The Dehydration Decomposition of Formic Acid over Alumina Catalyst

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The existence of a certain adsorbed species on the catalyst surface in its working state does not necessarily imply that it is really a reaction intermediate. A new approach to this problem is to employ a dynamic treatment of chemisorbed species by means of the infrared spectroscopy to study their kinetic behaviour in their working condition.

In the dehydration decomposition of formic acid on various metals and alumina, it has been reported that formate ion can be observed on the catalyst surfaces,[1] but it is necessary for elucidating the reaction mechanism to determine whether the formate ion is a reaction intermediate.

The apparatus to study adsorption on alumina under the reaction conditions by means of the infrared technique is consisted of a closed circulating system and the reaction cell which serves as the infrared cell to measure the adsorption on the alumina by the infrared spectroscopy. The alumina catalyst obtained from Degussa Co., Ltd. was pressed to form a disc, calcined at 400°C for 2 hr prior to the use, and the decomposition reaction was carried out in the temperature range between 170 and 190°C. No reaction took place without the catalysts in the temperature range studied. An alumina disc was heated to the reaction temperature, and then DCOOD was first introduced in the system. In the stationary state of the decomposition, DCOOD in the ambient gas was replaced by HCOOH and the decomposition was continued, and the rate of the overall reaction as well as the change in the spectra of the chemisorbed species was followed simultaneously. If the formate ion is the reaction intermediate, $DCOO^-$ on the catalyst surface should be replaced by $HCOO^-$ with a rate corresponding to the overall reaction rate, but if it is not, it might remain unchanged provided no exchange reaction is involved.

The infrared spectra of the adsorbed species were studied in the range from 4000 to 2000 cm^{-1}, and the amounts of formate ions on the catalyst surface were estimated from the C-H (2915 cm^{-1}) and C-D (2220 cm^{-1}) stretching vibrations. The amounts of HCOOH (or HCOOD) and DCOOD (or DCOOH) in the gas phase were also estimated.

It was accordingly demonstrated that a part of the adsorbed $DCOO^-$ on the catalyst surface disappears during the reaction, but the corresponding amount appears in the gas phase as formic acid vapour, which shows that some formate ions on the catalyst surface can exchange with formic acid vapour without going directly to the reaction products. The surface hydroxyl group originally retained on alumina remained unchanged by the formic acid vapour, but a part of the hydroxyl group from the dissociative adsorption of formic acid was readily exchanged by its isotopic compound (DCOOD), and also by D_2O.

In the stationary state of the reaction, it was revealed by means of the adsorption measurements during the reaction that the decomposition rate is proportional to the amount of formic acid adsorbed and is expressed by the following equation

$$r = k(\mathrm{H}^+)_{\mathrm{ads.}} P_{\mathrm{HCOOH}}/(1 + b(\mathrm{H_2O})_{\mathrm{ads.}})$$

where $(H^+)_{ads.}$ and $(H_2O)_{ads.}$ designate the amounts of formic acid and water adsorbed respectively, which were estimated from the total amounts of adsorbed hydrogen, oxygen and carbon.

In order to examine the role of hydrogen from the dissociative adsorption of formic acid on the catalyst surface, the relative activities of formate ion and proton on the surface was purposely modified by adsorbing acetic acid before the decomposition. On admitting acetic acid to alumina, dissociative adsorption to CH_3COO^- and proton (OH) took place, and the decomposition of the chemisorbed species scarcely took place at the decomposition temperature of formic acid. Then, formic acid was admitted, where the exchange of CH_3COO^- with $HCOO^-$ did not take place appreciably during the reaction, and the adsorption of formate ion on the pretreated alumina dropped to about one tenth of that in the case without acetic acid pretreatment, whereas the number of adsorbed proton was the same. The rate of the decomposition of formic acid was approximately the same in both cases, which strongly supports that the overall decomposition proceeds between formic acid molecule from the gas phase and the surface proton supplied from the dissociative adsorption of formic acid and the formate ion observable on the catalyst surface during the reaction is not the reaction intermediate.

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1) K. Hirota, K. Kuwata, T. Otaki and S. Asai, Actes du Deuxieme Congrès International de Catalyse, Paris, 1960, p. 809.