THE CATALYSIS OF NICKEL ON THE THERMAL DECOMPOSITION OF METHANE.

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The catalytic decomposition of methane has been studied by Kunsetzow[1], Sabatier and Sendrens[2], Slater[3] and recently by Cantelo[4]. Nickel is generally known as the most excellent catalyst for hydrogenation and dehydrogenation in organic chemistry. It is, however, to be remarked that the efficiency of the catalyst depends greatly upon the conditions of preparing and reducing of it.

As seen from Cantelo's experiment[4], nickel is the most efficient catalyst also for the thermal decomposition of methane. But it is doubtful whether the conditions to prepare an efficient catalyst may be identical both for methane decomposition and for hydrogenation or not, i.e. whether an catalyst suitable for hydrogenation may be equally efficient for methane decomposition or not. The author has made some investigations on this point.

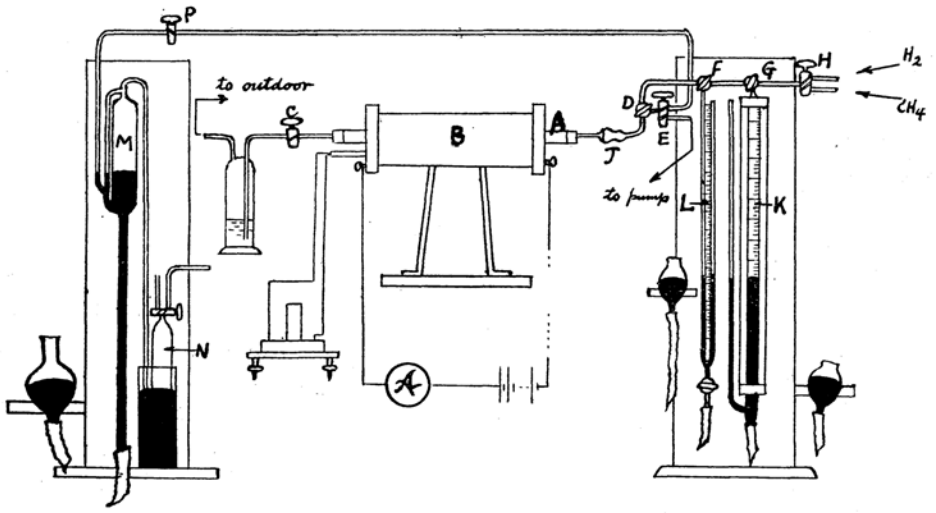

Fig. 1.

(1) *Ber.*, **40** (1907), 2871.
(2) *Ann. chim. phys.*, **4** (1905), 435.
(3) *J. Chem. Soc.*, **109** (1916), 106.
(4) *J. Phys. Chem.*, **28** (1924), 1036.

Experimental Part.

In experiments the author has employed an apparatus shown in Fig. 1 which is practically identical with Slater's apparatus except some modifications.

The boats, filled with definite amounts of powdered catalyst are carefully pushed into the silica tube A (length 400 mm. and internal bore 15 mm.) through the joint J. Hydrogen is then passed through the cocks H, G, F and D for a definite time in order to reduce the catalyst, the silica tube being heated to a desired temperature by means of the electric furnace B. When the reduction finishes, stop-cocks C and F are closed and E opend, the whole is exhausted to a vacuum by an oil pump and further by the Töpler's pump M.

Methane is introduced into the burette K through the cock H. The mercury in the manometer must have been previously raised to the stop-cock F.

In the next place the electric furnace is adjusted by the help of a variable resistance to a desired temperature and then methane is introduced into the tube A through the cocks G and F until the manometer L shows the atmospheric pressure. Immediately, the methane in the tube is decomposed and the manometer L shows a gradual increase of the internal pressure. The reaction is allowed to proceed for the required time (10 minutes), and at the end of it, F is closed and E opened, thus allowing most of the gas to be drawn over into the vacuous portion of the Töpler's pump M.

Lastly, a sample of the gas is pumped out into the burette N and analysed for the determination of hydrogen content in it. The rate and degree of the decomposition of methane on each catalyst can be also examined, although in a rough manner, by observing the manometer L.

As it has been found very convenient for the experimental work to be possible to reproduce catalysts of consistent activity, the author has used the following method to prepare a catalyst according to E.F. Armstrong and T. P. Hilditch.[1] A boiling aqueous sodium carbonate is added in slight exess to a boiling solution of nickel sulphate. The precipitated hydroxide and basic carbonate are collected on a filter and throughly washed, until the filtrate shows no reaction for sulphate or carbonate, and then dried at 100°C.

Before proceeding to the study of the activity of the catalyst, the catalytic effect of the walls of the silica tube and porcelain boats employed has been examined in the absence of catalyst in various temperatures. The results are shown in Table 1.

(1) *Proc. Roy. Soc.* (London), A. 103 (1923), 586.

TABLE. 1.

Reaction temperature	Hydrogen produced	Reaction temperature	Hydrogen produced
600°C	0.2%	850°C	3.4%
650	0.6	900	14.7
700	0.9	950	22.1
750	1.6	1000	37.5
800	2.1		

The amount of hydrogen produced in consequence of the decomposition of methane by the mere catalysis of the walls is thus found to be not more than 15% even at 900°C. and only 3.4% at 850°C.

For reducing the catalyst hydrogen is, in all the experiments, streamed through the tube at the rate of 1 litre per hour, as it has been ascertained by a preliminary experiment that this rate is nearly enough (see Table 2). In this case reducing is conducted at 600°C., streaming hydrogen over one gram of the catalyst for one hour.

TABLE. 2.

Velocity of H_2-stream	Hydrogen produced	Velocity of H_2-stream	Hydrogen produced
$1\frac{\text{litre}}{\text{hour}}$	15.60%	$4\frac{\text{litre}}{\text{hour}}$	16.01%
2	16.26	5	16.20
3	16.18		

The Effect of Reduction Temperature. The boats, each filled with 1.5 gr. of the catalyst is pushed into the reaction tube, and the catalyst is reduced by passing hydrogen through the tube at various temperature with the velocity of 1 litre per hour.

When the reduction finishes, the temperature of the furnace is raised to 850°C. and the activity of the catalyst is examined, introducing methane in the tube and allowing the reaction to proceed for 10 minutes.

Table 3 and Fig. 2 show the effect of reduction temperature of the catalyst on the yield of hydrogen.

TABLE 3.

Reduction temperature	Hydrogen produced	Reduction temperature	Hydrogen produced
300°C	22.10%	600°C	51.13%
400	32.54	700	48.50
500	41.75	800	46.51

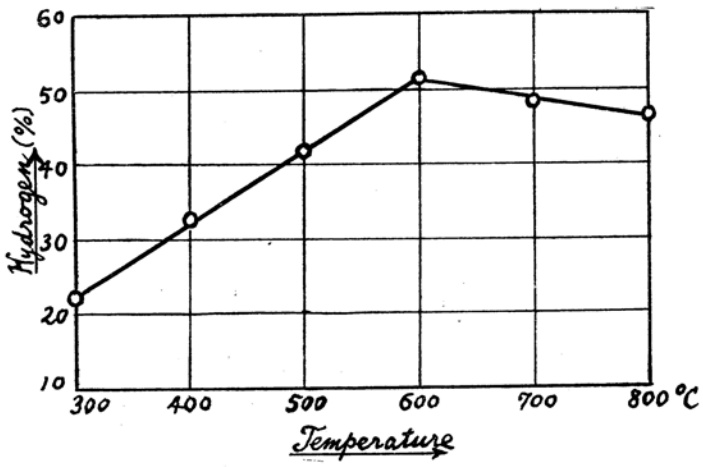

Fig. 2.

The catalyst becomes more active in a notable extent with the increase of reduction temperature until it reaches 600°C., while above this temperature its increase causes, on the contrary, a gradual decrease of activity. In order to give the highest activity to the catalyst, therefore, reduction must be conducted at 600°C. This conclusion is very interesting in contrast with the results obtained by many authors in the studies of hydrogenation where the optimal temperature of reduction has been determined to be about 400°C. and a catalyst reduced at above 500°C. has been generally known to be poor in activity.

The Effect of Reducing Duration. In order to know the effect of reducing duration, each catalyst reduced for different duration is tested on its activity in the same way as above. The result is shown in Table 4. and Fig. 3.

TABLE 4.

Reduction temperature : 600°C.
Reaction temperature : 850°C.
Reaction time : 10 minutes.

Reducing duration	Hydrogen produced	Manometer reading	Reducing duration	Hydrogen produced	Manometer reading
8 hour	45.99%	20 cm.	19 hour	53.55%	24 cm.
10	48.23	23	20	31.00	15
12	51.13	25	22	30.10	14
14	53.09	29	24	30.14	14
16	57.20	32	26	30.08	14
18	63.50	28.5 34.	30	30.20	14

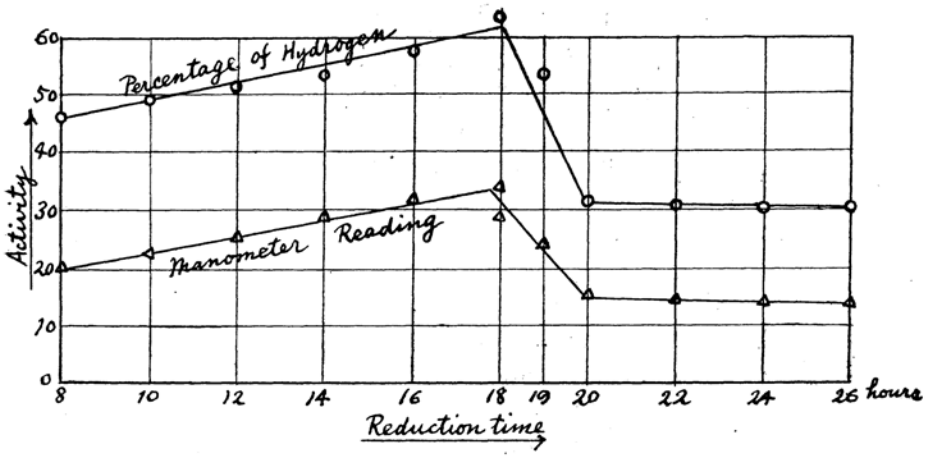

Fig. 3.

It is seen that the activity of the catalyst increases in proportion with duration of the reduction until it reaches to 18 hours, while a little longer reduction than that time causes, on the contrary, a sudden decrease of activity. The highest activity is thus obtained by reducing the catalyst for 18 hours. In order to determine the extent to which the reduction has taken place in the case of the maximum activity, the catalyst is analysed by the ferric chloride method for the determination of nickel in the presence of its oxide[1] and found to contain 79.5 per cent of the total nickel as reduced metallic one.

This result leads to the conclusion that also for the decomposition of methane, a partially reduced nickel catalyst (Ni-NiO) is better than a completely reduced one, what has been already ascertained in the case of hydrogenation by Boswell and other investigators.

The poor activity attained after 20 hours reduction is no more altered by reducing the catalyst further, and this seem to show that at least the surface of it has been completely reduced and accordingly has become very poor in activity.

The lower curve in Fig. 3 indicates the readings of the manometer in the experiments, of course giving a parallel result to that of the analysis.

The Durability of Activity. To study the durability of catalystic activity in an exact manner it is necessary to construct a more suitable apparatus than that described above. However, the author has tried to examine how the activity of the catalyst has been affected by the carbon deposited on its surface in consequence of the decomposition of methane, simply using the same apparatus as in the above cases.

(1) Treadwell-Hall, "Analytical Chemistry," 1919, Vol. 2, p. 612.

Methane is introduced in the tube, as above described, which contains a boat filled with 1 gram of catalyst reduced at 600°C. for 9 hours, and the reaction is allowed to proceed at 850°C. After ten minutes the gas produced by the decomposition of methane is pumped out in the burette by the Töpler's pump and determined the hydrogen contained in it. Methane is again introduced in the same tube and after ten minutes the produced gas is similarly pumped out and analysed. In this manner the process has been repeated 30 times.

In the first time the manometer reading reaches 30 cm. corresponding to 57.5% yield of hydrogen and in the second time it decreases to 29 cm. corresponding to 56.8% hydrogen.

But in all the cases from the third to the thirtieth time, the manometer shows invariably the same reading with the second time, meaning no more decrease of the activity of the catalyst.

As the total quantity of methane used in the repeated reactions amounts to 3.6 litres of which about 40 per cent may be regarded to be decomposed into hydrogen and carbon, the amount of carbon deposited on one gram of the catalyst can be calculated approximately to be 0.6 gram. From this it is perceived that such a quantity of carbon deposit seems to have almost no effect on the activity of the catalyst.

In conclusion the author wishes to express his cordial thanks to Prof. M. Katayama for his valuable advices during the work and also to Mr. Z. Simizu for his earnest assistance.

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