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— **Note** —

NUMBER OF ACTIVE SITES AND TURNOVER NUMBER FOR HETEROGENEOUS CATALYSIS

By

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The activity of heterogeneous catalysis is kinetically controlled by two principal factors, *i.e.*, the number of active sites on catalyst surface and the turnover number of reaction on each active site. The former is usually evaluated by chemisorption of appropriate component of reaction, however, there is no proof of all sites for chemisorption being active for catalysis; for instance, catalysis may be retarded by strong and irreversible adsorption of some components. Selective poisoning of catalyst by some appropriate compounds is useful for the cases of enzyme and organometallic catalysts in homogeneous phase, however, it is rather useless for solid catalysts because of some irreversible chemical changes of their surfaces probably affecting the reaction mechanism, accordingly the turnover number.

We have previously proposed[1)] a method of evaluating the lower limit of the number of active sites on catalyst surface from the observation of dependences of a steady rate of heterogeneous catalysis upon the reaction temperature and partial pressures of reacting components. This method is based on a statistical mechanical expression of the forward unidirectional rate of a surface process assumed to be rate-determining and to take place on physically identical active sites, on which adsorbed species are affecting with each other repulsive interactions proportional to their coverage fraction. The concluding expression for the steady rate, V, of catalysis was

$$\log V = \log N_0 - \frac{E}{2.3RT} + \log\frac{ekT}{h} - \sum_j x_j\left(\log\frac{Q_j}{C_j} + T\frac{\partial \log Q_j}{\partial T}\right) - A, \tag{1}$$

where N_0 is the lower limit of the number of active sites to be evaluated with neglection of the additional term A, which is a function of surface coverage of adsorption and temperatute and is evaluated[1)] to be smaller than *ca.* 6 except

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the case of catalyst surface being sparsely covered by adsorption. E and x_j are the observed activation heat and reaction order with repect to j th component of reaction of a concentration C_j (molecules/mℓ), respectively. R and kT/h have their usual meanings and Q_j is the state sum of a molecule of j th component excluding of its energy term, exp $(-\varepsilon_j/kT)$.

Sum of the second, third and fourth terms of the above expression of log V give

$$\log\frac{V}{N_0} \cong \log n \qquad (2)$$

which is the turnover number (molecules/sec) on each site of catalyst under consideration.

In a recent review[2)] Maatman has emphasized the utility of calculation of the active site density and turnover numbers of heterogeneous catalysis. He has calculated them similarly based on the transition state theory, however, the results may be doubtful because of his too much simplification of rate equation with neglection of the activation entropy term and hence with neglection of the fourth term as well as A in the right-hand side of Eq. (1). The activation energy or entropy of heterogeneous catalysis is usually measured with reference to the state in homogeneous phase *prior* to adsorption and hence the contribution of heat of adsorption or entropy of adsorption might be not negligible. For instance, the fourth term in the right-hand side of Eq. (1) amounts to -13.521 or -10.326 in the case of adsorption of nitrogen or hydrogenation of ethylene on metal catalyst, respectively, at 473° K and 10 mmHg of partial pressure.

The log N_0 and log n are now evaluated at 473° K and 10 mmHg of partial pressures of each component for available kinetic observations with various metallic catalysts, most of which are cited in the previous paper[1)] and supplemented by observations on isotopic mixing of nitrogen gas[3),4)], ammonia decomposition on iron catalysts[5)] and ethylene hydrogenation on evaporated metal films[6)]. The results are summerized in Figs. 1 and 2 where only the order of magnitudes of log N_0 and log n are taken into consideration. Probably on account of large errors of estimation of surface area and extraporation of kinetics to 473° K and 10 mmHg, the value of log N_0 is widely dispersed as shown in Fig. 1 We have $4.2\times10^{14}\,\mathrm{cm}^{-2}$ for log N_0 on the average for 69 cases. Fig. 2 shows that the turnover number is characteristic of the sort of catalyzed reaction irrespective of catalysts and is clearly classified into two groups, that is, the one for nitrogen fixation and the other for transfer of hydrogen atoms. The value of log n for ammonia decomposition included in the former group suggests that this reaction is rate-determined by the combination of adsorbed nitrogen atoms into N_2.

The log N_0 and log n are evaluated for hydrogenation of acetone on powdered

ZnO[7] at 140~180°C; the results are 15.50 per gram of catalyst and 1.02 on their average, respectively. This valus of log n is close to that of the group of transfer of hydrogen atoms given in Fig. 2. Assuming the surface area of powdered ZnO surface is more than several square meter per gram, we see that only a little part of ZnO surface are active for the hydrogenation, in agreement with the observed result that H_2-D_2 equilibration was completely retarded by adsorption of acetone or 2-propanol amounting to only *ca.* 4% of saturated adsorption. This result suggests that ZnO surface is nearly saturated by strongly adsorbed acetone and/or 2-propanol and only few percents available for hydrogen chemisorption offer the active sites for hydrogenation.

It is intersting to elucidate which the promoter of catalyst raises, the number of active sites or the turnover number. TAKEZAWA and TOYOSHIMA[5] have observed the isotopic mixing of nitrogen gas on doubly promoted iron catalysts and obtained a common kinetics as

$$V \propto P_{N_2}^{0.5} \quad \text{and} \quad E = 33\,\text{kcal/mol}$$

with catalysts preliminarily reduced by hydrogen at 450°C (A) and further at

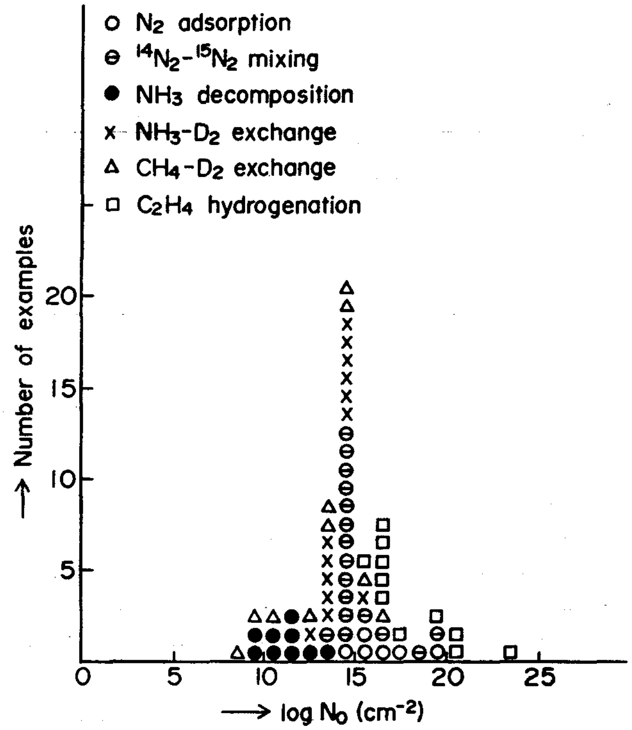

Fig. 1. Number of active sites on the surfaces of metal catalysts.

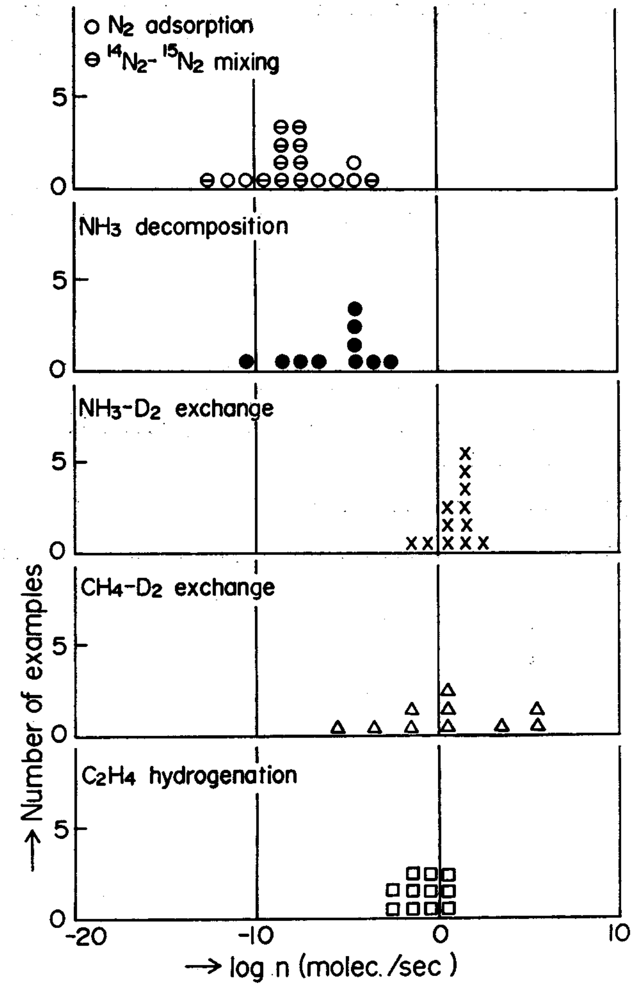

Fig. 2. Turnover numbers of various catalyses on metal catalysts.

600°C (B) both for 50 hr. The reaction on catalyst A was accelerated by coexisting hydrogen gas, but not with catalyst B. The log N_0 and log n are evaluated at 700°K and 10 mmHg as given in Table 1. As seen from the common kinetics and Eq. (1), log n should have a common value and coexisting hydrogen affects the value of N_0 alone. With catalyst A coexisting hydrogen increases the number of active sites, while it decreases with catalyst B probably by strong chemisorption of hydrogen.

The kinetics of ammonia decomposition was considerably different with catalysts A and B[3]. The results are given in Table 2, from which we see severe

TABLE 1. $^{14}N_2$-$^{15}N_2$ mixing reaction on doubly promoted iron catalysts

Catalyst	React. temp. °C	P mmHg	H_2	V mℓ STP/hr	log N_0*) (cm^{-2})	log n*) (molec./sec)
A	433	78	+	8.0	15.09	−4.43
	433	198	−	9.6	14.97	
	351	74	+	1.8	15.70	
	351	74	−	0.3	14.03	
B	408	160	+	5.6	15.07	−4.43
	408	129	−	6.3	15.16	

*) Calculated at 700°K and 10 mmHg.

TABLE 2. Ammonia decomposition on doubly propoted iron catalysts. 423°C, $V \propto P_{NH_3}^{x_A} P_{H_2}^{x_H}$

Catalyst	V mℓ STP/min	E kcal/mole	x_A	x_H	logN_0*) cm^{-2})	log n*) (molec./sec)
A	27.5	43.5	0.17	−0.07	14.34	−1.55
B	14.7	48.0	0.41	−0.41	13.31	0.04

*) Calculated at 700 °K and $P_{NH_3} = P_{H_2} = 10$ mmHg.

TABLE 3. K_2O effect on $^{14}N_2$-$^{15}N_2$ mixing reaction at 403°C and 188 mmHg over singly promoted iron catalyst reduced at 600°C for 72 hr

K_2O wt %	E kcal/mole	x_A	log N_0*) (cm^{-2})	log n*) (molec./sec)
0	25.2	0.1	15.24	−3.97
0.33	32.6	0.5	14.32	−3.14
0.58			14.25	
1.54			14.31	

*) Calculated at 700°K and 10 mmHg.

reduction of catalyst decreases N_0, but considerably increases n, suggesting that by severe reduction the catalyst surface is covered more by K_2O and some special interaction is formed between surface iron and K_2O to accelerate the ammonia decomposition. The promoting action of K_2O for isotopic mixing of nitrogen gas was investigated by one of the present authors (A. K.)[3]. Table 3 shows that K_2O similarly decreases N_0 and inrceases n.

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