As the limiting case, we get

$$\frac{dx}{dt} = \frac{A_2 - (x_2)_0^2}{1 + (A_2 - (x_2)_0) K_1 p}$$

which has an implicit expression as to $x$. Putting $(A_2 - (x_2)_0) K_1 p = \alpha$ and $(A_2 - (x_2)_0) = \beta^2$, we can rewrite the equation (6) as,

$$\beta \left( \frac{dx}{dt} \right)^{-\frac{1}{2}} = 1 + \alpha$$

which corresponds to the linear relationship between $\left( \frac{dx}{dt} \right)^{-\frac{1}{2}}$ and $t$. This relation was verified on the results of the authors for the adsorption of $H_2$ on Ni (2) and (3) Cu, carried by kieselguhr respectively, and those of Soller and others (4). The test of the equation showed that it was correct for the results observed under comparatively low pressure, e.g. 1/50 atms, pressure. The equation, however, was found not to hold under higher pressures.

This might be probably of the dependence of each elementary process or so remarkable inter-actions between the processes (1) and (2) that can not be neglected.

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22. Studies on the Rate of Reaction of $CH_4$ and $CO_2$. (II)

The Reaction of $H_2$ and $CO_2$.

Kimio Tarama, Syuichi Hayakawa, Hiroshi Ichikawa
and Shinji Funakoshi.

The rate of reaction of $CO_2$ and $H_2$, one of the reactions which might occur in the thermal reaction of $CH_4$ and $CO_2$, was measured by the flow method under the atm. pressure. Under the condition of the reaction temp. 1210-1310°K and the contact time 0.1-1.0 sec., the effects on the degree of conversion in compliance with the alteration of ratio of $CO_2/H_2$ were observed and the following results were obtained.

1. This reaction is heterogeneous because the rate of reaction is accelerated in the reaction vessel when packed with some quartz fragments.

2. Under the constant velocity of total flow, the reaction rate seems to increase according to the increase of $CO_2$ content, while there is no apparent change in the range of the ratio $CO_2/H_2$ larger than unity.

3. When the velocity of $CO_2$ flow is constant, the conversion of $CO_2$ decreases according to the increase of $H_2$ quantity, but when the velocity of $H_2$ flow is constant, the conversion of $H_2$ increases, though slightly, as $CO_2$ increases in spite of shortening the contact time.
4. These results are qualitatively explained by the velocity equation which is derived from the assumption that the reaction of $\text{H}_2$ with $\text{CO}_2$ activated by the adsorption on the quartz surface is the rate determining step, and that the $\text{CO}_2$ adsorption is retarded markedly by the adsorptions of $\text{H}_2\text{O}$ produced.

5. The apparent Arrhenius' activation energy of this reaction is 25 Kcal.

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Kimio Tarama and Toshiaki Kubota.

To clarify the mechanism of the catalytic isomerization, decomposition and alkylation reactions of n-heptane by $\text{AlCl}_3$, the conductivities of catalyst layers were measured. The change of conductivities did not occur under anhydrous condition, but were found to be more remarkable according to the increase of water content in catalyst. The most remarkable change occurred under the condition of the mol. ratio of $\text{H}_2\text{O}/\text{AlCl}_3=0.015$, where the catalyst is most active for the isomerization.

From these results, the following mechanism is proposed, i.e. the reaction proceeds through the ionic intermediate complex between heptane and $\text{Al}_{2}\text{Cl}_{(6-n)} \cdot (\text{OH})_n$, produced from $\text{AlCl}_3$ and $\text{H}_2\text{O}$, in which $n$ is smaller than 0.5 (simply represented by $\text{OHA1Cl}_2$).

\[
\begin{align*}
\text{CH}_3\text{-CH}_2\ldots\text{CH}_2\text{-CH}_3 + \text{HOA1Cl}_2 & \rightarrow \text{CH}_3\text{-CH}_2\ldots\text{CH}_2\text{-CH}_3\text{Cl}\text{OH} \\
\rightarrow \text{CH}_3\text{-CH}_2\ldots\text{CH}_2\text{-CH}_3 & \rightarrow \text{CH}_3\text{-CH}_2\ldots\text{CH}_2\text{-CH}_3\text{Cl-}\text{Al-H} \\
& \vdots \text{CH}_3\text{-CH}_2\ldots\text{CH}_2\text{-CH}_3 + \text{HOA1Cl}_2
\end{align*}
\]

The fact of progress of decomposition in case of larger water content, is considered that the transfer of II-atom combined with attached to Al in $\text{CH}_3\text{-CH}_2\ldots\text{CH}_2\text{-CH}_3$ will be interfered. This supposition might be emphasized by the facts that the decomposition is promoted by the supply of D.S. voltage in the reaction system, and, on the other hand, n-heptane he is predominantly decomposed, II-atom disappears in the form of chloroform by the catalyst, mixture of $\text{CCl}_4$ and $\text{AlCl}_3$, instead of $\text{H}_2\text{O}$.

Finally, in case of much more water content, no decomposition occurred probably of the interference of the formation of ionic intermediate complex.