BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 270—272 (1969)

Poisoning Effect of Carbon Disulfide on the Liquid-phase Hydrogenation of Acetone over a Raney-Nickel Catalyst

Sanae KISHIDA and Shiichiro TERANISHI

Department of Chemical Engineering, Faculty of Engineering Science, Osaka Uniwersity, Machikaneyama-cho, Toyonaka, Osaka

(Received June 17, 1968)

Recently the present authors have reported[1] that the liquid-phase hydrogenation of open-chain ketones over a Raney-nickel catalyst could reasonably be interpreted by the rate equation derived from the Langmuir-Hinshelwood mechanism;

$$v = k \cdot a \cdot C_R/(1 + a \cdot C_R), \qquad (1)$$

where k refers to the rate constant; C_R, the concentration of reactant to be hydrogenated, and a, the equilibrium constant concerning the adsorption strength of hydrogen and the reactant.*1

In a previous paper[2] the authors also studied the hydrogenation of mesityl oxide over a Raney-nickel catalyst poisoned by potassium iodide, and found that the equilibrium constant, a, and the rate constant decrease upon the poisoning. The authors, therefore, pointed out that not only the behavior of the rate, but also the change in the kinetics due to the poisoning, has to be taken into account in considering a mechanism of the poisoning in heterogeneous catalysis.

In the present study, the kinetics of acetone hydrogenation over a Raney-nickel catalyst progressively poisoned by carbon disulfide is investigated in detail. A poisoning curve and a mechanism of the poisoning are then discussed accordingly.

Experimental

Catalyst. 1.00 g of Raney-alloy (50.0% Ni) was leached with 50 m*l* of a 20% sodium hydroxide solution at 100°C for 60 min. The sample was then washed 5 times with 100 m*l* of water, 5 times with 25 m*l* of isopropyl alcohol, and 10 times with 25 m*l* of *n*-hexane under hydrogen. The sample was then poisoned by CS_2, and diluted with *n*-hexane. The concentrations were so low that the CS_2 in solution was completely adsorbed by the catalyst. The sample was then washed 5 more times with 25 m*l* of *n*-hexane.

Apparatus and Procedure. For the rate measurements they were as previously reported.[1]

Results

The concentration dependence of the initial rates at 30°C over the catalyst progressively poisoned are shown in Fig. 1. The peak shifts to higher concentrations with the progressive poisoning. The

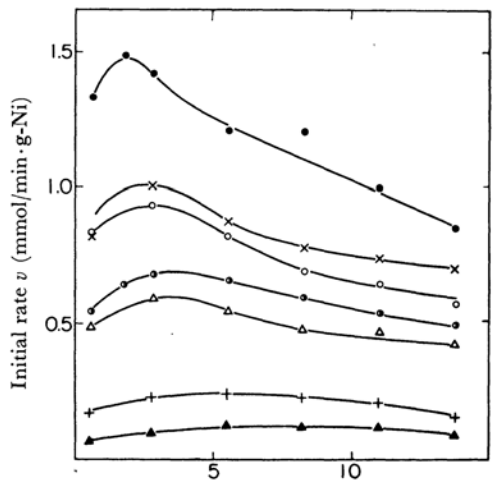

Fig. 1. Acetone hydrogenation over Raney-nickel catalyst progressively poisoned by CS_2.
The amount of CS_2 adsorbed are; ●, 0.0; ×, 0.0167; ○, 0.0474; ◑, 0.0660; △, 0.0835; +, 0.1885; ▲, 0.2505 mmol/g-Ni.

values of k and a for the poisoned catalyst were evaluated from the plots of $\sqrt{C_R/v}$ *vs.* C_R. It was found that k and a decrease in an exponential manner with the amount of carbon disulfide adsorbed, as is shown in Fig. 2; that is, k and a over the poisoned catalyst can be expressed as;

$$k = k_0 \exp(-\beta \cdot x),$$

$$a = a_0 \exp(-\alpha \cdot x),$$

where k_0 and a_0 refer to the rate constant and the equilibrium constant respectively over the un-

1) S. Kishida, S. Kajimoto and S. Teranishi, *Shokubai (Catalyst)*, **9**, 58 (1967); *J. Catalysis*, in printing.

*1 The accurate definition of a is: $a=(1/C_H) \cdot \exp(-\delta\Delta G/RT)$, where C_H refers to the liquid-phase concentration of hydrogen and where $\delta\Delta G$ is the difference in the free energies of the adsorption of hydrogen and a reactant. See Refs. 1 and 2.

2) S. Kishida and S. Teranishi, This Bulletin, **41**, (1968).

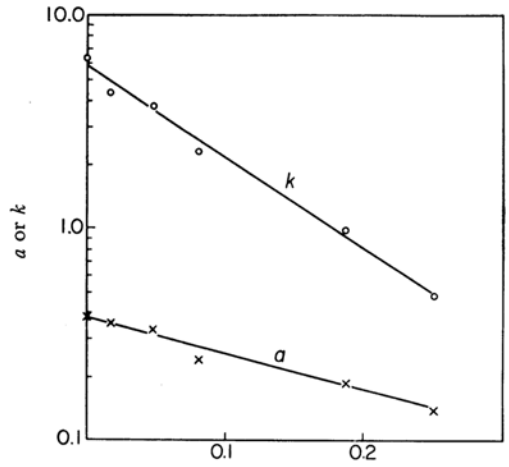

Fig. 2. Plotts of the logarithms of k and a *vs.* x.

poisoned catalyst, and x, the amount of carbon disulfide adsorbed. The β and α can be termed the poisoning coefficients for k and a respectively. From Fig. 2, the values of α and β are found to be 1.04 and 2.47 respectively. By substituting the above relations into Eq. (1), the rate equation available for the unpoisoned and poisoned catalyst can be obtained as:

$$v(x) = \frac{k_0 \cdot \exp(-\beta \cdot x) \cdot a_0 \cdot \exp(-\alpha \cdot x) \cdot C_R}{(1 + a_0 \cdot \exp(-\alpha \cdot x) \cdot C_R)^2}, \qquad (2)$$

where $v(x)$ is the reaction rate over the catalyst poisoned with x mmol of carbon disulfide per gram of Ni.

Discussion

The experimental finding that the peak of the rate *vs.* concentration plot shifts upon the poisoning seems to indicate that the adsorption coefficients of acetone or/and hydrogen are influenced in the presence of carbon disulfide.

Recently, Kishi, Ikeda and Hirota[3] have observed that the ultraviolet and visible absorption bands of acetylacetone adsorbed on evaporated iron shift in the presence of oxygen or water vapor. Eischens and Pliskin[4] reported many observations that the addition of a gas to a chemisorbed CO system shifts the frequency of the CO stretching bands. Blyholder[5] has lately proposed a qualitative interpretation of the phenomenon, applying the molecular orbital theory to a carbon-oxygen-metal system. He has shown that the shift of absorption could be explained as a result of the adsorption of a gas, by which an electron is added to or removed from the metal, with a consequent addition or removal of an electron from the chemisorbed CO. These results indicate an interaction among the adsorbed molecules.

It is necessary to mention that the hydrogenation of benzaldehyde over a Raney-nickel catalyst is markedly promoted in the presence of trimethylamine.[6] This indicates that the reaction rate of heterogeneous catalysis does not always decrease in the presence of a "poison." This so-called promoting effect must also be taken into account in discussing a poisoning mechanism.

As has been previously reported by the present authors[7] in connection with hydrogenation of isobutyl methyl ketone, the fractional surface coverage of adsorbed hydrogen during the reaction is increased by the poisoning. This phenomenon was interpreted as being due to the change in the adsorption strength of the ketone or/and hydrogen, a change caused by the potassium iodide adsorbed.

It seems that these and other phenomena can be reasonably explained and correlated by recognizing that adsorbed molecules interact directly or through the catalyst.[8] The poisoning can then be considered as a phenomenon caused by the interaction of "third material" with reacting molecules,*2 with a consequent change in the adsorption strength and hence, in the reactivity of the latter.

In view of this, a reaction rate over a catalyst progressively poisoned can generally be given by Eq. (2), which also gives a poisoning curve when $v(x)$ is plotted *vs.* x by fixing C_R. If $a_0 \cdot C_R \ll 1$, Eq. (2) becomes; $v(x) = k_0 \cdot a_0 \cdot C_R \cdot \exp(-(\beta+\alpha)x)$, and if $a_0 \cdot C_R \gg 1$, $v(x) = (k_0/a_0 \cdot C_R) \cdot \exp(-(\beta-\alpha)x)$. These are generally written as: $v(x) = (\text{constant}) \times \exp(-\gamma \cdot x)$, which can be expanded as:

$$v(x) = (\text{Constant}) \times (1 - \gamma \cdot x) \qquad (3)$$

in a small range of x, indicating that the rate first falls in a linear manner with poisoning if γ is positive. The poisoning curve of a flexed linear type[9] can now be reasonably interpreted by considering that Eq. (3) does not hold as x increases. Equation

3) K. Kishi, S. Ikeda and K. Hirota, *J. Phys. Chem.*, **71**, 4384 (1967).

4) R. P. Eischens and W. A. Pliskin, *Advan. Catalysis*, **10**, 1 (1958).

5) G. Blyholder, *J. Phys. Chem.*, **68**, 2772 (1964).

6) D. R. Levering, *J. Am. Chem. Soc.*, **71**, 1515 (1949).

7) S. Kishida, Y. Tanaka and S. Teranishi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **89**, 271 (1968).

8) M. Boudart, *J. Am. Chem. Soc.*, **74**, 3556 (1952).

*2 The fact that the kinetics of acetone hydrogenation are explained by the Langmuir-Hinshelwood mechanism can be interpreted as suggesting that the interactions of acetone-acetone, acetone-hydrogen, and hydrogen-hydrogen are not important enough to be taken into account in discussing the kinetics.

9) J. N. Pattison and E. F. Degering, *ibid.*, **73**, 611 (1951); E. F. G. Herington and E. K. Rideal, *Trans. Faraday Soc.*, **40**, 505 (1944).

(3) is substantially the same as that proposed by Maxted.[10]

The values of α and β are naturally different for different reactions, since they depend on the values of an interaction between a poisoning material and a reacting material. A given poison can, therefore, give different poisoning curves, especially in different types of reactions. In Fig. 3, three types of poisoning curves, predictable when α and β are positive, are shown. It can be seen that the reaction rate does not change or even increases, although the rate constant of a given reaction decreases, in the presence of a poison. It has been believed, according to the so-called "active patch" theory, that two different types of active sites can be experimentally distinguished when a given poison inhibits one reaction but does not influence another one.[11] Figure 3, however, suggests another possibility in interpreting the phenomenon. Since there is a possibility that α and β are negative, three more cases have to be taken into account in order to consider all of the poisoning curves predictable from Eq. (2), that is: (1) $\alpha<0$, $\beta<0$, (2) $\alpha<0$, $\beta>0$ and (3) $\alpha>0$, $\beta<0$. Nine other types of poisoning curves can, then, be deduced.

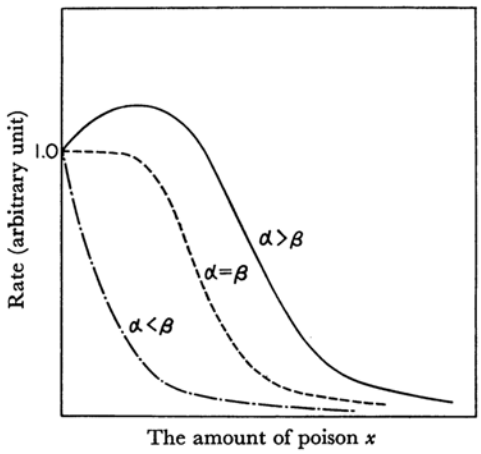

Fig. 3. Poisoning curves predictable from Eq. (2) in the case where α and β are positive

It can now be concluded that various types of observed poisoning curves can be interpreted by considering the poisoning as a phenomenon due to an interaction between a "third material" and the reacting molecules.

10) E. B. Maxted and V. Stone, *J. Chem. Soc.*, **1934**, 672.

11) J. Medema and J. P. W. Houtman, *J. Catalysis*, **6**, 322 (1966); *ibid.*, **8**, 298 (1967).