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METHANE FORMATION FROM SOLID CARBON AND HYDROGEN BY THE USE OF PHYSICALLY MIXED CATALYSTS

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Methane formation from active carbon and H_2 by the use of physically mixed metal on silica catalysts was investigated. Methane formation was found only in the initial several ten minutes, by the end of which oxygen-containing functional groups on the surface of active carbon had been depleted. The reactivity of carbon was regenerated by the contact with gaseous oxygen. It is concluded that hydrogen atoms, dissociated on metal surface and transferred to the carbon surface by interparticle spillover, react with surface functional groups to yield methane.

The importance of coal gasification has stimulated interest in the hydrogenation of solid carbon yielding methane. "Catalytic Effect" on the reaction has already reported by many investigators[1-4]. Most of them used transition metals directly supported on a solid carbon, which ensures the direct contact of the two reactant, solid carbon and hydrogen , with the catalyst. From practical point of view, however, it is disadvantageous because metal catalysts lose their activities as the solid carbon is converted to gaseous products.

Only a few studies have been done on the "Catalytic Effect" of physically mixed catalyst -carbon system. It has been expected that conversion is limited by a poor contact of catalyst and carbon.[1] The objective of the present report is to show the catalytic effect of physically mixed catalyst-carbon system and to elucidate the nature of solid-solid contact catalysis. Also emphasis is placed on the method to increase the conversion of carbon.

All the catalysts, $Ni\text{-}SiO_2$, $Ni\text{-}Al_2O_3$, $Rh\text{-}SiO_2$ and $CoO\text{-}MoO_3\text{-}Al_2O_3$, were prepared by a conventional impregnation method. They were prereduced at 550°C. Active carbon (from Wako Pure Chem. Co.) was used as a reactant, the surface area of which was 1360 m^2/g. The mixture of carbon and catalyst, 1 : 1 of weight ratio and 100-150 mesh size fraction, was packed in an U-tube reactor. It was heated in helium flow up to 550°C and then was kept at the temperature for 30 min. The reaction was started by changing helium flow to hydrogen. Flow rate of hydrogen was 10 cm^3-STP/min.

Eluted gas was occasionally taken out by a sampling valve and analysed by gas chromatography, equipped with FID detector and a Goray column U. As an illustration of figures, methane concentration in effluent gas was plotted.

Fig. 1 shows methane formation from cargon without catalyst and from carbon-catalyst physical mixtures. Catalytic effect is apparent. Methane formation decreased with process time. Integration of the curve from 0 to 3 hr gives total conversion of carbon to methane to be 2 - 3%.[5)]

Significant characteristic is that the same curve of methane formation vs. time was observed both for Ni-SiO_2(5 wt% Ni) and Rh-SiO_2 (5 wt% Rh). Completely the same profile was observed also for Ni-SiO_2(20 wt% Ni) and Ni-Al_2O_3(5 wt% Ni).[7)] This indicates that the decline of the methane formation is not due to the decrease of catalytic activity but due to the decrease of carbon reactivity. This is contrary to the findings[2,3)] for various directly supported metal-carbon systems, where methane formation rate is significantly different from one another.

fig. 2 shows the effect of O_2-treatment for the catalyst-carbon mixture. The reactivity was regene-

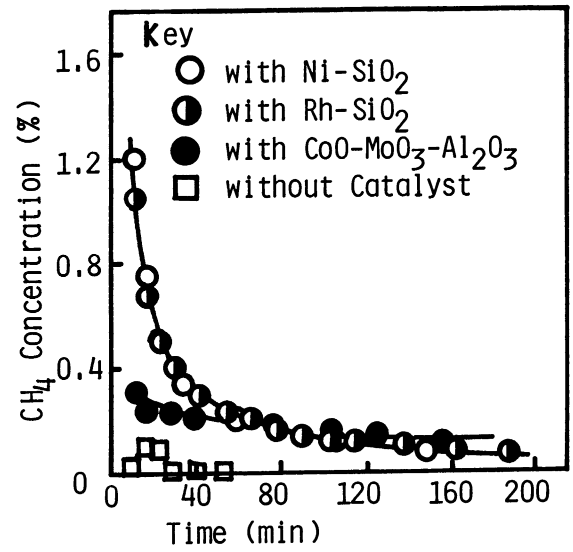

Fig. 1 Methane formation vs process time, with or without catalyst.
Reaction conditions: Temp.; 550°C, Catalyst; 1.0 g, Active carbon; 1.0 g H_2 flow rate; 10 cm^3-STP/min

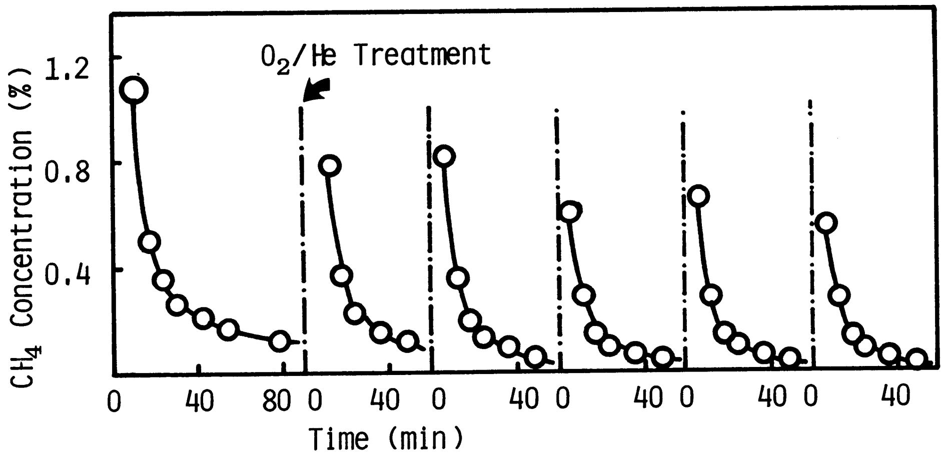

Fig. 2 Methane formation with physically mixed Ni-SiO_2: Effect of O_2/He treatment.
Reaction conditions: the same as given in Fig.1
Treatment conditions: 20%O_2-He flow, 5 min, at 550°C

rated by the treatment. Sequential cycles of the treatment-reaction were repeated for 5 times and total conversion of 5%5) was attained. It is noteworthy that all carbon may be catalytically converted to methane at 550°C by these cycles.

It is well known that various oxygen containing functional groups exist on the surface of active carbon. They decompose at an elevated temperature, giving CO_2 or CO. Thermal decomposition of active carbon in helium flow was studied by the use of conventional TPD (Temperature Programmed Desorption) apparatus, equipped with TCD detector for monitoring total response. Fig. 3 shows the results. The decomposed products were mostly CO_2 but small amount of CO was also formed at high temperature. Formation of H_2O was also observed, however, it did not contribute to the recorder response because effluent gas passed through a dryice - Methanol trap.

Comparison of curve a and b indicates that a considerable amount of functional groups remained even after heating at 550°C. The amount of CO_2, remained after treatment at 550°C but decomposed at 650°C, was amounted to 0.9×10^{-3} mol/g-A.C.. The value is comparable to the amount of methane produced by the hydrogenation, $0,5 \times 10^{-3}$ mol/g-A.C.. 0.5×10^{-3} mol/g-A.C. in the first 30 min and 1.7×10^{-3} mol/g-A.C. in 3 hours. Curve c and d shows the same experiments for the used catalyst - carbon mixture; curve c, after the reaction and curve d, after the reoxidation. No CO_2 was produced from the mixture after the reaction, but it appeared after the reoxidation. This clearly demonstrates the participation of oxygen containing functional groups in the methane formation. Rather surprisingly, all the functional groups, not only some special one which directly contacted with metal surface by chanee, were converted to methane.

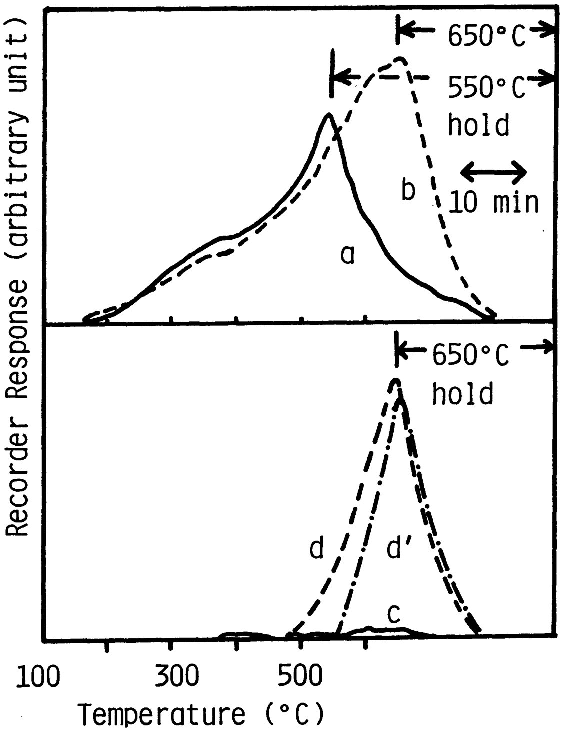

Fig. 3 Thermal decomposition of oxygen-containing functional groups.
Carrier gas: He, Temperature raise: 10°C/min
a, b: fresh active carbon,(without any pretreatment) c: catalyst-carbon mixture after the use for the reaction, d, d' : catalyst-carbon mixture after the reaction-reoxidation treatments. d being 5 min and d being 1 hr of helium purge(550°C)after the reoxidation(550°C). Arrows indicate that the temperature was held as indicated.

From these findings, following mechanisms can be depicted. H_2 dissociate on the metal surface. Resultant H atoms transfer to carbon surface through inert support (nórmal spillorver) and through the point of contact between catalyst and carbon. Then H atoms and surface functional groups react to yield methane without participation of the catalyst.

If the H_2 dissociation activity and the rate of hydrogen spillover are high enough, methane yield vs. time will show the same profile regardless of the employed catalysts, because over-all rate is limited by the non-catalytic process. This is the situation for Ni-SiO_2, Ni-Al_2O_3 or Rh-SiO_2. If, on the other hand, rate of H_2-dissociation is low, a different profile will be observed as for CoO-MoO_3-Al_2O_3 which is known as a "mild" hydrogenation catalyst.

Another possible mechanism for the formation of methane may be as follows: Thermal decomposition of functional groups gives CO_2 and CO and subsequent hydrogenation of CO_2/CO yields methane. Since Ni is an active catalyst for CO_2/CO methanation, the mechanism may be convincing. However, this is not the case because the thermal decomposition ceases to occur after 2 hr (see Fig. 3) while the formation of methane occurred to an extent of 0.35×10^{-3}mol/gA.C. even when the catalyst - carbon mixture was pretreated in helium flow for 2hr and then subjected to the reaction. Participation of water in the formation of methane can also be excluded because no effect was found when 20 Torr of water was added in H_2 flow.

It is suggested from our results that methane will not be formed by the reaction of lattice carbon and hydrogen if dissociated hydrogen atoms are supplied as a reactant. Direct methanation of carbon to methane needs a direct contact of carbon and hydrogen with the catalyst. Oxygen containing functional groups can be hydrogenated at 550°C if H atoms are supplied by any means. "Interparticle spillover"$^{6)}$ will be a practical method to produce H atoms on the surface of active carbon.

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References and Note

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7) In order to reduce too much complexity, data points were omitted for the results of Ni-SiO_2(20wt% Ni) and Ni-Al_2O_3.

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