JOURNAL OF CATALYSIS 55, 36–42 (1978)

Studies on the Catalysis by the Molten Metal

XI. An Analysis of an Anomalous Catalytic Activity of In–Sn Liquid Alloy in the Dehydrogenation of 2-Butanol

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Received January 4, 1978; revised June 16, 1978

Measurements of the rate of 2-butanol dehydrogenation over the In–Sn liquid alloy catalyst have been carried out. In addition, the surface tension of the liquid alloy has been measured at high temperatures and under the atmosphere of 2-butanol vapor. It has been found that the catalytic activity vs catalyst composition curve has a maximum at In/Sn ≒ 1. Furthermore, interesting information about the adsorption of 2-butanol has been obtained from the surface tension data. By assuming a surface unimolecular reaction mechanism, the Hinshelwood–Lindemann's theory has been applied to analyze the experimental data. Thus, it has been shown that the curious relation between the catalytic activity and the catalyst composition is ascribed to the following reasons. (i) The admolecules at In/Sn ≒ 1 have the largest effective internal freedom. (ii) The admolecules with the largest internal freedom must have the smallest chance to be activated. (iii) If activated, however, such admolecules are brought to the most strongly energized state. (iv) Hence the admolecules at In/Sn ≒ 1 are able to have the shortest lifetime and decompose with the highest rate.

INTRODUCTION

Much scientific information concerning the catalysis by the liquid metal has been accumulated by the present authors (*1–10*), and a practical application of the liquid metal catalyst has been shown to be promising (*11*). On the contrary, except for the review of Schwab (*12*), little information about the catalysis of liquid alloy is available. Considering this situation, the present authors have attempted to clarify the mechanism of the catalysis of the binary liquid alloy.

The purpose of this paper is to report the result of a kinetic study on the catalytic dehydrogenation of 2-butanol over In–Sn liquid alloy. Surface tension data have been added to discuss the role of adsorption in catalysis.

EXPERIMENTAL METHODS

Catalysts

Indium (In, 99.999%) and tin (Sn, 99.999%) were commercially obtained and used as raw materials to make In–Sn alloys of various compositions. Nearly the same techniques as those reported in a previous paper (*6*) were used in alloy making. Briefly speaking, they are as follows. Namely, the crude alloy was made by means of a vacuum melting followed by a reduction with purified hydrogen, and then only the purified part of the liquid

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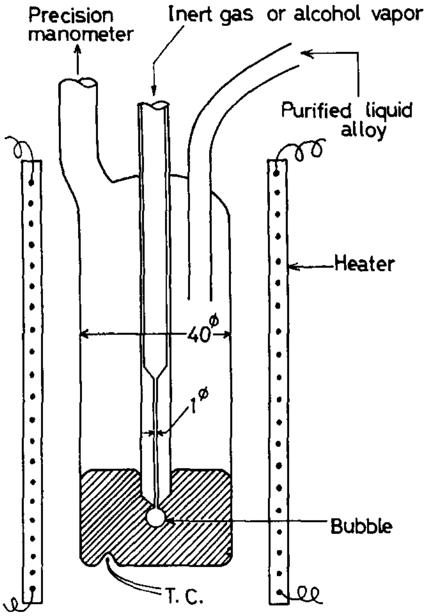

FIG. 1. A schematic drawing for the surface tension cell designed on the basis of the maximum bubble pressure method.

alloy was transferred through a vacuum line into the reactor.

Activity Measurements

The activity of the liquid alloy catalyst was measured by a flow type apparatus equipped with a rectangular duct reactor (*5*). The dehydrogenation of 2-butanol was chosen as a test reaction, and the apparent first order rate constant k_{app} was evaluated by the method reported previously (*5*). The experimental conditions were as follows: temperature = 465, 485, and 500°C; pressure = 1 atm; molar feed rate of 2-butanol vapor = 0.0954 mole/hr. The reaction products were analyzed by means of a gas chromatography under the following conditions: column = activated charcoal, 2.3 m (for gaseous products) or polyethylene glycol-6000, 2.5 m (for liquid products); carrier gas = He; temperature = 100°C.

Surface Tension

In order to obtain information about the adsorption of 2-butanol vapor on the surface of the liquid alloy, the surface tension of the catalyst at high temperature (250–380°C) was measured by applying the maximum bubble pressure method (*13*). The surface tension cell used for this measurement is schematically shown in Fig. 1. The reliability of this cell was ascertained by measuring the surface tension of pure In or Sn under the atmosphere of an inert gas (He or H_2) and by comparing the result with the literature value (*14*). In the present paper, the surface tension data obtained in the atmosphere of an inert gas are expressed by σ_0, and those obtained in the atmosphere of 2-butanol vapor are expressed by σ. As shown below, the difference between σ_0 and σ is available for the discussion of the adsorption of 2-butanol vapor on the liquid alloy catalyst.

RESULTS AND DISCUSSION

Catalytic Activity

The observed relation between the catalytic activity k_{app} and the alloy composition C_1^b (atomic fraction of In) is shown in Fig. 2. As shown in Fig. 2, each activity vs composition curve has a maximum and a minimum. In other words, the curve deviates greatly from the straight line representing the additivity of the catalytic activities of the alloy components (In and Sn). This result cannot be attributed to experimental errors. The application of the first order kinetics to the dehydrogenation of a secondary aliphatic alcohol had been justified in previous works (*5, 6*). Furthermore, the reproducibility of the experimental result was good (within a few percent deviation), and the selectivity of the reaction was excellent (over 95%). Therefore, the complex activity vs composition curve observed in the present work has to be regarded as a manifestation of the intrinsic activity of the In–Sn liquid alloy system.

Surface Tension and Adsorption of 2-Butanol Vapor

It is reasonable to expect that adsorption data would provide useful information for the interpretation of the observed catalytic activity, i.e., k_{app} vs C_1^b relation. It is apparent from the surface tension data given in Fig. 3 that the adsorption of 2-butanol vapor on the liquid alloy catalyst is appreciable. On contacting the 2-butanol vapor with the liquid alloy, the surface tension (σ) decreased appreciably from the reference value (σ_0) which was determined in He atmosphere. This indicates that the adsorption of 2-butanol vapor took place. On the other hand, Fig. 3 shows that the surface tension measured in H_2 atmosphere was essentially the same as that measured in He atmosphere. This means that the adsorption of H_2 did not take place.

According to the theory of surface tension (*13*), the change in the surface tension ($d\sigma$) of a binary liquid mixture which is in equilibrium with a gas of pressure p is given by

$$-d\sigma = \Gamma_1 kT\left\{\frac{1+\partial\ln\gamma_1/\partial\ln x_1^b}{x_1^b(1-x_1^b)}\right\}dx_1^b + \Gamma kTd\ln p, \qquad (1)$$

where k is the Boltzmann's constant, T is the absolute temperature, γ_1 is the activity coefficient of the component specified as 1, x_1^b is the mole fraction of the component 1, Γ_1 is the surface excess of 1, and Γ is the adsorption of the gas (or vapor).

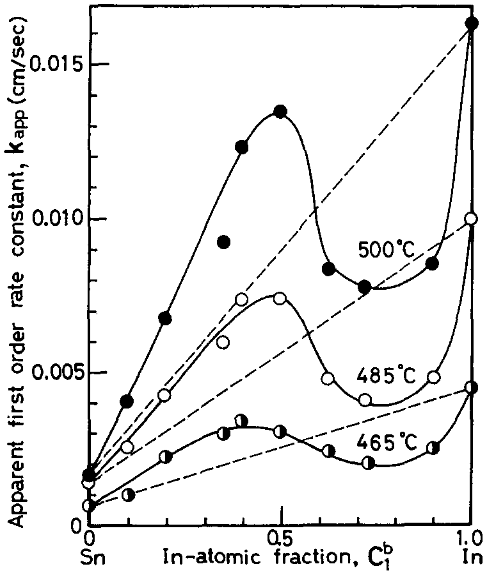

FIG. 2. Relations between the catalytic activity and the composition of the In–Sn liquid alloy.

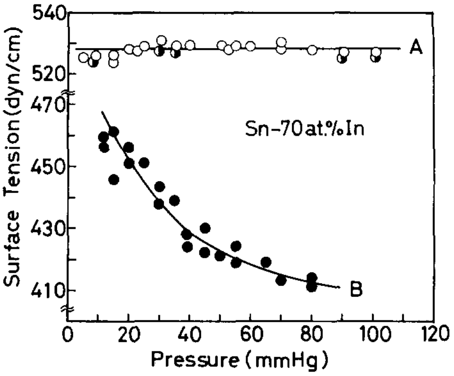

FIG. 3. A typical change of surface tension at 350°C; (A) in H_2(○) and He(◐); (B) in 2-butanol vapor.

When the composition (x_1^b) of the liquid mixture is held constant ($dx_1^b = 0$) and the pressure (p) is taken as a variable, Eq. (1) gives

$$-d\sigma = kT\Gamma d\ln p \qquad (2)$$

or

$$F = \sigma_0 - \sigma = kT\int_0^p \Gamma d\ln p. \qquad (3)$$

In this equation, the adsorption Γ must have a form capable of representing the experimental $F - p$ relation.

In the present work, the Langmuir adsorption isotherm was assumed for Γ to integrate the right side of Eq. (3). The result is

$$(\sigma_0 - \sigma)/N_s kT = \ln(1 + K_a p), \qquad (4)$$

where N_s is the number of adsorption sites

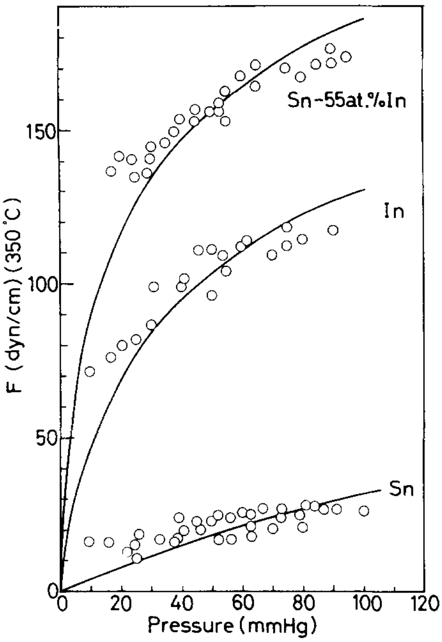

FIG. 4. Examples of the surface tension change accompanied with the adsorption of 2-butanol vapor.

per unit surface area of the liquid alloy, and K_a is the adsorption coefficient (adsorption equilibrium constant) for the 2-butanol vapor.

Applications of Eq. (4) to the experimental data give Fig. 4 and Fig. 5. As illustrated in Fig. 4, the Langmuir adsorption isotherm agreed fairly well with the experimental data. The number of adsorption sites N_s was evaluated to be 3 to $7 \times 10^{14}/\mathrm{cm}^2$. This value suggests that almost all of the surface atoms are available as the adsorption sites. Further it was found that the value of N_s is insensitive to the variation of the catalyst composition. Namely, the value of N_s varied little with the change in the composition of the liquid alloy. On the contrary, as shown in Fig. 5, the value of K_a was found to depend much upon the composition of the liquid alloy.

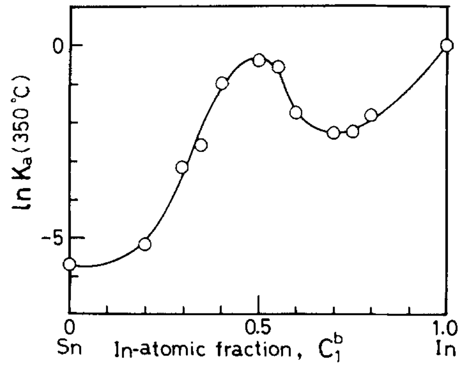

FIG. 5. The relation between the adsorption coefficient (K_a) and the bulk composition of the liquid alloy.

A striking parallelism between the k_{app} vs C_1^b relation (Fig. 2) and the K_a vs C_1^b relation (Fig. 5) suggests that the adsorption of 2-butanol vapor plays some important roles in the catalysis over the liquid alloy. In order to serve further discussions on the relation between the adsorption and catalysis, the heat of adsorption ($-\Delta H_{\mathrm{ads}}$) and the entropy of adsorption (ΔS_{ads}) were evaluated from the temperature dependence of K_a or $\sigma_0 - \sigma$. The results are shown in Fig. 6a and b. It must be pointed out that both $-\Delta H_{\mathrm{ads}}$ and $-\Delta S_{\mathrm{ads}}$ have their respective maximum and minimum at In/Sn ≒ 1 where the catalytic activity k_{app} was found to have the maximum value.

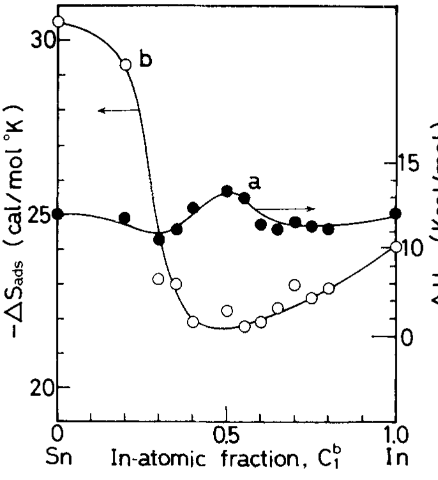

FIG. 6. Variations of the heat of adsorption and the entropy of adsorption on changing the composition of the liquid alloy.

Reaction Mechanism and Kinetic Parameters

In order to have a clear understanding of the relation between the catalytic activity (k_{app}) and the adsorption characteristics ($-\Delta H_{ads}$ and $-\Delta S_{ads}$), it is necessary to have information about the reaction mechanism. For this purpose, the results of previous works (*5*, *6*) are useful. These works had revealed that the molecules adsorbed on the catalyst are mobile and the dehydrogenation of alcohol over the liquid metal catalyst proceeds by a surface unimolecular reaction mechanism, i.e.,

$$A \overset{K_a}{\rightleftharpoons} A_{ads},$$

$$A_{ads} + A_{ads} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^*_{ads} + A_{ads}, \qquad (5)$$

$$A^*_{ads} \xrightarrow{k_3} \text{products},$$

where * indicates an activated molecule and k_1, k_2, and k_3 are the rate constants.

On the basis of the reaction mechanism given by Eq. (5), it had been shown (*6*) that, when the adsorption is almost saturated, the apparent first order rate constant is expressed by

$$k_{app} = N_s K_a k_3 (k_1/k_2)/(1 + K_a p). \qquad (6)$$

The value of k_{app} has already been obtained by the activity measurements, and the value of K_a at the reaction temperature is obtainable by extrapolating the temperature dependence of the surface tension $(\sigma_0 - \sigma)$. Thus, it is possible to evaluate the composite rate constant $k_3(k_1/k_2)$ from Eq. (6).

According to the theory of Hinshelwood–Lindemann (*15*), the composite rate constant is given by

$$k_3(k_1/k_2) = k_3 \frac{1}{(s-1)!} (E_0/kT)^{s-1} \times \exp(-E_0/kT), \qquad (7)$$

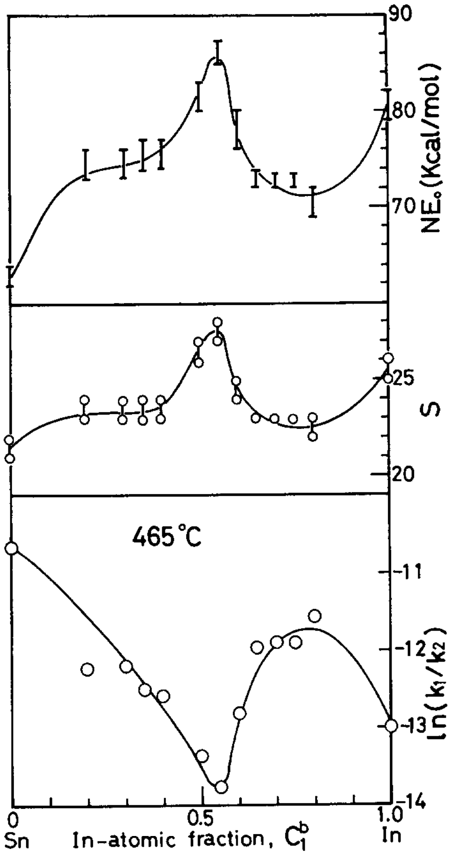

FIG. 7. Variations of kinetic parameters s, E_0 and k_1/k_2 on changing the composition of the liquid alloy.

where s is the effective internal freedom of the reacting molecule, E_0 is the critical energy per molecule required to bring about unimolecular reaction.

Although the original purpose of the Hinshelwood–Lindemann's theory is to treat the unimolecular reaction in a homogeneous gaseous phase, there seems no reason to deny the extended application of Eq. (7) to the present case where a two-dimensional (surface) unimolecular reaction is considered to be taking place. Of course, s and E_0 have to be regarded as the kinetic parameters for the adsorbed molecules, and $1/k_3 = \tau$ has to be considered as the lifetime of an adsorbed energized molecule.

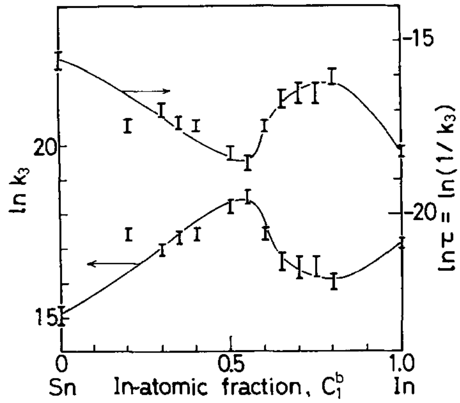

FIG. 8. Variations of kinetic parameters k_3 and τ on changing the compositions of the liquid alloy.

Interpretation of the Catalytic Activity (k_{app} vs $C_1{}^b$)

Interesting results have been obtained by applying the above-mentioned theory to our experimental data. Namely, the relations s vs $C_1{}^b$, NE_0 vs $C_1{}^b$ (N, Avogadro's number), $\ln k_3$ vs $C_1{}^b$ which are shown in Figs. 7 and 8 indicate that the respective maxima of s, E_0 and k_3 appear at In/Sn $\fallingdotseq$ 1. Furthermore, Figs. 7 and 8 show that the respective minima of k_1/k_2 and $1/k_3$ (lifetime τ) also appear at In/Sn $\fallingdotseq$ 1. As already mentioned, the composition In/Sn $\fallingdotseq$ 1 was the special point where K_a and $-\Delta H_{\text{ads}}$ became maximum and $-\Delta S_{\text{ads}}$ became minimum. Thus it seems worthwhile to discuss why the kinetic parameters (k_{app}, s, NE_0, k_1/k_2, τ) show anomalies at In/Sn $\fallingdotseq$ 1 where the adsorption parameters also show anomalies.

Probably, the smallest entropy of adsorption ($-\Delta S_{\text{ads}}$) at In/Sn $\fallingdotseq$ 1 indicates that every admolecule is able to have a variety of adsorbed states during its stay on the liquid alloy of this composition. According to this view, the majority of atoms in the admolecule would have a chance to interact with the catalyst surface. Such a situation in the admolecule would result in the largest increase in the effective number of bonds in the admolecule participating the reaction. In other words, the situation would enable the admolecule to have the largest effective internal freedom s. Furthermore, when the energy of interaction between the catalyst surface and any one atom constituting the admolecule is not much different from a certain average value, the heat of adsorption $-\Delta H_{\text{ads}}$ would have the largest value at In/Sn $\fallingdotseq$ 1 where the number of atoms interacting with the catalyst surface is probably the largest.

The largest effective internal freedom of the admolecule on the catalyst of In/Sn $\fallingdotseq$ 1 seems to be responsible for the largest activation energy E_0 at this composition (Fig. 7). When an admolecule has a large s value, the total internal energy is distributed among a number of internal freedoms, and hence only a part of the total energy is stored in the >CH–OH group which has to be activated in the dehydrogenation reaction. Therefore the largest activation energy per molecule (E_0) is required to activate the >CH–OH group of the admolecule with the largest s value. On the other hand, the chance for an admolecule to get such a high activation energy by a surface collision would be small. Therefore, it is quite reasonable that k_1/k_2 became minimum at In/Sn $\fallingdotseq$ 1 where E_0 is maximum. On the contrary, the highly energized admolecule is able to decompose rapidly, and hence its lifetime τ would be shortest. Thus the smallest τ value at In/Sn $\fallingdotseq$ 1 is reasonable.

As mentioned above, the kinetic aspects of the activity versus composition anomaly observed at In/Sn $\fallingdotseq$ 1 were explained on the basis of the Hinshelwood–Lindemann's theory of unimolecular reaction and the surface tension data (adsorption data). It is expected that applications of more advanced theories of unimolecular reaction (*15*) would clarify further details of the reaction mechanism. Furthermore, structures and physical properties of the liquid alloy surface which govern the adsorption and catalysis have not yet been clarified. Probably, the anomalous catalytic behavior of the In–Sn alloy is caused by some changes in the surface composition. All these problems are open to future study.

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