17. The Activated Adsorption of Methane on Reduced Nickel.

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It is well known that a nickel catalyst is highly active for the decomposition of methane, but the mechanism of the catalysis is still unknown. Some studies on catalysis in connection with activated adsorption have recently been done, but the system of methane-nickel has not yet been investigated. O. Schmidt reported that methane is not so much adsorbed on nickel and a simple adsorption isobar indicating no occurrence of activated adsorption was obtained in the temperature range between room temperature and 230°C. H. S. Taylor and others, however, concluded from their researches upon the exchange reactions between methane and CD₄ or D₂ that the activated adsorption of methane of a dissociative type took place on the surface of nickel above 138°C. Under Prof. S. Horiba’s guidance, the author attempted

![Diagram of experimental setup](image)

Fig. 1.—Apparatus.

- S Sorption vessel.
- T Automatic Töpler pump.
- D Diffusion pump.
- M₁ McLeod manometer.
- M₂ Ordinary manometer.
- A Apparatus for gas analysis by thermal conductivity.
- B Gas burette for ordinary gas analysis.
- V Standard volume of 220 c.c.

to elucidate the nature of the activated adsorption by direct measurement of the adsorption using nickel carefully prepared.

Experimental\(^3\)

The main part of the apparatus used is shown in Fig. 1. The experiments were carried out at low pressures (10^{-3}–5 mm.). Methane were prepared from aluminium carbide and water.\(^2\) Nickel oxide was prepared by calcination of the nitrate at 350°C. The oxide of 15 g. was put in a sorption vessel (S) and thoroughly reduced by hydrogen. Hydrogen was passed for 3 days at 350°C. in the case of Ni(I) and for 5 days at 250°C. in the case of Ni(II).

Results

Adsorption at Low Temperatures.

In the temperature range between −112°C and 20°C., adsorption equilibrium was established within several minutes after methane was introduced. The gas adsorbed was easily removed. The value of the heat of adsorption obtained was 1 kcal./g. mol for both Ni(I) and Ni(II). It is evident that the adsorption in this temperature range is van der Waals’ adsorption.

Adsorption above 40°C.

At high temperatures above room temperature, an adsorption different from that of van der Waals was observed, which we call activated adsorption. The activated adsorption took place in measurable rate at 100°C. in Ni(I), and even at 40°C. in Ni(II) which was more active. At such a low temperature, however, adsorption equilibrium was hard to be established. At 100°C., 130°C. and 170°C. it took more than 5 days, 3 days and 1 hour respectively for Ni(I) to reach equilibrium. As to Ni(II), equilibrium was established more rapidly. The adsorbed amount rapidly decreased with the rise of temperature.

To obtain the adsorption isobar, a number of experiments were carried out at various temperatures and pressures. An isobar at 0.01 cm. with Ni(I) is shown in Fig. 2 and at 0.0001 cm. with Ni(II) in Fig. 3.

On the Reproducibility of Results.

Methane adsorbed above room temperature can be desorbed by evacuation at high temperatures. At 200°C. it was completely desorbed in 1 hour and reproducible results were obtained. The adsorbability of surface, however, is decreased after methane has been adsorbed at higher temperatures than 250°C. This may be attributed to the formation of nickel carbide above that temperature,\(^5\) but the activity could be recovered to its original value by passing hydrogen at the same temperature for 24 hours.

2) Kubokawa, ibid., 11, 82 (1937).
3) Scheffer, Dokkum and Al, Rec. trav., 45, 803 (1926).
Fig. 2.—Adsorption isobar of methane at 0.01 cm. for Ni(I).

Fig. 3.—Adsorption isobar of methane at 0.0001 cm. for Ni(II).
Allmand and Chaplin suggested that the activated adsorption may not be a new type of adsorption but the phenomenon of displacement of such a surface impurity as adsorbed oxygen or unreduced oxide. This interpretation, however, cannot be applied to the present experiments, because the adsorbability of the surface remained constant in repeated experiments at various temperatures and moreover the activated adsorption disappeared when nickel was poisoned with a small quantity of air.

Then, the question is whether the activated adsorption of methane is a dissociative adsorption which severs the C-H bond or not. The following experiments were carried out to solve the question.

**Analysis of the Desorbed Gas.**

Methane which was in the state of activated adsorption was taken out by means of an automatic Topler pump and analysed by the thermal conductivity method. After Ni(I) was highly evacuated at high temperatures, methane was adsorbed at 150°C for 5 days. One of the experiments showed that the gas desorbed for the first 1 minute was pure methane while in the gas desorbed for the next 30 minutes 14% of hydrogen was detected, and then hydrogen gradually became rich. This evidence leads to the conclusion that the activated adsorption of methane is a dissociative adsorption severing the C-H bond and that the dissociated hydrogen is strongly adsorbed on the surface or diffused into the nickel lattice, so that it is difficult to escape into the gas phase. It follows, therefore, that the adsorbability of hydrogen has much influence upon the measurement.

**Kinetics of the Activated Adsorption.**

It is necessary to know whether the measured velocity of the activated adsorption of methane is the velocity of the dissociation of the C-H bond or the diffusion velocity of the dissociated hydrogen into the interior of the catalyst. Therefore, the velocity of the adsorption of hydrogen as well as the adsorption isotherm and isobar were measured with the same catalyst.

It was found that the sorption velocity of hydrogen was very large compared with that of methane and moreover the measured velocity did not obey the diffusion law. Hence, the observed velocity should be the surface reaction velocity. Hydrogen was found to be adsorbed so much, e.g. 100 times as much as methane at 130°C.

From the reversibility of the surface reaction the rate of sorption is expressed by the equation

$$-\frac{dp}{dt} = k_1 p (1-\theta) - k_2 \theta,$$

where $p$ is the pressure of methane, $k_1$ and $k_2$ constants, and $\theta$ the fraction of the surface covered with the adsorbed methane. Taking

(1−θ) to be 1 when the adsorbed amount is small, the equation reduces to
\[ -\frac{dp}{dt} = k(p - p_e), \]
where \( p_e \) is the equilibrium pressure, as a limiting expression both for adsorption and desorption.\(^1\)

Integrating this, we have
\[ \log(p - p_e) = \log(p_o - p_e) - 0.4343kt, \]
where \( p_o \) is the initial pressure of methane. The linear relation between \( \log(p - p_e) \) and \( t \) in this equation was always satisfied as is shown in Fig. 4, and hence the velocity constant of the activated adsorption, \( k \), was easily obtained. The linear relation between the logarithm of \( k \) and \( \frac{1}{T} \) as required by Arrhenius’ equation is shown in Fig. 5. As the activation energy for the activated adsorption of methane 7 kcal./g. mol was obtained in both Ni(I) and Ni(II).

**Discussion**

The activated adsorption of methane is considered to be followed by a successive dissociation of the C−H bonds, such as
\[ \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \rightarrow \text{CH}_2 + 2\text{H} \rightarrow \text{CH} + 3\text{H} \rightarrow \text{C} + 4\text{H}. \]

Methane will be formed and desorbed by the reverse process of the hydrogenation of the C–H radicals. Carbon crystals will be also formed during the course of the experiments which was confirmed by the fact that the adsorbed amount by the activated adsorption was considerably large compared with the saturation value of van der Waals' adsorption of methane. But the adsorption on the separated carbon or the formation of nickel carbide will be negligible in the present experiments as justified by the reproducibility of the experimental results already mentioned.

The obtained activation energy is for the initial stage of the adsorption, and so it is regarded as that for the 1st stage, \( \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \), of the catalytic decomposition of methane on the surface of nickel; the following consideration is possible in comparison with the data of Taylor and his coworkers\(^1\) They obtained 19 kcal./g. mol as the activation energy for the exchange reaction between \( \text{CH}_4 \) and \( \text{CD}_4 \) on the surface of nickel. This value is considered to be nearly equal to the activation energy for the desorption of methane which is dissociated in \( \text{H} \), \( \text{CH}_3 \), \( \text{CD}_3 \), etc. Accordingly, when the difference between the zero point energy of the C–H bond and that of the C–D bond is neglected, the following value is obtained as the heat of activated adsorption of methane on the surface of nickel: \( \Delta H = 19 - 7 = 12 \text{ kcal./g. mol} \).

It is note-worthy that the value of 100 kcal.\(^2\) for the activation energy of the reaction \( \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \) in the gaseous phase is reduced only to 7 kcal., if the reaction occurs on the surface of nickel.

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1) Loc. cit.
2) e. g. Rice and Dooley, *J. Am. Chem. Soc.*, 56, 2747 (1934).