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MEASUREMENT OF ACTIVE SITE DENSITY ON A SULFIDED NICKEL CATALYST

By

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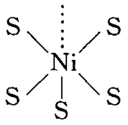
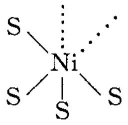
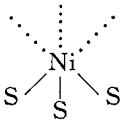
Modification of nickel catalyst with a small amount of sulfur caused selective inhibition for ethylene hydrogenation and H_2-D_2 equilibration; the catalyst was still active for acetylene hydrogenation and hydrogen exchange between ethylene and deuteroethylene.1) This fact was well accounted2) for with a model of active sites similar to one proposed by Siegel.3) The model consists of surface nickel atom of three types with respect to coordinative unsaturation by sulfur atoms as follows.



(A)



(B)



(C)

Site A is effective only for adsorption of acetylene or olefin; site B with a coordinated hydrogen atom is active for hydrogen exchange and isomerization of olefin, but lacks activity for hydrogenation and H_2-D_2 equilibration which are solely due to site C. The catalytic selectivity of molybdenum disulfide was elucidated also by this model of active sites.4)

These active sites were allowed to catalyze just as mononuclear metal complex in a liquid phase; hence they should be distributed on catalyst surface so sparsely as to catalyze independently from one another. On this point of view, the authors tried in this report to estimate their densities.

The denstiy of active site on catalyst surface is estimated usually by an amount of catalytic poison completely inhibiting catalysis, according to a known stoichiometry between poison and active site. The present model of active site,

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however, affords none of such stoichiometry because poison may fill every coordinative unsaturation of sites A and B as well as C and, furthermore, hydrogenation of olefin taking place soley on sites C can be inhibited by occupation of any one of its three coordinative unsaturation by poison. Accordingly, too much strong poison irreversibly coordinating to nickel atom of every type of active sites, A, B and C, is inadequate to estimate respective densities of these active sites.

Acetylene was hydrogenated to ethylene but not to ethane on nickel also in the presence of a small amount of carbon monoxide, but activity of nickel to form ethane was recovered easily by a simple evacuation of reacting gas containing carbon monoxide.5) Sulfided nickel freshly prepared, on the other hand, lacked activity for hydrogenation but became active in contact with acetylene, bringing about an induction period. The catalyst showed a brief activity for ethylene hydrogenation after completion of acetylene hydrogenation to ethylene.2) These facts suggest that the strength of coordination to surface nickel atom is $C_2H_2 > CO$, $S > C_2H_4$, H_2; hence, at least, the density of site C can be estimated by adsorption of carbon monoxide in course of acetylene hydrogenation.

Nickel wire of 0.1 mm diameter and *ca.* 1000 m length was preliminarily oxidized, reduced by hydrogen and evacuated at 500°C; finally treated with a small amount of hydrogen sulfide for a few minutes and evacuated at 300°C. Auger electron spectroscopy indicated2) the surface composition of nickel thus sulfided to be Ni_3S_2 and that sulfur penetrated into nickel by *ca.* 500 A depth. Reaction was carried out at 120°C with gas mixture of *ca.* 20 Torr acetylene and *ca.* 40 Torr hydrogen, which was admixed with known amounts of carbon-^{13}C monoxide and argon in an usual circulation system of *ca.* 220 mℓ and all made of glass. Decrease of total pressure was followed by a manometer and a small portion of reacting gas was sampled at times for gaschromatometric and mass-spectrometric analyses. Carbon-^{13}C monoxide was used to discriminate it from ethylene in mass-spectrometric measurement and its partial pressure was determined with reference to Ar^+ peak height.

A typical time course of the reaction is given in Fig. 1, where partial pressure of carbon monoxide decreased gradually with progress of acetylene hydrogenation to a steady value attainable after consumption of acetylene. Decrease of total pressure beyond the initial pressure of acetylene was caused by formation of butene.2,5) None of change in reaction gas was observed without catalyst and none of oxygen compound was found over catalyst even at 200°C. Partial pressure of carbon monoxide did not change when it was introduced with acetylene over catalyst at 120°C. Inhibition of ethylene hydrogenation over nickel caused by carbon monoxide was erased easily by a brief evacuation at 120°C. Accor-

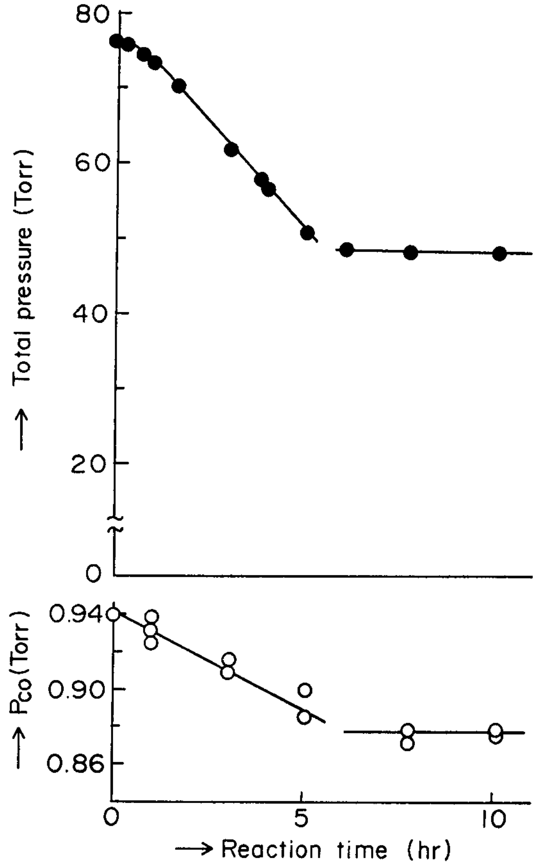

Fig. 1. Typical time courses of acetylene partial hydrogenation on sulfided nickel catalyst and adsorption of CO at 120°C. The initial pressures are $C_2H_2=20.1$, $H_2=44.7$, $CO=0.94$ and $Ar=10.1$ Torr.

dingly, the decrease of carbon monoxide pressure shown in Fig. 1 is attributed to its simple adsorption.

The decrement, $-\Delta P_{CO}$, of carbon monoxide partial pressure observed at various catalytic activity is plotted in Fig. 2 against the catalytic hydrogenation activity roughly estimated by $-\Delta P_T/\Delta t$, where $-\Delta P_T$ is a decrement of the total pressure and Δt the reaction time elapsed for consumption of acetylene. $-\Delta P_{CO}$ increased in proportion to catalytic activity, *i.e.*, amount of adsorbed carbon monoxide is proportional to density of site C active for hydrogenation.

Increase of $-\Delta P_{CO}$ with rise of initial pressure of carbon monoxide (P'_{CO}) was rapid in a range of $0 < P'_{CO} <$ *ca.* 1 Torr and slow to 10 Torr as high as

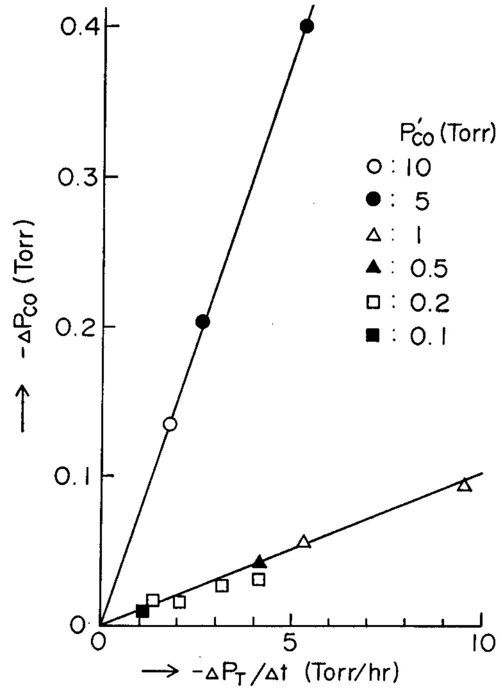

Fig. 2. Proportionarity between amount of adsorbed CO ($-\Delta P_{\mathrm{CO}}$) and hydrogenation activity ($-\Delta P_{\mathrm{T}}/\Delta t$) over sulfided nickel catalyst. Figures are the initial pressure of CO mixed with reactant.

observed. $-\Delta P_{\mathrm{CO}}$ estimated with P'_{CO} above 5 Torr is *ca.* ten times as large as that obtained with P_{CO} below 1 Torr. This difference can be understood as follows. Carbon monoxide coordinates competitively with acetylene as indicated by the fact of Fig. 1 that adsorption of carbon monoxide occured gradually with progress of acetylene hydrogenation, but not at once when acetylene was consumed. Figure 3 shows an effect of 2.3 Torr carbon monoxide admixed on the way of 1-butene hydrogenation. In the absence of carbon monoxide, isomerization of 1-butene proceeded without induction period, whereas hydrogenation to butane did not occur.[2] Evidently differing from the result of Fig. 1, adsorption of carbon monoxide took place as soon as it was admixed, coinciding with supposed order of adsorption strength, CO > olefin. However, admixed carbon monoxide as much as 2.3 Torr slowed, but not completely inhibited, the isomerization, indicating that site B is more resistive for coordination of carbon monoxide than site C. Accordingly, carbon monoxide is estimated to coordinate more easily, the higher the degree of coordinative unsaturation of surface nickel atom, and we can assumed that only a part of unsaturated coordination of site C is occu-

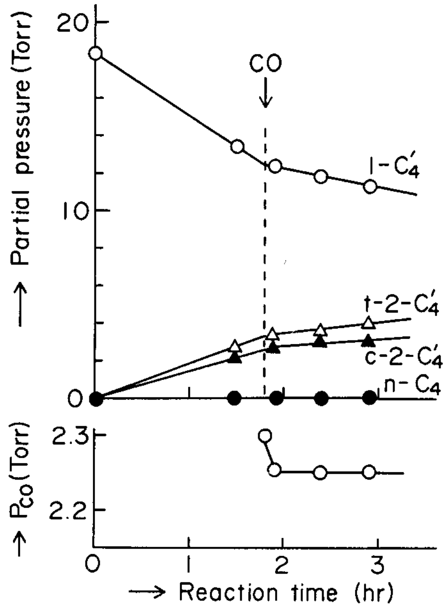

Fig. 3. Effect of 2.3 Torr CO admixed on the way of hydrogenation of 1-butene over sulfided nickel catalyst at 120°C.

pied with carbon monoxide below *ca.* 1 Torr, which does not coordinate onto sites A and B with lower unsaturation. On the other hand, the majority of unsaturated coordination of whole active sites are occupied by carbon monoxide in the case of the upper line of Fig. 2 observed at higher partial pressure of carbon monoxide.

BET area of a catalyst with a catalytic activity of $-\Delta P_T/\Delta t=5$ Torr/hr was determined by adsorption of kripton as 3.9×10^3 cm^2, assuming one kripton atom occupied 19.4 A^2 of surface. An upper bound of the density of site C on this catalyst can be estimated as follows with reference to the lower line of Fig. 2. From the value of $-\Delta P_{CO}=0.05$ Torr at $-\Delta P_T/\Delta t=5$ Torr/hr, we have 6.4×10^{13} cm^{-2} as an upper bound of the density of site C, assuming that one unsaturated coordination of every site C is occupied by a carbon monoxide molecule. On the other hand, from the value of $-\Delta P_{CO}=0.38$ Torr at $-P_T/\Delta t=5$ Torr/hr of the upper line of Fig. 2, we have 4.8×10^{14} cm^{-2} as a number of carbon monoxide molecules adsorbed on whole sites, A, B and C, in which $3\times6.4\times10^{13}$ cm^{-2} at most is responsible to site C. Attributing the other part of adsorbed carbon monoxide to sites A and B, we have 2.9×10^{14} or 1.5×10^{14} cm^{-2} as an upper bound of site A or B, respectively. Carbon monoxide trapped on catalyst surface other than by simple adsorption, *e.g.*, by formation of surface carbonyl, if any, does not affect the values of these upper bounds of site density.

The density of site A or B estimated above is ten or more times as small as that of surface atoms, *ca.* $6\times10^{15}\,\mathrm{cm}^{-2}$, evaluated on the basis of crystal plane of nickel metal.6) The density of site C is 10^{-2} times as small as that of whole atoms on catalyst surface, indicating sparse distribution of site C on sulfided nickel surface.

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