Decrease of the Surface Area of Raney-type Catalysts in the Aluminium-dissolution Process

By Masaki SATO and Nobuto OHTA

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Introduction

Some authors have shown$^{1-5)}$ that the surface areas or the catalytic activities of Raney nickel catalysts decrease on reserving. The present authors suggested in the studies on Raney copper catalyst for the dehydrogenation of cyclohexanol to cyclohexanone,$^{6)}$ that the similar, but much more rapid decrease of the surface area might occur in the process of dissolving aluminium with alkali.

It has been confirmed that this suggestion was right and applicable also to the usual Raney nickel catalyst.

Experimental Procedure

(1) Preparation of the Catalysts.

a) *Starting alloy*.—The starting alloy for the catalyst No. 16* was obtained as follows.

Firstly, 40 parts of aluminium were melted in an electrically heated furnace or Tammann furnace and then 5 parts of zinc, 50 parts of copper, and 5 parts of nickel were put into it in the above order.

The fused solution was stirred with a silica tube to be homogenized, the temperature being raised to about 900°C. After cooling the alloy was powdered and 200 mesh powders were used as the sample. The content of aluminium was 40.6%.

As Raney nickel, a commercial one containing 48.9% of aluminium was used.

b) *Dissolving of aluminium*.—The dissolution of aluminium was carried out using 30% NaOH aqueous solution in an open vessel. After dissolution, the remaining catalyst was taken out of the alkali solution and washed with cold water till the washed water became neutral to litmus-paper. The time required for this treatment was always 3 to 4 hrs.

As soon as the washing was finished the sample was put into a vessel for the measurement of the surface area and dried at 20° to 30°C under the reduced pressure until the pressure of the system reached about 10^{-4} mm Hg.

(2) Measurement of the Surface Area.—The surface area was determined by using the usual method of low temperature adsorption of carbondioxide and making use of the B. E. T. equation. Nitrogen gas was used to the measurement of the dead space of the apparatus.

The carbondioxide that we used was a commercial one stored in an iron cylinder. It was purified by the usual cleaning up system, consisting of a copper sulfate bottle for scrubbing out hydrogen-sulfide, a concentrated sulfuric acid bottle for drying and a phosphorus pentoxide tube for removing the trace of moisture.

After the system was pumped out to high vacuum (about 10^{-4} mm Hg), the first adsorption test of carbon dioxide was carried out at -78.5°C. To avoid errors based on the probable presence of a trace of alkali on the surface of the catalyst, the system was degassed by a diffusion pump for an hour at 0°C after the first test and the adsorption test was repeated again at -78.5°C.

The surface area was calculated from the V_m value (the volume of gas required to form a monomolecular layer all over the surface) obtained from the second isotherm, where the cross-sectional area of carbondioxide molecule was assumed to be 17.0 Å^2.

Results

The experimental results are shown in Fig. 1, Fig. 2, Table I–a and Table I–b.

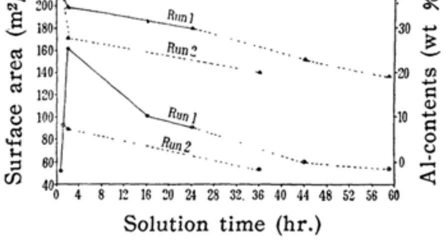

Fig. 1. The relationship between the surface area and the condition of aluminium-dissolution, on the catalyst " No. 16 ".
⊙ Surface area. ⚠ Content of aluminium. (Temperature of dissolution are 10° to 15°C at solid lines and 70° to 80°C at dotted lines.)

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* One of the best catalysts for the dehydrogenation of cyclohexanol to cyclohexanone which was discovered by the present authors.$^{7)}$

1) J. Aubry, *Bull. soc. chim.* (France), 5, 1333 (1938).

2) R. Schröter, *Angew. Chem.*, 54, 229, 252 (1941).

3) A. A. Pavlic and H. Adkins, *J. Am. Chem. Soc.*, 68, 1471 (1946).

4) H. A. Smith, W. C. Bedoit and J. F. Fuzek, *J. Am. Chem. Soc.*, 71, 3769 (1949).

5) J. H. Pattison and F. Degering, *J. Am. Chem. Soc.*, 73, 486 (1951).

6) This suggestion was presented at the 6th Annual Meeting of the Chemical Society of Japan held at Kyoto, April, 1953.

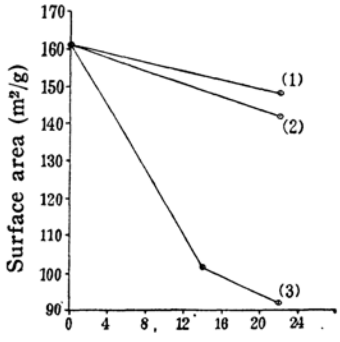


Fig. 2. Variations of the surface area of the catalyst "No. 16" on standing.

Note: Dissolution of aluminium was carried out at 10° to 15°C. for 2 hrs. Each sample was reserved in a following condition.

(1) 70° to 80° C, in vacuum.
(2) room temperature (20°C), in water.
(3) 10° to 15°C, in 30% NaOH aq. solution.

TABLE I–a

VARIATION OF THE SURFACE AREA IN THE ALUMINIUM DISSOLUTION PROCESS ON RANEY NICKEL CATALYST

Condition of the solution		Surface area ($m^2/g.$)	Al-content (wt%)
1 hr.	10° to 15°C	48.2	33.0
2 hrs.	10° to 15°C	58.8	31.0
24 hrs.	10° to 15°C	47.0	
1 hr. +1 hr.	10° to 15°C 70° to 80°C	43.0	24.8
1 hr.	70° to 80°C	46.5	29.5

TABLE I–b

THERMOSTABILITY OF CATALYST "NO. 16" OBTAINED BY A SEVERE DISSOLUTION PROCESS

(24 hrs., 10° to 15°C+35 hrs., 70° to 80°C)

	Surface area ($m^2/g.$)	Al-content (wt%)
Original	55.5	19.8
After heating at 400°C for 3 hrs. in vacuum	55.5	19.8

Discussion

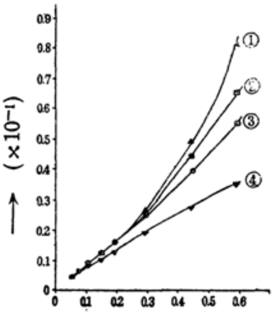
From the experimental results above mentioned the following is obvious.

1) At an initial step of the dissolution-process, the content of aluminium becomes lower on the surface of the catalyst and bare copper or nickel atoms, active centers for catalysis, increase in number to form abnormally uneven surfaces having a large area.

At the next step of this process, where the velocity of dissolution of aluminium is rather small and the internal aluminium may be dissolved out, the surface area decreases in spite of successive dissolution of aluminium. It surely leads to a conclusion that during this step nascent bare atoms of nickel or copper formed by dissolution of aluminium move so as to reconfigurate the surface-structure to a more stable one. This kind of reconfiguration (or decrease of surface area) may be sufficiently reasonable, but has not been reported on the Raney type catalyst. As anticipated, the rate of this decrease is higher as the temperature of the dissolution process is higher (Fig. 1 and Table I–a).

2) It is valid to say on the catalyst "No. 16" (Fig. 1 and Fig.2), that the decrease of surface area during the aluminium-dissolution process is more rapid when compared with that during reserving in dried state or in water. Smith,

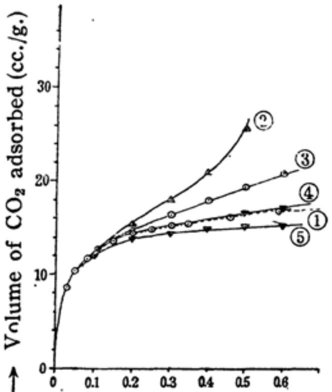
Fig. 3 The catalyst "No. 16" prepared by an exhaustive dissolution-process (24 hrs. at 10° to 15°C and next 20 hrs., at 70° to 80°C).



→ Relative pressure (x)

Fig. 3–A

(1) B. E. T.-line. (2) Hüttig-line.
(2) Anderson-line. (4) Langmuir-line.



→ Relative pressure (x)

Fig. 3–B

(1) observed-curve. (4) modified B. E. T. -curve (n=2.0).
(2) B. E. T.-curve.
(3) Hüttig-curve. (5) Langmuir-curve.

Bedoit and Fuzek[4] reported the aging of the Raney nickel "W–2", of which the surface area originally was 38.0 m²/g. and which, after ten or 40 days, decreased to 31.0 or 26.0 m²/g. respectively. The rate of decrease of surface is merely less than one-tenth compared to that shown in Table I–a.

3) From Table I–b, it can be understood that the catalyst prepared by an exhaustive dissolution-process (24 hrs. at 10° to 15°C, and next 35 hrs. at 70° to 80°C) has a very heat-stable surface. This must be one of the causes that the catalyst maintained the most suitable activity for a long time[8].

4) In Fig. 3–A, the abscissa represents the relative pressure x ($=p/p_0$), the ordinate $x/v(1-x)$, $x/v(1-0.8x)$, $x(1+x)/x$ or x/v in the case of the B. E. T.[9], Anderson[10], Hüttig[11] or Langmuir[12] equation, respectively (the v is the volume of CO_2 adsorbed).

In each case, the rigid linearity exists at 0.05 to 0.25, 0.05 to 0.25, 0.05 to 0.35 or 0.15 to 0.15 of x, respectively; that is, the Hüttig line shows the linearity in the widest range. (Fig. 3–A)

In Fig. 3–B, solid lines were shown to represent the relations between the relative pressure and the volume of adsorbed carbon-dioxide, calculated by putting each V_m found in Fig. 3–A into the corresponding Hüttig, Langmuir, B. E. T. and modified B. E. T. equation (1)[13] in which the maximum numbers of adsorbed molecules are assumed to be finite.

$$V=\frac{V_m\cdot C\cdot X}{1-x}\cdot\frac{1-(n+1)\cdot x+n\cdot x^{n+1}}{1+(C-1)\cdot x-n\cdot x^{n+1}}, \tag{1}$$

where C is a constant, and n is the maximum numbers of adsorbed molecules.

A dotted line is the observed curve, which accords best with the modified B. E. T. line ($n=2$).

5) In Fig. 4–5, calculated values of the adsorbed carbon-dioxide (V_{cal})$\sim$the relative pressure lines are shown as dotted lines. The V_{cal} were obtained by putting various finite values in "n" of the modified B. E. T. equation (1), where the V_m found from the B. E. T. line of $x/v(1-x)\sim x$ was always used. Observed curves of the same relation were shown as the solid lines.

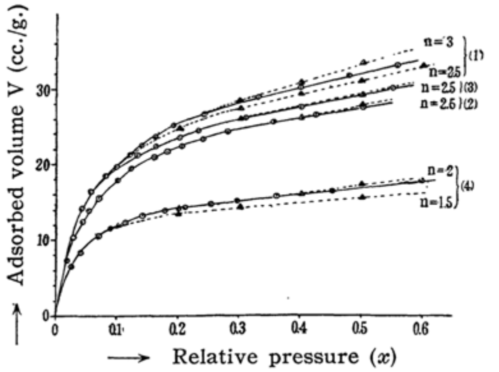


Fig. 4. Alloy-catalyst "No. 16"

Run No.	Condition of aluminium dissolution	n
(1)	16 hrs., 10° to 15°C	2.5–3
(2)	24 hrs., 10° to 15°C	2.5
(3)	1 hr, 10° to 15°C, +1 hr, 70° to 80°C	2.5
(4)	24 hrs, 10° to 15°C+20 hrs, 70° to 80°C	2.0

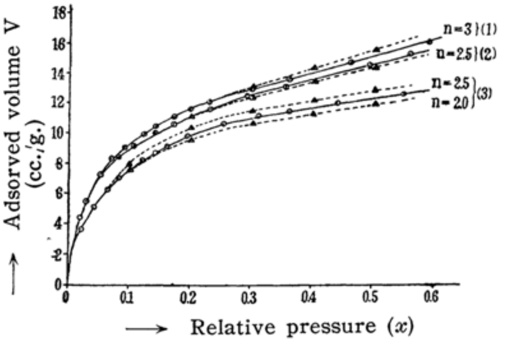


Fig. 5. Raney-nickel

Run No.	Condition of aluminium dissolution	n
(1)	1 hr, 10° to 15°C	3.0
(2)	24 hrs, 10° to 15°C	2.5
(3)	1 hr, 10° to 15°C, +1 hr, 70° to 80°C	$2.0<n<2.5$

A comparison of the curves with the calculated ones shows that the severer the condition of dissolution is, the lower the reliable n-value is. As this value indicates the number of molecular layers adsorbed on the catalyst surface, it may be considered** as a factor indicating the adsorption affinity, which, in turn, probably is a variable having some relation with the catalytic activity.

On dehydrogenation of cyclohexanol to cyclohexanone at 275°C, the catalyst "No. 16" prepared by a mild dissolution process[6] (12°C, 75 hrs.) showed a very high activity in the initial period as compared with the same catalyst prepared by the above exhausive dissolution. But the activity of the former decreased rapidly to a degree lower than that of the latter catalyst, which

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[7] N. Ohta and M. Sato, *J. Chem. Soc. Japan* (Ind. Chem. Section), **56**, 153, 250 (1953).

[8] N. Ohta, M. Sato and J. Imamura, *J. Chem. Soc. Japan*, (Ind. Chem. Section) **56**, 495 (1953).

[9] S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

[10] R. B. Anderson, *J. Am. Chem. Soc.*, **68**, 686 (1946).

[11] G. F. Hüttig, *Kolloid-Z.*, **121**, 50 (1951).

[12] I. Langmuir, *J. Am. Chem. Soc.*, **37**, 1139 (1915), **38**, 2221 (1916).

[13] T. L. Hill, *J. Chem. Phys.*, **14**, 263 (1946).

maintained the initial activity for a long time.

It was concluded from these facts that a very active, but unstable surface is left at an initial step of dissolution process in dissolution at a low temperature, while a less active, but more stable surface appears in process of dissolution or the severe dissolution process.

Furthermore, the reconfiguration pointed out at 1) may be an important cause of this decrease of catalytic activity. Active centers on the Raney nickel "W-6"[14], which is the most active catalyst of this type particularly at low temperatures, may seem to be nascent bare nickel atoms formed at the low temperature dissolution.

Summary

Variations of the surface area in the dissolution process were investigated on a Raney copper catalyst "No. 16" (for dehydrogenation of cyclohexanol) and a Raney nickel catalyst.

It has been found that nascent bare atoms of copper or nickel formed at the initial step move rapidly, perhaps particularly in alkali solution, to reconfigurate the surface-structure to a more stable one.

That is to say, the surface area reaches a maximum at an initial step, where only a small quantity of aluminium is dissolved out, then rapidly decreases to a stable value in spite of successive dissolution of aluminium. The rate of decrease is much greater than that recognized on reserving the catalyst in its dried state or in water.

By calculating reliable "n" values, the number of adsorbed molecular layers on the surface area from the modified B. E. T. equation, it has been deduced that the average catalytic activity per unit area of the surface may be decreased in process of dissolution of aluminium.

The Government Chemical Industrial
Research Institute, Tokyo
Hatagaya

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[14] H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, 70, 695 (1948).

** The n-value may not be considered as a factor indicating the variation of pore- radius at the catalyst from the adsorption-desorption isotherm.