 ppm; NH_3, 0–400 ppm; O_2, 3%; N_2 balance. Temperature: 350 °C. Space velocity: 30 000 h^{-1}.

less than 0.3% of inlet NH_3 even at 425 °C.

Reaction Ratio of NO with NH_3. To clarify the reaction equation of NO with NH_3, it is of importance to determine the reaction ratio of NO with NH_3. Therefore the NO conversion as a function of the NH_3/NO ratio was studied under a variety of conditions. Test gas mixtures containing 300 ppm NO, 0–350 ppm NH_3, 3% O_2, and the remainder N_2 were used in the experiments. It has been found that in the absence of H_2O the NO–NH_3 reaction proceeds more than 2 times faster than that in the presence of 12% H_2O as shown in Figure 2. Under these conditions the reaction proceeds completely in such a way that either of the two reactants, NO or NH_3, is consumed entirely. The result is shown in Figure 4. It is clearly seen that the NO conversion is equal to the NH_3/NO ratio. It is also shown that the relation between the NO conversion and the NH_3/NO ratio was unchanged under such a condition that the gas contained SO_2, CO_2, and H_2O.

To determine the reaction ratio of NO with NH_3, we simultaneously measured the amount of reacted NH_3 and reacted NO. Figure 5 shows the NO conversion and the outlet NH_3 concentration as a function of the NH_3/NO ratio. It is seen that the NO conversion is equal to the NH_3/NO ratio and that the concentration of NH_3 in the exit gas is negligible in the experiments performed with the NH_3/NO ratio less than unity. When the ratio was more than unity, unreacted NH_3 increased linearly with the excess NH_3. These results suggest that NO reacts with NH_3 at a 1:1 mole ratio. The dashed line shows the outlet NH_3 concentration if NH_3 reacts with NO at a 1:1 mole ratio and NH_3 is not decomposed by O_2. Since the catalyst has activity for the NH_3 decomposition by O_2, the observed outlet NH_3 concentration is less than the value of the dashed line. These experimental results seem to indicate that NH_3 reacts with NO preferentially in the presence of a large excess of O_2 and that the NH_3 decomposition by O_2 proceeds after NO is consumed completely.

It may be argued that the reaction ratio of NH_3 with NO is coincidentally 1:1, if the NH_3 decomposition occurs in the experiments performed with the NH_3/NO ratio less than unity. The reaction of NO with NH_3 has been conventionally written as in eq 2. Summation of reactions

$$6NO + 4NH_3 = 5N_2 + 6H_2O \qquad (2)$$

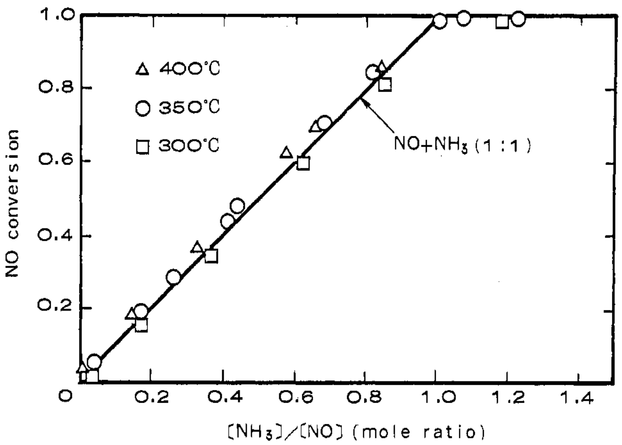

Figure 6. NO conversion as a function of $(NH_3)/(NO)$ ratio—effect of temperature. Gas composition: NO, 300 ppm; NH_3, 0–370 ppm; O_2, 3%; N_2 balance. Temperature: 300–400 °C. Space velocity: 30 000 h^{-1}.

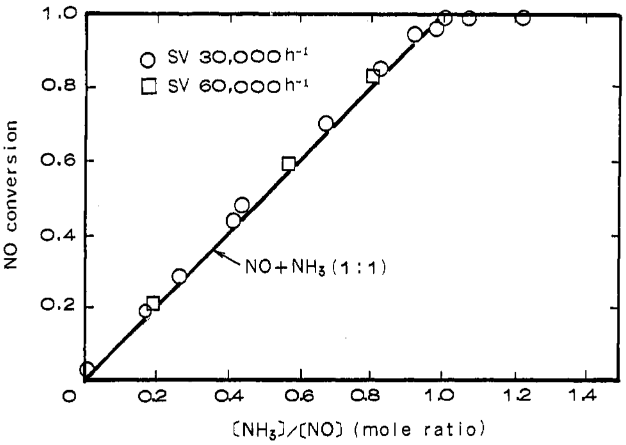

Figure 7. NO conversion as a function of $(NH_3)/(NO)$ ratio—effect of space velocity. Gas composition: NO, 300 ppm; NH_3 0–370 ppm; O_2, 3%; N_2 balance. Temperature: 350 °C. Space velocity: 30 000–60 000 h^{-1}.

1 and 2 may give the NO–NH_3 reaction ratio of unity under some reaction conditions. The decomposition rate of NH_3, however, has a large temperature dependence between 300 and 400 °C as shown in Figure 3. It may be said that the reaction ratio of NH_3 with NO is unity if the reaction between the NO conversion and the NH_3/NO ratio is unchanged in the temperature range. Figure 6 shows the NO conversion as a function of the NH_3/NO ratio at 300, 350, and 400 °C. It is seen that the NO conversion is equal to the NH_3/NO ratio at 300 °C where no substantial NH_3 decomposition occurs. The same relationship was obtained at 400 °C where the NH_3 decomposition by O_2 is more than 95% in the absence of NO (see Figure 3).

We have also studied the reaction ratio of NO with NH_3 by using a catalyst which has a high activity for the NH_3 decomposition ($CuO–TiO_2$ catalyst) and a catalyst which does not decompose NH_3 ($WO_3–TiO_2$ catalyst). It was found that the NO conversion was equal to the NH_3/NO ratio. Figure 7 shows the effect of space velocity. Under different space velocities, the same relationship was obtained. From the above results it can be concluded that NO reacts with NH_3 at a 1:1 mole ratio.

An effect of O_2 on the NO–NH_3 reaction was studied by using a test gas containing 300 ppm NO, 360 ppm NH_3, 0 or 3% O_2, and the remainder N_2. The change of the NO conversion as a function of time in the absence or presence of O_2 is shown in Figure 8. The NO conversion decreased gradually to almost zero in the absence of O_2, but it quickly returned to the initial value when O_2 supply was resumed. This observation clearly indicates the involvement of O_2 in the NO–NH_3 reaction, and the reaction is inhibited by the absence of O_2. To clarify the reaction equation, the effect of O_2 concentration on the reaction ratio of NO with NH_3 was studied. Figure 9 shows the effect of O_2. It was found that the NO conversion was equal to the NH_3/NO ratio over an O_2 concentration of 0.5–11.1%. The formation of N_2O was studied, since considerable formation of N_2O has been reported on $Pt–Al_2O_3$[9] and CuO.[11] A gas mixture containing 1000 ppm NO, 1200 ppm NH_3, 3% O_2, and the remainder N_2 was passed through the catalyst bed at 300–400 °C and a space velocity of 30 000 h^{-1}. The N_2O concentration was monitored by an IR spectrophotometer at 4.5 μm. N_2O was not detected in all experiments (<10 ppm). From the above experimental results the overall reaction in the NO–NH_3–O_2 system under the present conditions is given by eq 3.

$$NO + NH_3 + {}^1/_4O_2 = N_2 + {}^3/_2H_2O \qquad (3)$$

Reaction Mechanism of NO with NH_3. The enhancement of the NO–NH_3 reaction by O_2 observed in the present study is qualitatively in agreement with the experimental results obtained by Markvart and Pour[15] and Bauerle et al.[12-14] The former used $Pt–Al_2O_3$ catalyst, and the latter $V_2O_5–Al_2O_3$ and iron–chromium oxides. Otto and Shelef[11] studied the reaction on a CuO catalyst using

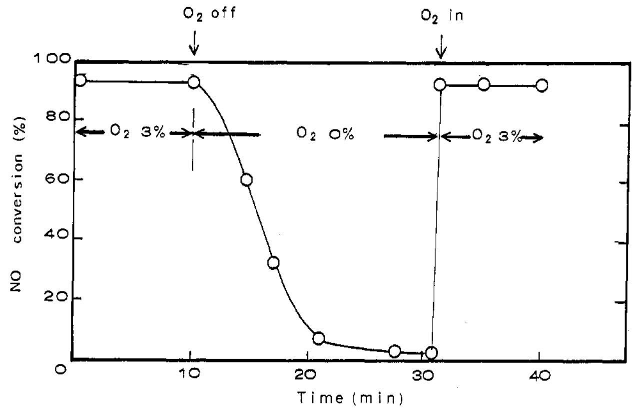

Figure 8. Effect of oxygen on NO–NH_3 reaction. Gas composition: NO, 300 ppm; NH_3, 330 ppm; SO_2, 500 ppm; O_2, 3%; CO_2, 12%; H_2O, 12%; N_2, balance. Temperature: 350 °C. Space velocity: 60 000 h^{-1}.

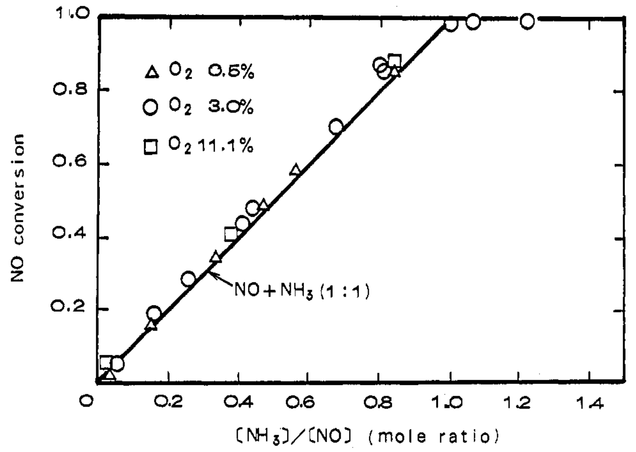

Figure 9. NO conversion as a function of $(NH_3)/(NO)$ ratio—effect of O_2 concentration. Gas composition: NO, 300 ppm; NH_3 0–370 ppm; O_2, 0.5–11.1%; N_2, balance. Temperature: 350 °C. Space velocity: 30 000 h^{-1}.

a gaseous mixture containing ^{14}NO and $^{15}NH_3$. At the early stage of the reaction the only product besides water was mixed nitrogen $^{14}N^{15}N$, which directly indicates that 1 mol of NO reacts with 1 mol of NH_3. In their experiments O_2 was not added to the reaction mixture. It was found that the CuO catalyst was reduced to Cu_2O or Cu during the course of the reaction and that the formation of N_2O and $^{14}N^{14}N$ occurred at the later stage of the reaction. Therefore, if the reaction were carried out with excess O_2, the nitrogen product would be always $^{14}N^{15}N$.

Otto et al.[9] proposed a mechanism for the production of N_2 and N_2O in the absence of O_2. The mechanism included primary and secondary reaction steps for the formation of each product as in eq 4–9. For the overall

$$NH_3(ads) = NH_2(ads) + H(ads) \qquad (4)$$

$$NO(ads) + NH_2(ads) = N_2 + H_2O(ads) \qquad (5)$$

$$NO(ads) + NH_2(ads) = N_2O + 2H(ads) \qquad (6)$$

$$NO(ads) + H(ads) = HNO(ads) \qquad (7)$$

$$2HNO(ads) = N_2O(ads) + H_2O(ads) \qquad (8)$$

$$2H(ads) + 2HNO(ads) = N_2 + 2H_2O(ads) \qquad (9)$$

reaction, the surface dissociation of NH_3 (eq 3) is considered to be the rate-controlling step. In the present study the formation of N_2O was negligible on the iron oxide–titanium oxide catalyst. Therefore reactions 5–8 are considered to be minor reactions.

Tamaru et al.[16] postulated NO_2-like species for the adsorbed state of NO on V_2O_5 catalyst. We have also studied the reaction of NO_2 with NH_3. Contrary to the case of NO–NH_3 reaction, the reaction ratio of NO_2 with NH_3 is 3:4. Although we did not try to observe the adsorbed state of NO, it seems to us that NO_2-like species are of minor importance in the iron oxide–titanium oxide catalyst.

From the information obtained in the present study and the previous studies, the following reaction mechanism for NO with NH_3 in the presence of excess O_2 is proposed:

$$NH_3(ads) + NO(ads) = N_2 + H_2O + H(ads) \qquad (10)$$

$$2H(ads) + O = H_2O + \square \qquad (11)$$

$$O_2 + 2\square = 2O \qquad (12)$$

O = adsorbed oxygen or lattice oxygen; $\square$ = oxygen adsorption site or lattice site. First, the reaction between adsorbed NH_3 and adsorbed NO takes place and adsorbed hydrogen is produced. Then, adsorbed hydrogen is consumed by adsorbed oxygen or lattice oxygen. The oxygen adsorption site or lattice site is reproduced by adsorption of gaseous oxygen. Reaction 10 plus one-half reaction 11 plus one-quarter reaction 12 gives reaction 3. In the absence of oxygen, reaction 12 cannot proceed. The catalyst is reduced by adsorbed hydrogen, or adsorbed oxygen is consumed by adsorbed hydrogen. As a result the active site of the catalyst decreases, and reaction 10 does not proceed. Although we did not observe a reduction state of the catalyst in the absence of O_2, Otto et al. observed that CuO catalyst was reduced to Cu_2O or Cu. Therefore it is probable that the iron oxide–titanium oxide is reduced in the absence of O_2. Reaction 10 is the summation of reactions 4 and 5. NH_3 reacts with O_2 at a considerable rate, for example, at 350 °C. However, NH_3 reacts preferentially with NO in the presence of O_2. Therefore it seems that reaction 10 or 5 must be faster than a reaction between NH_3(ads) and adsorbed oxygen species. Reaction 10 seems to be more probable than reactions 4 and 5, because the decomposition of NH_3 by O_2 was completely inhibited by the presence of NO. If the dissociation of NH_3 were the first step in the NO–NH_3 reaction, the decomposition of NH_3 should proceed competitively with the NO–NH_3 reaction.

As mentioned before in the present paper, the reaction rate of NO with NH_3 is retarded by H_2O. It is considered that H_2O adsorbs competitively with NH_3 on the active site of the catalyst.

The reaction mechanism proposed above gives a good explanation of the results obtained in this study. The reaction of NO_2 and a mixture of NO–NO_2 with NH_3 was also investigated. Details of the reaction mechanism of NO_x with NH_3 will be reported later.

Standard Reduction Potential of the Indium–Indium(III) Electrode

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The standard reduction potential of the indium–indium(III) electrode has been determined at 25.0 °C in the absence of hydrolysis and complex formation. A value of −322.6 mV has been found, differing considerably from the values published before.

Introduction

Several investigators[1–5] have attempted to determine the standard reduction potential of the In;In^{3+} electrode using electrochemical cells. The reported values range between −335 and −341 mV. In most of these investigations the calculations are based on the assumption that the indium salt dissociates completely in aqueous solution. For indium chloride, however, this assumption can seriously be questioned. It has been found by Ferri[6] and De Poorter[7] that chloride forms with In^{3+} relatively stable complexes. As hydrolysis of In^{3+} becomes more and more important in dilute solutions, the extrapolation of experimental data to ionic strength zero can also be a possible source of error.

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