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Activity and Hydrogen Content of a Plate-Type Raney Nickel Catalyst

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A constant-potential electrolysis technique was found to be applicable to determination of the hydrogen content of a plate-type Raney nickel catalyst. The hydrogen was anodically removed in a definite amount according to the potential applied. Relationships between the hydrogen content, the BET surface area, and the activity for acetone hydrogenation were also investigated for the cases of electrolytic and thermal removal. On the basis of the data, combined with observation by means of an electron scanning microscope, it was concluded that removal of the hydrogen originally held by the catalyst inevitably caused a decrease in the activity. Electrolytic removal did not change the fine-structure of the bulk of the catalyst layer as remarkably as thermal removal. Though the catalyst that partly or completely lost its original hydrogen was able to resorb a considerable amount of hydrogen, it had no relation to the activity for acetone hydrogenation. A rough estimate of the atom ratio for the catalyst, H_{ads}:H_{abs}:Ni:Al, was 2:22:22:1.

INTRODUCTION

Numerous conflicting opinions have been reported so far about the relationship between the activity and the hydrogen content of Raney nickel catalysts. Some investigators (*1*) took the position that the amount of hydrogen held in the catalyst essentially controlled its activity; others (*2*) claimed that there was no fundamental relationship. Kubomatsu *et al.* (*3*) ascribed the controversy to the extraordinary difficulties in obtaining a reliable value of the hydrogen content and in changing the hydrogen content without changing the fine structure of the catalyst.

Though a variety of methods for determining the content have so far been used, electrochemical methods seem to have scarcely been reported probably because the usual finely pulverized form of the catalyst appeared to be unsuitable for any of the methods. A plate type of the catalyst, originally developed by Yasumura *et al.* (*4*), however, makes it easy to use electrochemical methods in the hydrogen content determination. The purpose of the present work is first to examine the applicability of electrochemical techniques to the determination by using plate-type Raney nickel, and then to obtain information concerning the relationship between the hydrogen content and the activity.

EXPERIMENTAL

Preparation of plate Raney nickel catalyst and measurement of its activity. Nickel plate (99.9% pure), about 1 mm thick, that had thinly been coated on both sides with aluminum (99%) by means of a metal-spray apparatus was heated at 700°C for 30 min, then rolled to a thickness of about 0.5 mm while hot, followed by an additional

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heat-treating for 30 min at 700°C. During these treatments a thin layer of Ni–Al alloys is formed between the coated aluminum layer and the nickel substrate. The plate was cut into small pieces, (4–5) × (25–40) mm in size, so as to be suitable for the present electrochemical treatments. The aluminum of these pieces was leached out just before use with a 20% sodium hydroxide solution at 50°C until hydrogen ceased to evolve. The layer of Raney nickel on the substrate was 25 μm thick on the average as measured by means of a scanning electron microscope.

The above-described are, as already shown by one of the present authors (*5*), optimum conditions for preparing the most active catalyst of this type. He also remarked there that a Ni–Al alloy formed at 700°C had a composition of $NiAl_3$ with a very little Ni_2Al_3, which was consistent with the recent, detailed investigation by Baird and Steffgen (*6*). They reported that alloying at or ~725°C produced the most active catalysts for methanation of carbon monoxide–hydrogen mixtures. The alloy used in the present work, therefore, would have almost the same elementary composition as that described by these authors.

The activity was measured for hydrogenation of acetone. Because a piece of the catalyst sample had an insufficient surface area, 2–4 cm^2, three to six pieces were used together in each run. Their total geometrical surface area were adjusted before leaching so as to come to just 12 cm^2, which was suitable for the measuring apparatus used. The apparatus having a capacity of about 600 ml was filled with nitrogen at 1 atm and cooled to 0°C prior to measurement. Sample pieces were quickly placed in a 260-ml glass vessel which was a part of the apparatus. After injection of 1 ml of acetone into the vessel, the nitrogen was replaced by hydrogen, then the whole system was dipped into a hot bath thermostated at 70°C. A decrease in gas volume during 1 hr was regarded for convenience as the catalytic activity. The resulting product was confirmed to be 2-propanol by means of a gas chromatograph.

Cyclic voltammetry and controlled potential electrolysis. For these, the conventional apparatuses and an H-cell divided in two compartments by a sintered glass disk were used. The electrolyte was 100 ml of a 20% sodium hydroxide solution, the same concentration as used in preparing the catalyst, and the temperature was always kept at 20°C. The cathode was a platinum plate and the reference a saturated calomel electrode (SCE). The usual precautions such as elimination of dissolved oxygen or hydrogen in solution were properly taken. In the solution all the catalyst samples, regardless of their history, exhibited the same rest potential of −1.080 V vs SCE at 20°C whenever they were saturated with hydrogen. The saturation was done electrolytically with special care so as not to cause any Raney nickel particles to fall off the sample. Thus the vigorous evolution of hydrogen was avoided; a very small cathodic current was allowed to flow until the rest potential of a sample attained to a stable value of −1.080 V. The whole hydrogen content of a sample was determined on the basis of the automatically recorded current–time curve for the electrolysis in which the electrode potential of the sample was controlled at −0.2 V vs SCE.

Thickness, surface morphology, crystallographic fine-structure, and true surface area of catalyst layer. The first two properties were examined by means of a scanning electron microscope (JOEL Ltd. Model 50-A) and the third by an X-ray diffractometer (Rigakudenki Ltd.). The last was determined on a BET system using nitrogen as the adsorbate. The apparatus required the specimen to have an apparent surface area of 50 cm^2 at least.

Treatment of data. Properties of the catalyst were expressed in relative values to facilitate discussion of the relationship

between the hydrogen content and the activity. The reference values for the hydrogen content, activity, and BET surface area were those of the fresh catalyst, i.e., 22.4 C per 1 cm^2 of apparent surface area (cm^2-app), 421 ml, and 0.90 m^2 per cm^2-app, respectively. From absolute values experimentally determined, a set of points over the curves of Fig. 4 was derived by the following procedure consisting of six steps. As an example the case of treatment at −0.7 V was described; the numerical values cited were the averages of replicate measurements. Samples of the same sort, of course, were used throughout the steps.

(1) A fresh catalyst sample was subjected to the electrolysis at −0.7 V; the amount of electricity consumed was 20.2 C/cm^2-app or 90.2% of the originally held hydrogen, the remaining hydrogen being 9.8% (Curve 1). (2) The sample was electrolytically saturated with hydrogen, followed by electrolysis again at the same potential as in Step 1; 5.8 C/cm^2-app was consumed, corresponding to the amount of resorbed hydrogen. (3) In succession, the remaining hydrogen was completely removed at −0.2 V, corresponding to 2.2 C/cm^2-app. Thus the original hydrogen content was 2.2 + 20.2 = 22.4, which supported the soundness of the reference value. The sum of residual and resorbed hydrogen was 5.8 + 2.2 = 8.0 or 35.7% (Curve 2). (4) Several pieces of the catalyst cuts were each subjected to electrolysis at −0.7 V, then together they all underwent the activity measurement, giving a gas-volume decrease of 266 ml or 63.2% of the reference value, 421 ml (Curve 3). (5) The hydrogen saturation (Step 2) succeeding Step 1 resulted in almost the same activity value as in Step 4. (6) A group of samples having undergone Step 1 treatment showed a BET surface area of 0.79 m^2/cm^2-app, or 88% of the reference.

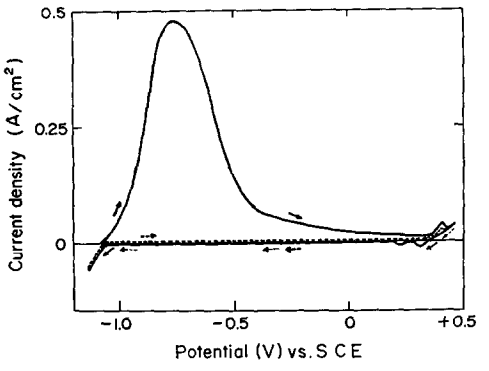

FIG. 1. Cyclic voltammogram on plate Raney nickel catalyst in 20% NaOH solution at 20°C. Sweep rate = 20 mV/sec; ——, first sweep; – – –, second sweep after hydrogen saturation at about −1.1 V.

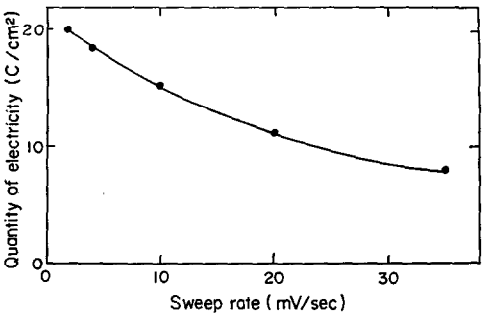

FIG. 2. Change in quantity of electricity for oxidation with sweep rate.

RESULTS AND DISCUSSION

Determination of hydrogen content by electrochemical techniques. A typical cyclic voltammogram on a plate Raney nickel catalyst as freshly prepared is shown in Fig. 1. On the first anodic sweep two current peaks are seen; the large one at about −0.8 V corresponds to the massive oxidation of the hydrogen held by the catalyst, and the small one at +0.4 V is well known to be due to oxidation of metallic nickel. Two small peaks on the return sweep correspond to the successive reductions of the two kinds of nickel oxides. Immediately after the saturation of this sample with electrolytic hydrogen the second cycle is initiated; its anodic curve is obviously different from the first

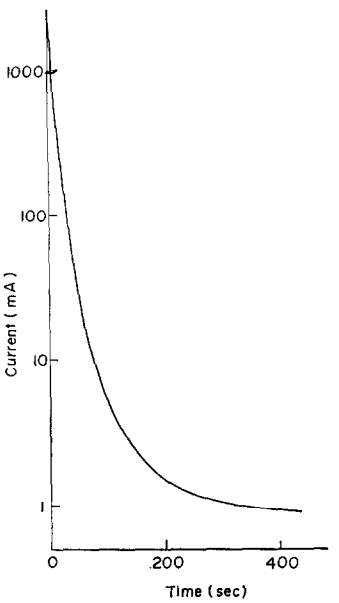

FIG. 3. Typical log i vs t curve in electrolytic determination of hydrogen at −0.2 V. Before determination, the sample was heat-treated at 400°C for 20 min under nitrogen atmosphere. Size = 4.8 × 40 mm.

one. No significant flow of current due to oxidation of hydrogen occurs, whereas the cathodic curve is identical with that during the first cycle. Moreover, any sample that had once undergone such a deep anodic sweep no longer showed the catalytic activity for hydrogenation of acetone.

Though the total quantity of electricity consumed during oxidation is obtainable on the basis of the anodic curve and sweep rate, it cannot be used as a measure of the hydrogen content of the catalyst because of the experimental fact that first the total quantity of electricity consumed largely depended on the sweep rate of potential (Fig. 2), and second, the value of current just before the beginning of the nickel oxidation was too large to neglect even with a very small sweep rate such as 4 mV/sec.

On the other hand, the controlled potential electrolysis technique was found to be satisfactory for the hydrogen content determination. Figure 3 shows a typical log i (current) vs t (time) curve, which was reconstructed from the automatically recorded i–t curve during the controlled-potential anodic dissolution of the hydrogen. Though the curve appears to have a linear portion, it is not a straight line in the strict sense, which differs a little from the well-known fact that an ordinary controlled potential electrolysis such as the anodic dissolution of a metal electrode itself always gives a linear log i vs t relationship (*7*). The present departure from linearity may be ascribed to the following circumstances. The activity of the hydrogen undergoing oxidative dissolution at the catalyst surface cannot remain constant for the entire period of electrolysis, since the hydrogen must be supplied by a very slow diffusion from the bulk to the surface of the catalyst layer. Moreover, the bulk itself is too thin, only about 25 μm, to afford to establish a diffusion layer of constant thickness, which may be an indispensable factor in bringing about a linear relationship between log i and t.

The total quantity of electricity consumed in oxidation of hydrogen can be determined by the graphical integration of the current between the limits $t = 0$ and t at which the current falls to, e.g., 1 mA. The amount of hydrogen thus ignored would be very small compared with the whole amount since the catalyst layer is very thin. Any potential between −0.2 and +0.2 V applied to freshly prepared samples of the same sort resulted in almost the same value of the quantity of electricity, i.e., 22.4 C/cm²-app, which is regarded as the whole amount of hydrogen held by the catalyst.

Estimation of atom ratio in plate Raney nickel catalyst. The amounts of hydrogen adsorbed on and absorbed in the catalyst can roughly be estimated on the assumptions that the surface of the hydrogen-saturated catalyst is completely covered with a monolayer of hydrogen atoms, one hydrogen atom per one site of nickel, and

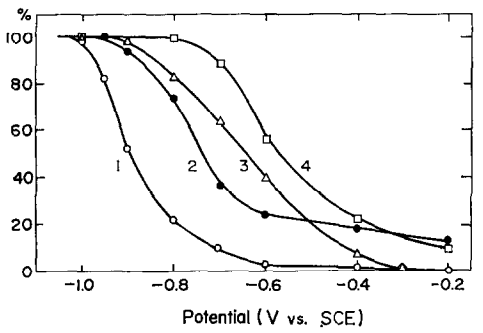

FIG. 4. Effects of electrolytic removal of hydrogen on properties of catalyst. Curves: (1) amount of residual hydrogen after constant potential electrolysis; (2) sum of resorbed and residual hydrogen; (3) activity of catalyst containing hydrogen corresponding in amount to (1) or (2); (4) BET surface area after removal of hydrogen. The numbers on vertical axis are relative values for the properties, the references being those of freshly prepared catalysts.

that the effective area per site of nickel is 6.7 Å^2 (*8*). Then the number of hydrogen atoms present per 1 cm^2 of true surface area would be 1.5×10^{15} atoms. The hydrogen atoms of this quantity liberate an amount of electricity $1.5 \times 10^{15} \times 96{,}500/(6.02 \times 10^{23}) = 0.24 \times 10^{-3}$ C. Accordingly, the amount of hydrogen atoms adsorbed on the fresh catalyst with a true surface area of 0.90 m^2/cm^2-app is 0.14×10^{20} atoms/cm^2-app or 2.2 C/cm^2-app, and then the amount absorbed in the catalyst layer is 22.4 − 2.2 = 20.2 C/cm^2-app, or 1.26×10^{20} atoms/cm^2-app. From the viewpoint of electrochemistry, the numerical value 2.2 seems too high, and therefore the assumption of the full coverage with atomic hydrogen may justly be criticized. Nevertheless, the value was tentatively adopted for the purpose of making a rough estimate of the atom ratio, H_{abs}:Ni, in the catalyst layer of the plate type. If the values 5.2 g/cm^3 as the density and 25 μm as the thickness of the layer are used, and the presence of aluminum species is ignored for convenience, the amount of nickel present in the layer with 1 cm^2-app would be 13 mg or 1.3×10^{20} atoms. Thus the ratio H_{abs}:Ni = 1.26:1.3 $\simeq$ 1:1. The catalyst layer was analyzed for aluminum and nickel by atomic absorption spectrometry; the atom ratio Al:Ni was 1:22. To sum up, a rough estimate of

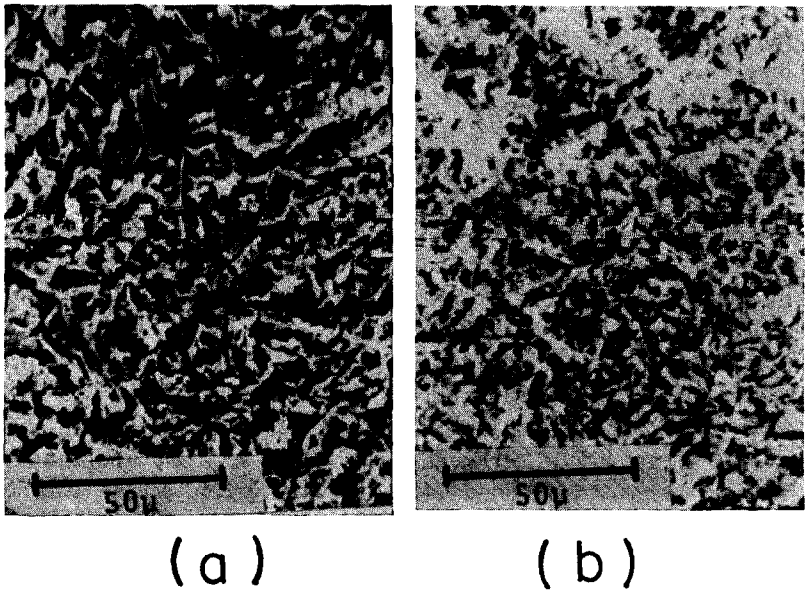

FIG. 5. Secondary electron images of catalyst surface: (a) freshly prepared catalyst; (b) hydrogen was electrolytically removed at −0.6 V.

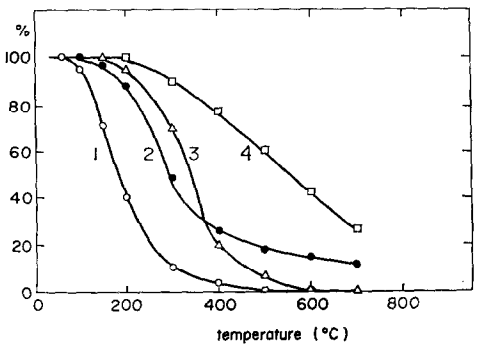

FIG. 6. Effects of a 30-min heat-treatment at various temperatures under nitrogen atmosphere on properties of catalyst. Curves: (1) amount of residual hydrogen after heat-treatment; (2) sum of residual and electrolytically resorbed hydrogen; (3) catalytic activity, as explained in Fig. 4; (4) BET surface area after thermal removal.

the atom ratio $H_{ads}:H_{abs}:Ni:Al$ was 2:22:22:1.

There may naturally be a doubt whether, in the electrolytic determination of the hydrogen, the aluminum in the catalyst caused higher values, but samples of the same catalyst as used in the main investigation were found by mean of atomic absorption analysis to contain on the average 0.25 mg of the whole aluminum per 1 cm^2-app. This amount is equivalent only to 2.7 C even if all the aluminum is assumed to be present in the zero oxidation state and oxidized to the trivalent state. A sample whose aluminum content was as high as 3.5 mg per 1 cm^2-app (equivalent to 37 C) as a result of incomplete leaching of the aluminum from the same source alloy consumed 12 C/cm^2-app in the electrolytic determination of hydrogen at −0.2 V. On the basis of these findings it can be said that the aluminum species in the catalyst used did not cause serious errors in the determination of hydrogen, though the errors could not be estimated quantitatively.

Relationship between hydrogen content and catalytic activity. It was found that the amount of hydrogen electrolytically removed from the catalyst depended on the potential applied, provided it lay between −1.0 and −0.2 V. The relationship is shown by Curve 1 in Fig. 4. When a sample that had partially or completely lost its hydrogen was kept for a while at a hydrogen evolution potential, it resorbed a considerable amount of hydrogen. Then the sample was again subjected to the hydrogen removal electrolysis at the same potential as that in the preceding removal; the difference in quantity of electricity was considered to correspond to the amount of resorbed hydrogen, and the vertical distance between Curves 1 and 2 corresponds to the amount of resorbed hydrogen. Curve 3 represents the activity when the catalyst contains hydrogen corresponding in amount to Curve 1 or 2, and Curve 4 represents the corresponding change in BET surface area of the catalyst. It is interesting to note that the activities before and after the resorption of hydrogen are practically the same. In other words, resorbed hydrogen in considerable amounts is not responsible for the activity at all. On the other hand, the activity is still high even when the hydrogen content is reduced to a low value; for example, a specimen that had lost 90% of its original hydrogen by the electrolytic treatment at −0.7 V still exhibited as much as 63% of its original activity.

A fresh sample had a BET surface area of 70 m^2/g Ni, or 0.9 m^2/cm^2-app, which remained practically unchanged until more than about 80% of the original hydrogen was removed. These findings are consistent with those reported by Kokes and Emmett (*9*) for the thermal removal of hydrogen from an ordinary pulverized Raney nickel catalyst.

Figure 5 shows secondary electron images of the catalyst surface; (a) is for a fresh catalyst and (b) for a catalyst from which hydrogen was electrolytically removed at −0.6 V. Close inspection of these shows that the removal made the grain boundaries obscure; that is, the clefts separating each

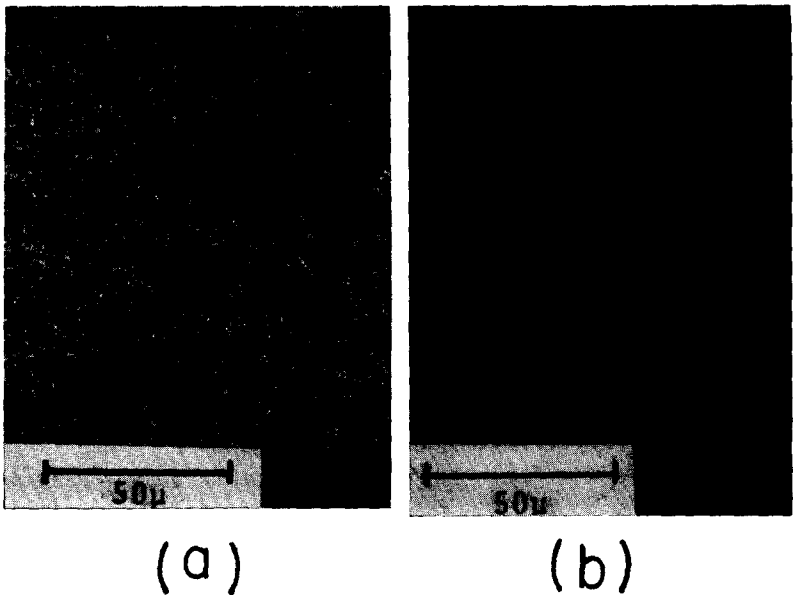

FIG. 7. Sulfur distribution on catalyst surface: (a) freshly prepared catalyst; (b) after complete removal of hydrogen at −0.2 V.

grain from others appeared to have been buried considerably, though the size of each grain seemingly remained almost unchanged. The change in surface texture was naturally considered to be associated with a progress of recrystallization of nickel in the bulk of catalyst layer. Contrary to expectation, the X-ray diffraction patterns for the catalyst from which hydrogen was electrolytically removed failed to provide positive evidence for the recrystallization, although the patterns for the fresh and the hydrogen-removed catalysts were not entirely the same. The reverse was found for thermal removal; the patterns obviously provided evidence for recrystallization (*5*). Naturally, temperature would make such a large difference. In order to see whether there was any essential difference between electrolytic and thermal removal, the effects of the latter on catalytic properties were observed. Samples were heat-treated at various temperatures for 30 min under an atmosphere of nitrogen, and the amounts of remaining hydrogen were electrolytically determined. The result is shown in Fig. 6. No essential difference can be seen compared with Fig. 4, but the activity, in proportion to the BET surface area, decreased more intensely than it did in the case of the electrolytic removal. It is already known that nickel sulfide forms at the places where the catalytic activity is high when the catalyst is immersed in a saturated aqueous solution of hydrogen sulfide (*10*). The formation did not occur at all on the surface of the catalyst from which the hydrogen had completely been removed by the thermal treatment at 600°C, the temperature at which the activity just fell to zero (Fig. 6). On the contrary, it occurred as shown in Fig. 7(b) when all of the hydrogen had been electrolytically removed at −0.2 V. In other words, the electrolysis is obviously a milder way of removing the hydrogen if it must be done.

To sum up, the hydrogen held by a plate Raney nickel catalyst was successfully determined by means of controlled potential electrolysis, and partial removal of the hydrogen which originated during

preparation of the catalyst was inevitably accompanied by diminution of the activity for acetone hydrogenation. Electrolytic removal did not alter the fine structure of the bulk of the catalyst as remarkably as thermal removal. Though the catalyst that partly or completely lost its original hydrogen was able to resorb a considerable amount of hydrogen, it had no relation to the activity.

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