May, 1983] © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***56***, *1301—1304 (1983)* 1301

Effect of Adsorption of Potassium Iodide on Catalytic Activity of Plate-type Raney Nickel

Tomio Yoshino* and Tuneyo Abe
Faculty of Pharmaceutical Science, Tokushima University of Arts and Science,
Yamashiro-cho, Tokushima 770

(Received June 25, 1982)

An experimental investigation was made of the adsorptive activity of Raney nickel catalyst toward potassium iodide over a wide KI concentration range and of the change with KI adsorption of hydrogenating activity toward unsaturated alcohol and ketone. Adsorbed amounts of K^+ and I^- ions were determined by potentiometry and radioactivity measurement. The adsorptive activity *vs.* I^- concentration relation yields a definitive break at equilibrium concentration 5.5×10^{-5} mol dm^{-3} (surface coverage 26%), the adsorption features in the lower and higher ranges relative to the break point being approximately represented by Freundlich's and BET equations, respectively. Adsorption sites effective for I^- ion in the Freundlich region disappear almost completely when the catalyst is preheated at 600 °C. The surface coverage causing the hydrogenation activity to decrease by 50% is 3% for allyl alcohol and 0.3% for 2-butanone. With allyl alcohol, however, even such a catalyst as has preadsorbed *ca.* 5-monolayer amount of I^- ions possesses a 33% residual activity, though catalyst coverages over 26% result in only a little decrease in activity. These results suggest that the adsorption sites in the Freundlich region may function as strong catalytically active centers for the hydrogenation, which are unstable to heating.

Many reports have dealt with the relation between adsorption of halogen compounds on Raney nickel and catalysis by Raney nickel with preadsorbed halogen compounds. Pattison and Degering[1)] reported that the rate of catalytic reduction of styrene was remarkably decreased when the concentration of chloride ion to be preadsorbed exceeded 4.2×10^{-4} mol/g RNi. On reduction of carbonyl groups in unsaturated ketones by Raney nickel, Hoshiai *et al.*[2,3)] reported that a complete loss of the hydrogenation activity of catalyst occurred when Raney nickel had preadsorbed more than 4.1×10^{-4} mol of iodide ion per gram of Raney nickel. Sokol'skii and Zakumbaeva[4)] reported that catalytic reduction of *p*-nitrophenol and similar compounds was decelerated in the coexistence of alkali halides.

Recent reports[5,6)] indicate that preadsorption of NaBr on a modified Raney nickel for asymmetric hydrogenation results in a marked increase in yield owing to enantioface-differentiating hydrogenation and that this increase is caused by selective adsorption of NaBr at active centers involving aluminium compounds[7—9)] lacking asymmetric selectivity. Little has yet been clarified of the relation between the adsorption on catalyst surface and the change in catalytic activity.

The present paper deals with the relation between the adsorptive activity of Raney nickel for KI and the catalytic activity of KI-preadsorbed Raney nickel for hydrogenation of unsaturated alcohols or ketones, with particular reference to the nature of surfaces of such catalyst preparations.

Experimental

Materials. Raney alloy was prepared by placing a nickel plate, 0.05 mm thick and 99.96% pure, between aluminium plates, 0.1 mm thick and 99.995% pure, and subjecting the sandwich heated at 630 °C in a nitrogen stream to hot-rolling with a dental roller. A plate-type Raney nickel catalyst,[10,11)] suited for the present experiment, was prepared by treating the Raney alloy with a solution of 20 wt% sodium hydroxide at 50 °C for 1 h. The catalyst, thus obtained or further preannealed in a hydrogen atmosphere at 30—600 °C for 1 h, was used to determine the adsorption and hydrogenation activities; the catalyst was divided before use into portions of 16 cm^2 in apparent area (BET specific surface area 4.2×10^2 cm^2/cm^2).

Allyl alcohol, 2-butanone, and mesityl oxide (4-methyl-3-penten-2-one) were of special grade and used without further purification. Solutions of potassium iodide (special grade) were prepared by use of distilled water.

Procedures. The adsorption experiment was carried out by shaking the catalyst, in 100 ml aqueous solution of initial concentration 10^{-7}—10^{-2} mol dm^{-3} of KI labeled with 0.3 μCi of ^{131}I, in an atmosphere of nitrogen at 20—30 °C for 1 h. The catalyst was washed twice with 10 ml ethanol and then twice with 10 ml of a reactant before being used for reduction experiments. Adsorbed and desorbed amounts of iodide ion were determined with a well-type scintillation counter (Fuji Electric Model NHS 2) by measuring radioactivities on 1 ml portions taken from the adsorbate solution and the liquid employed for desorption experiment, respectively. Potentiometric measurement with a microprocessor ionalyzer (Orion Research Model 901) was employed to determine the amount of potassium ion adsorbed from aqueous solution.

The activity of catalysts was determined by use of liquid-phase hydrogenation on 3 ml allyl alcohol, 2-butanone, or mesityl oxide at 1 atm and 70 °C. Products were analyzed with a gas chromatograph (Yanagimoto Model G 180).

Results

Adsorbed Amount and Adsorption Isotherm. Both the time required for saturation adsorption to be reached and the adsorbed amount of I^- ion depend on temperature; with initial concentration 10^{-4} mol dm^{-3}, these values are about 60 min and 4.5×10^{-10} mol/BET cm^2 at 20 °C and about 30 min and 3.1×10^{-10} mol/BET cm^2 at 30 °C. It is noticed that the adsorbed amount may be estimated with a relative error less than about 10% under the same experimental conditions.

Figure 1 illustrates the effect of equilibrium concentration, *C*, on adsorbed amounts, *v*, of K^+ and

Table 1. Desorption of iodide ion from the catalyst in ethanol and reactant

Reactant	Initial [KI] mol/dm^3	Adsorbed I$^-$ mol/BET cm^2	Desorbed fraction/% of I$^-$			
			Ethanol	Reactant	Reaction	Total
Allyl alcohol	10^{-6}	5.70×10^{-12}	0.82	8.06	1.95	10.83
	10^{-3}	8.14×10^{-10}	1.35	4.63	1.61	7.59
2-Butanone	10^{-6}	5.70×10^{-12}	0.92	3.16	3.20	7.22
	10^{-3}	8.14×10^{-10}	1.19	2.80	0.80	4.79
4-Methyl-3-penten-2-one	10^{-6}	5.70×10^{-12}	0.84	4.27	0.70	5.77
	10^{-3}	8.14×10^{-10}	1.18	2.47	0.53	4.18

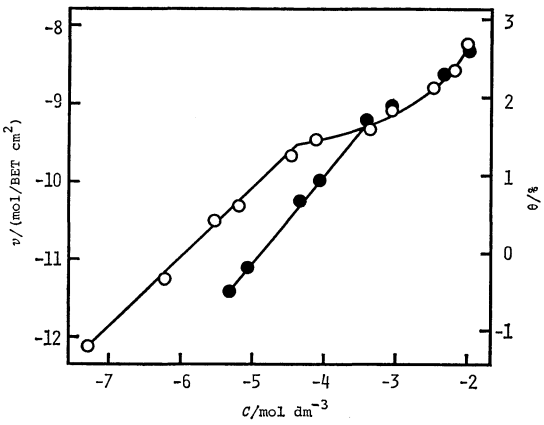

Fig. 1. Adsorption isotherm by the plot of the logarithm of the equilibrium concentration (C) on the logarithm of the adsorbed amount (v) (●: K$^+$ ion, ○: I$^-$ ion) and surface coverage (θ) of I$^-$ ion at 30 °C.

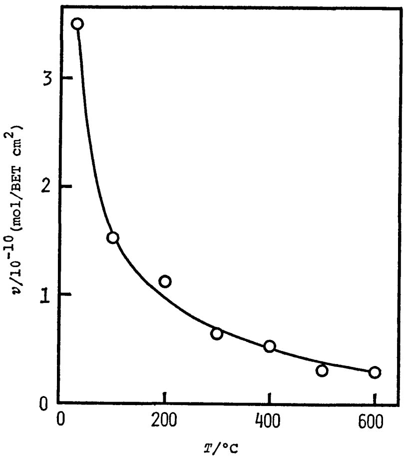

Fig. 2. Variation of I$^-$ adsorptivity at 30 °C of the catalyst preheated for 1 h in H_2. The initial concentration of the adsorbate was 10^{-4} mol dm^{-3}.

I$^-$ ions. Surface coverage, θ, of I$^-$ ion was obtained by a calculation using the value of 2.06 Å as the ionic radius of the ion adsorbed on the surface of Raney nickel. The adsorbed amount of I$^-$ ion, as shown in Fig. 1, yields a break at equilibrium concentration about 5.5×10^{-5} mol dm^{-3} ($v=3.2\times10^{-10}$ mol/BET cm^2; $\theta=26\%$). Below the break point, the adsorbed amount is given by Freundlich's equation[12]

$$\log v = a + \frac{1}{n}\log C,$$

where a is a constant, evaluated to be 1.2 from Fig. 1. Beyond the break point, the equilibrium data approximately obey a BET equation, suggesting a multilayer adsorption of I$^-$ ions. In fact, the 100% coverage is obtained at $C=2.1\times10^{-3}$ mol dm^{-3} and $v=1.2\times10^{-9}$ mol/BET cm^2, and the highest coverage, so far obtained, is 475%.

The isosteric differential heat of adsorption of I$^-$ ion, as obtained by processing the above results according to Clausius-Clapeyron's equation,[13] decreases exponentially with increasing surface coverage of I$^-$ ions in the Freundlich region, and is estimated to be 6.3×10^3 and 3.8×10^3 J/mol at coverages 3 and 25%, respectively.

The adsorbed amount of K$^+$ ion, as with the adsorption of I$^-$ ion, yields a break at equilibrium concentration about 4.3×10^{-4} mol dm^{-3} (adsorbed amount, 5.4×10^{-10} mol/BET cm^2; surface coverage of I$^-$ ion, 43%). Below the break point, the adsorbed amount is much less than that of I$^-$ ion. Beyond the point, however, both the adsorbates, K$^+$ and I$^-$ ions, give equimolar adsorbed amounts.

Adsorption on Preheated Catalyst. Figure 2 illustrates the variation of the I$^-$ adsorption activity of catalyst caused by application of sintering at 30—600 °C in a hydrogen atmosphere. The adsorptive activity of 3.5×10^{-10} mol/BET cm^2 ($\theta=28.1\%$) of the catalyst obtained by pretreatment at 30 °C was decreased by a 100 °C sintering to 1.5×10^{-10} mol/BET cm^2 (12.3%) corresponding to about 56% decrease and by a 600 °C sintering to 0.3×10^{-10} mol/BET cm^2 (2.4%) corresponding to about 91% decrease. These results suggest that many of the active centers for halogen adsorption are easily caused to disappear even by preheating at low temperature.

Desorption of the Adsorbate. The I$^-$ preadsorbed catalyst was used for the reduction experiment after being successively washed with ethanol and the reactant for the reduction. Table 1 indicates fractions of I$^-$ ions desorbed due to the washing with ethanol (the 4th col.), the washing with the reactant (the 5th col.), and the reduction (the 6th col.), the sum of these fractions being given in the 7th column. The desorption of I$^-$ ion, as seen from Table 1, obviously depends on the initial concentration, giving higher fractions at 10^{-6} mol dm^{-3} than at 10^{-3} mol dm^{-3}; most of the adsorbate is desorbed with allyl alcohol in contrast with 2-butanone and mesityl oxide, the desorptive capacity being in the decreasing order:

Table 2. Change in activity of the preadsorbed catalyst for hydrogenation

Adsorbed I^- mol/BET cm^2	Coverage %	Rate of hydrogenation[a)] mmol/h			
		Allyl alcohol	2-Butanone	4-Methyl-3-penten-2-one	
0	—	2.85	0.21	1.12[b)]	0.37[c)]
7.69×10^{-13}	0.06	2.13	0.17	0.57	0.32
5.70×10^{-12}	0.46	1.93	0.10	0.28	0.24
5.33×10^{-11}	4.28	1.27	0.08	0.22	0.15
3.11×10^{-10}	24.96	1.23	0.06	0.17	0.11
8.14×10^{-10}	65.41	1.21	0.04	—	—
5.92×10^{-9}	475.1	0.93	0.02	—	—

a) In the liquid phase at 1 atm and 70 °C. b) This column refers to product 4-methyl-2-pentanone produced from 4-methyl-3-penten-2-one. c) This column refers to product 4-methyl-2-pentanol.

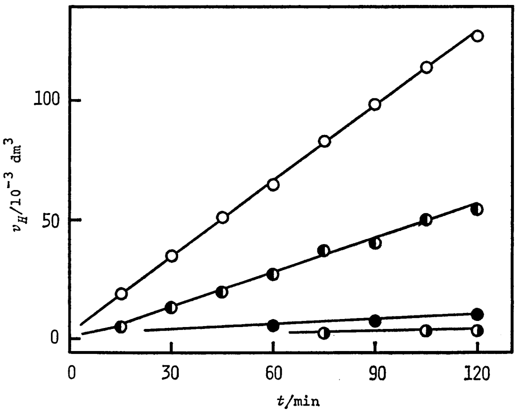

Fig. 3. Time dependences of hydrogen absorption (v_H) by allyl alcohol (○,◐) and by 2-butanone (●,◑) through the catalyst with (◐,◑) or without (○,●) preadsorption of KI. The initial concentration of the adsorbate was 10^{-5} mol dm^{-3}.

allyl alcohol>2-butanone>mesityl oxide.

Hydrogenation Activity of Preadsorbed Catalyst. Figure 3 illustrates the time dependence of the hydrogen adsorption by allyl alcohol or 2-butanone when the substrate is hydrogenated by catalysts with or without preadsorbed potassium iodide (adsorbed amount, 5.3×10^{-11} mol/BET cm^2; coverage, 4.3%). At 70 °C and 1 atm, the hydrogenation activity of catalyst remains constant over a period of 120 min, and is in general higher for the unsaturated alcohol than for the ketone. The hydrogenation activity is lowered by the preadsorption to 42.5% for the alcohol and 38.8% for the ketone.

Table 2 shows rates of hydrogenation of allyl alcohol, 2-butanone, and mesityl oxide on KI preadsorbed catalysts. The hydrogenation of the alcohol or the ketone yielded only 1-propanol or 2-butanol, respectively, but mesityl oxide gave both 4-methyl-2-pentanone and 4-methyl-2-pentanol. As seen from Table 2, the rate of hydrogenation of these compounds is highest for allyl alcohol regardless of the extent of preadsorption, and the rate for the alcohol by such a catalyst as has preadsorbed *ca.* 5-monolayer amount of adsorbate is 33% of that by the catalyst without preadsorption. It turns out that the rate of formation of 4-methyl-2-pentanone and 4-methyl-2-pentanol is remarkably decreased with increasing amount of preadsorbed I^- ions in the low adsorption phase; hydrogenation yields for the catalyst with 4.3% coverage are 71 and 29% for the carbon double bond and carbonyl group of mesityl oxide, respectively.

Discussion

As revealed from Fig. 1, the mode of adsorption of I^- ion is changed according as the adsorbate concentration falls in the lower or higher range relative to the definitive break. In the lower range, the Freundlich region, the isosteric heat of adsorption decreases exponentially with increasing adsorbed amount, and the surface coverage is so low (below 26%) that the surface interaction between adsorbate ions may be neglected and therefore the adsorbate ions may be considered to occupy heterogeneous adsorption sites successively with preference from higher to lower adsorption-activity sites. The number of ionic bonds of the K^+ with I^- ions adsorbed on the catalyst surface, in this region, seems to be smaller for the adsorbed amount than for that of adsorbed I^- ions, because a portion of the I^- ions may be stabilized electrostatically through the specific adsorption or may combine with H^+ instead of K^+ ion.[14)]

On the contrary, in the higher concentration range than the break point where the BET equation holds, the change in the mode of adsorption seems to be caused by strong ionic interaction between the adsorbates on the catalyst, as well as by capillary condensation on the porous surface. In addition, multilayer adsorption may be considered to take place at the catalytic surface with equimolar adsorption of counterionic adsorbates to form an ionic double layer at the solid/liquid interface.

As seen from Table 1, the greater portion of the amount of I^- desorbed from the catalyst surface is involved in the course of washing at room temperature, though the absolute fraction desorbed varies with the initial iodide and reactant concentrations and the desorption is made to proceed a little further during the following reduction run at 70 °C. These results suggest that capillary condensation is more important than the Langmuir type adsorption for the understanding of the mechanism of desorption.

As shown in Fig. 2, adsorption sites effective for halogen ions in the Freundlich region are so unstable to heating as to disappear to a considerable extent even at relatively low temperatures and almost completely at 600 °C. In a previous work,[15] it was reported that the catalytic activity of plate-type Raney nickel is decreased by thermal pretreatment, *e.g.*, a catalyst annealed at 600 °C has an activity as low as 16% of that of a 100 °C-annealed one for reduction of acetone and 29% of that of a 150 °C-annealed one for reduction of benzene. These facts indicate that both the adsorption sites and the active sites for hydrogenation are caused easily to disappear by preheating the catalyst.

The hydrogenation activity of catalyst lowers with increasing amount of I^- ions preadsorbed in the Freundlich region, this tendency being more pronounced in the lower adsorption phase, as seen from Table 2. Thus, the surface coverage at the 50% lowering is about 3% for allyl alcohol and about 0.3% for 2-butanone. For the latter compound, the relative catalytic activity lowers to 0.36 at surface coverage 3%; the activity for the reduction of carbonyl group in ketone is remarkably decreased by the preadsorption of I^- ion. Similarly, in the case of mesityl oxide, the hydrogenation of carbon double bond proceeds much more rapidly than that of carbonyl group on catalysts of the same coverage. These results suggest that the preadsorbed I^- ions preferentially occupy many of the strong adsorption sites at or near the active centers effective mainly for the reduction of carbonyl group.

In the case of the adsorption in the range beyond the Freundlich region, the hydrogenation activity of catalyst depends negligibly on surface coverage as seen from Table 2. The residual activity displayed at more than 100% coverage implies wide distribution of preadsorbed I^- ions over the heterogeneous surface of catalyst and partial desorption from the surface of those ions upon attack by the reactant.

The above results agree with previous results,[1–3] though no direct, quantitative comparision can be made for differences in adsorbate properties or adsorption conditions.

Hofer and Hintermann[16] examined properties of the active center of Raney nickel by X-Ray diffraction line broadening analysis and reported that annealed Raney nickel catalysts with much lowered activity had lost many of their surface structural defects. Pearce and Leuis,[17] using the same method, reported that a highly active Raney nickel catalyst was unstable for heating and possessed much more structural defects, microstrains, and stacking faults than an inactive catalyst. As mentioned above, we[15] also reported that active sites of Raney nickel are associated with lattice defects, vacancies and dislocations because the hydrogenation activity of preannealed catalyst was decreased in a temperature range where defects vanish.

It is concluded from the present results that the adsorption sites for I^- ions in the Freundlich region and the greater portion of the active sites for hydrogenation are the same sites on catalyst surface or are located very close to each other, and that they are related to heterogeneous lattice defects.

The authors wish to thank Professor Emeritus Jiro Yasumura (Tokushima University) for his helpful discussion.

References

1) J. N. Pattison and E. F. Degering, *J. Am. Chem. Soc.*, **73**, 611 (1951).

2) K. Hoshiai and J. Miyata, *Kogyo Kagaku Zasshi*, **60**, 253 (1957).

3) K. Hoshiai and I. Iwasawa, *Kogyo Kagaku Zasshi*, **61**, 846 (1958).

4) D. V. Sokol'skii and G. D. Zakumbaeva, *Tr. Inst. Khim. Nauk, Akad. Nauk Kaz. SSR*, **5**, 3 (1959).

5) T. Harada and Y. Izumi, *Chem. Lett.*, **1978**, 1195.

6) T. Harada, A. Tai, M. Yamamoto, H. Ozaki, and Y. Izumi, Proc. 7th Int. Congr. Catal. Part A, Tokyo (1980), pp. 364—375.

7) Y. Orito, S. Niwa, and S. Imai, *Yuki Gosei Kagaku Kyokai Shi*, **34**, 236 (1976).

8) T. Harada, S. Onaka, A. Tai, and Y. Izumi, *Chem. Lett.*, **1977**, 1131.

9) A. Hoek and W. M. H. Sachtler, *J. Catal.*, **58**, 276 (1979).

10) J. Yasumura, T. Yoshino, and S. Abe, *Ind. Eng. Chem., Pro. Res. Dev.*, **7**, 252 (1968).

11) T. Yoshino, H. Yagi, and Y. Tegawa, *Nippon Kagaku Kaishi*, **1980**, 16.

12) P. Fejes, "Contact Catalysis," ed by Z. G. Szabó and D. Kalló, Elsevier Scientific Publishing Co., Amsterdam (1976), Vol. 1, pp. 153—161.

13) T. Keii, "Kyuchaku," Kyoritsu Shuppan, Tokyo (1965), Chap. 2.

14) A. Kitahara and A. Watanabe, "Kaimen Denki Gensho," Kyoritsu Shuppan, Tokyo (1972), Chap. 2.

15) T. Yoshino, *Nippon Kagaku Zasshi*, **87**, 558 (1968).

16) E. M. Hofer and H. E. Hintermann, *Trans. Faraday Soc.*, **60**, 1457 (1964).

17) C. E. Pearce and D. Leuis, *J. Catal.*, **26**, 318 (1972)