CHEMISTRY LETTERS, pp. 611-612, 1973. Published by the Chemical Society of Japan

SELECTIVITY IN THE CATALYTIC FORMATION OF ACETALDEHYDE, ETHYLENE AND ETHYL ETHER FROM ETHYL ALCOHOL OVER POLYNAPHTHOQUINONE CONTAINING $FeCl_3$

Yasuhiro IWASAWA*, Sadao OGASAWARA*, Takaharu ONISHI+, and Kenzi TAMARU+
* Department of Applied Chemistry, Faculty of Engineering,
Yokohama National University, Ooka-cho, Minami-ku, Yokohama.
+ Department of Chemistry, University of Tokyo, Hongo, Bunkyo-ku, Tokyo.

Summary——— The rate as well as the selectivity of ethyl alcohol decomposition to acetaldehyde, ethylene and ethyl ether was markedly dependent on the $FeCl_3$ content in the polynaphthoquinone catalyst and the formation of ethylene and ether was considered to take place on the $FeCl_3$ coordinated to the quinone group of the catalyst.

The organic polymers containing quinone groups exhibit a considerable catalytic activity in various reactions, quinone groups playing a characteristic role as active sites[1). As was previously reported[2), the polynaphthoquinone obtained by the oxidation of 1,7-naphthalenediol by nitric acid in air catalyzed various reactions such as the dehydrogenations of formic acid, isopropyl alcohol and cyclohexene, and the isomerization of butene. However, the activity of the catalyst was mainly studied in those reactions, little attention being paid in the selectivity of the reactions. The decomposition of ethyl alcohol, accordingly, has been studied in this report and the selectivity of the dehydration and the dehdyrogenation was correlated with the structure and the composition of the polymer catalysts.

The polynaphthoquinones containing $FeCl_3$ were prepared by mixing the polynaphthoquinone(0.1g) and the known amounts of $FeCl_3$ in ethyl alcohol followed by gradually evaporating the solvent at room temperature under vacuum. The $FeCl_3$ coordinates to quinone groups in the catalysts[2). The polynaphthoquinone thus obtained were treated under vacuum at 250°C for 6 hours prior to each run.

When the adsorption of the reacting species on the catalyst was measured during the course of the reaction, it was revealed that the rate of the dehydrogenation of ethyl alcohol was proportional to the adsorbed amount of ethyl alcohol. The selectivity of the dehydrogenation was about 90% at 150°C. The activity of the dehydrogenation markedly increased with the increased amount of $FeCl_3$ contained in the catalysts, while that of isopropyl alcohol was much less affected by the amount of $FeCl_3$. Both ethylene and ethyl ether were produced by the dehydration of ethyl alcohol over the polynaphthoquinones in the temperature range from 150° to 230°C. The initial rates of the formation of ethylene and ethyl ether are expressed by the following equations; $d(\text{ethylene})/dt=k_1(\text{ethyl alcohol})_{ad}$ and $d(\text{ethyl ether})/dt=k_2(\text{ethyl alcohol})_{ad}^2$, which shows that ethylene and ethyl ether are formed by surface unimolecular and bimolecular processes, respectively, from the ethyl alcohol adsorbed on the catalyst. The dehydrogenation proceeded until the quinone groups in the catalyst were reduced by ethyl alcohol, while the dehydration was much less influenced by the reduction of the quinone groups, the dehydration, accordingly, being mainly observed over the reduced polynaphthoquinone.

The adsorption of ethyl alcohol over the polynaphthoquinone with or without $FeCl_3$ was of the Langmuir type. The heat of adsorption of ethyl alcohol was found to be 8.7 kcal/mol over the metal free polynaphthoquinone, which corresponds to one or two hydrogen bond energy. Ethyl alcohol may adsorb on quinone groups of the catalyst, forming the hydrogen bond. The heat of adsorption was 6.7 kcal/mol on the polynaphthoquinone containing $FeCl_3$, which was independent on the $FeCl_3$ content. The saturated amounts of adsorption of ethyl alcohol showed a linearity against the $FeCl_3$ content. These results demonstrate that ethyl alcohol is adsorbed selectively on $FeCl_3$ which is coordinated to quinone groups in the catalyst. The $FeCl_3$ coordinated to quinone groups changes its catalytic activity in addition to increasing the adsorbed amount of ethyl alcohol. As $FeCl_3$ behaves as a Lewis acid, $FeCl_3$ has an affinity to the hydroxy anion from ethyl alcohol to form either ethylene or ethyl ether.

The conversions of ethyl alcohol to ethylene and ethyl ether were markedly influenced by the amount of $FeCl_3$ contained in the catalysts. Higher $FeCl_3$ content exhibited higher rate of conversion to both ethylene and ethyl ether. The selectivity of the two conversions at 200°C are given in Fig.1. In the lower $FeCl_3$ content, ethylene was predominantly produced, whereas the formation of ethyl ether predominated over the dehydration in the higher $FeCl_3$ content. The rate of the ethyl ether formation had a good correlation with the square of the $FeCl_3$ content. It is accordingly indicated from these results and the rate equation that ethyl ether is formed via the surface bimolecular process between two ethyl alcohol molecules adsorbed on two $FeCl_3$ closely coordinated to quinone groups and the higher the surface $FeCl_3$ concentration, the higher probability for the bimolecular processes. It is consequently of interest that in the dehydration of ethyl alcohol the relative ratio of the formation of ethyl ether to that of ethylene was markedly affected by the $FeCl_3$ content of the catalysts.

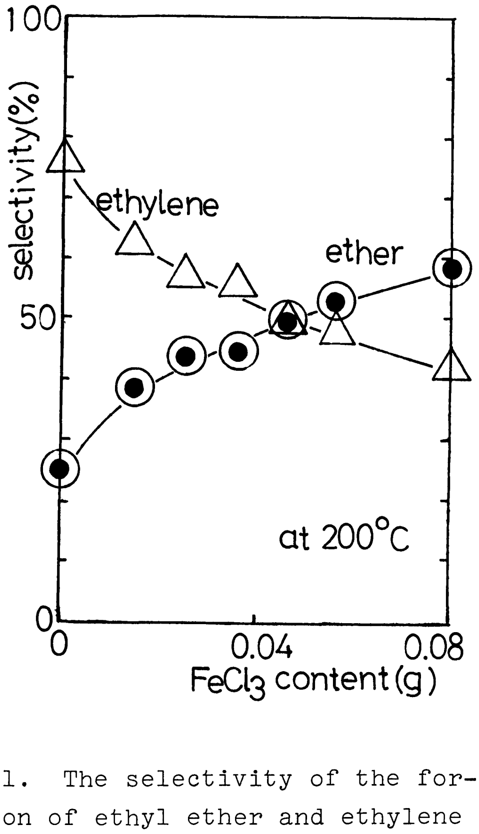

Fig.1. The selectivity of the formation of ethyl ether and ethylene in the dehydration over the catalysts containing various amounts of $FeCl_3$ per 0.1g of polynaphthoquinone; initial pressure of ethyl alcohol=2.3 cmHg.

References

1) J.Manassen and SH.Khalif, J.Catalysis, 13, 290 (1969)
2) Y.Iwasawa, M.Soma, T.Onishi and K.Tamaru, J.Chem.Soc.,Faraday I, 68, 1617 (1972)
Y.Iwasawa, T.Onishi and K.Tamaru, Chem.Comm., 1051 (1972)

(Received April 10, 1973)