CHEMISTRY LETTERS, pp. 121-122, 1981.

DEHYDROGENATION OF ETHANOL OVER ZSM-5 TYPE ZEOLITES

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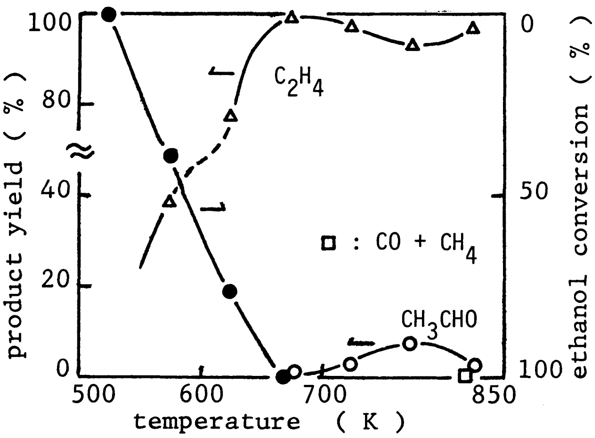
Decomposition of ethanol over ZSM-5 zeolite was investigated by use of a pulse microcatalytic reactor technique. Acetaldehyde and ethylene were formed over ZSM-5 and sodium enriched ZSM-5 was much more effective for the dehydrogenation than protonated one.

A new type zeolite, ZSM-5, developed by Mobile Oil Co. is a zeolite with high Si/Al ratio of a characteristic structure. It is known that the protonated ZSM-5 catalyzes the conversion of methanol and other compounds to higher hydrocarbons.[1,2] Chang and Silvestri proposed participation of basic sites in the methylene formation from CH_3OR (R = H, CH_3) to account for the reaction.[1] However, natures of the active sites in ZSM-5 have not been established. In order to clarify the natures, we carried out decomposition of ethanol over ZSM-5 and got the results suggesting existence of basic sites in ZSM-5.

The ZSM-5 zeolite was synthesized according to the patent of Mobile Oil Co.[3] Organic compounds (tetrapropylammonium is one of main components in the ZSM-5) were removed in a nitrogen stream at 773 K for 8 h. The sample will be simply denoted as ZSM. Sodium enriched ZSM and protonated ZSM were prepared by refluxing the ZSM in an aquaous solution of excess NaCl or a solution of 2 N HCl for 8 h, respectively. These will be denoted as Na-ZSM and H-ZSM. Analytical molar ratios $Na_2O:Al_2O_3:SiO_2$ are 0.68:1.00:189 for ZSM, 1.08:1.00:189 for Na-ZSM and 0.05:1.00:189 for H-ZSM. The samples were heated at 823 K in air for 1 h. The catalytic activities were measured by use of a pulse microcatalytic reactor technique. About 2×10^{-5} mol of ethanol was injected onto 100 mg of the sample under helium carrier: The rate of flow was 40 ml/min. Products were analyzed by gas chromatography.

Ethylene was mainly produced by the decomposition of ethanol over ZSM in the temperature range of 523 to 823 K, as shown in fig. 1. Diethyl ether was not detected in the whole range of temperature adopted. The dehydration of ethanol to ethylene is considered to occur on acid sites since dehydration of alcohol is usually catalyzed by acids;[4] the chemical formula of ZSM calculated from the molar ratio, $Si_{95.0}Al_{1.0}Na_{0.7}H_{0.3}O_{192}$, indicates the existence of the acid sites. At a temperature of 673 K or above, acetaldehyde was formed. Dehydrogenation of ethanol over a zeolite which does not contain transition metals has not been reported. As cationic iron impurity in faujasites catalyzed dehydrogenation of 2-propanol,[5] we suspected that the dehydrogenation over ZSM would be due to



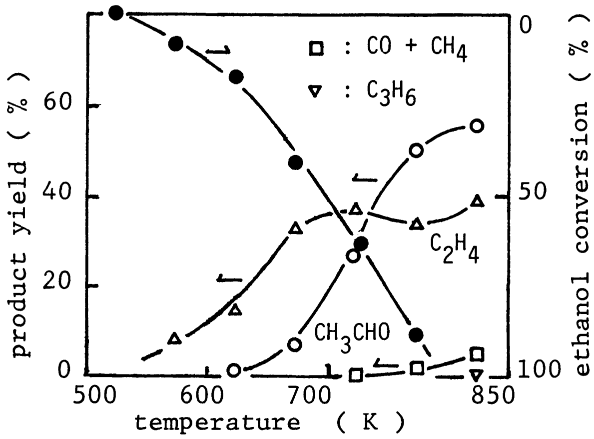


Fig.1. Conversion of ethanol over ZSM. Fig.2. Conversion of ethanol over Na-ZSM.

impurities. To confirm active sites for the dehydrogenation, the catalytic activities of Na-ZSM and H-ZSM were investigated. Fig.2 shows ethanol conversion and products yields distributions of ethanol decomposition over Na-ZSM. Acetaldehyde was produced as a main product at high temperatures. Hydrogen was detected in the temperature range of 673 to 823 K. Formation of carbon monoxide, methane and propylene may be due to conversion of acetaldehyde. On the other hand, H-ZSM catalyzed the dehydration effectively as shown in fig. 3. At high temperatures, acetaldehyde was formed. However, the yield was very small. The results show that the yield of acetaldehyde is dependent on amount of sodium ion in the ZSM-5 zeolite. This suggests that acetaldehyde is formed on basic sites in the zeolite: It was reported that dehydrogenation of 2-propanol proceeded on basic sites.[4]

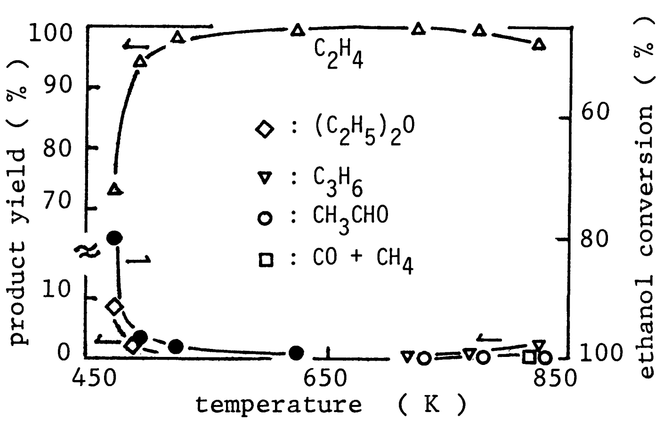


Fig.3. Conversion of ethanol over H-ZSM.

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(Received November 10, 1980)