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Dehydration of ethanol into ethylene over solid acid catalysts

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The dehydration of ethanol into ethylene was investigated over various solid acid catalysts, such as zeolites and silica–alumina, at temperatures ranging 453–573 K under atmospheric pressure. Ethylene was produced via diethyl ether during the dehydration process. H-mordenites were the most active for the dehydration. It was suggested that the catalyst activity could be correlated with the number of strong Brønsted acid sites in the catalyst. Further, the H-mordenite was more stable with a SiO_2/Al_2O_3 ratio of 90 than with a SiO_2/Al_2O_3 ratio of 20.

KEY WORDS: dehydration; ethanol; ethylene; solid acid.

1. Introduction

In recent times, the reduction of CO_2 emission has become a crucial problem in the chemical industry. The utilization of ethanol from biomass fermentation instead of petroleum as chemical feedstock may facilitate the reduction of CO_2 emission. Therefore, the authors have focused attention on the catalytic conversion of ethanol. At present, the authors are studying the dehydration of ethanol into ethylene. It is well known that this dehydration is catalyzed by various solid acid catalysts such as silica–alumina and zeolites [1–7].

In the present study, the dehydration of ethanol into ethylene was investigated over various solid acid catalysts such as zeolite and silica–alumina. First, in order to select highly active catalysts, the catalytic activities of various solid acid catalysts were compared at temperatures ranging from 453 to 573 K. Next, the relationship between the catalyst activity and the acid sites on the catalyst was discussed based on the results of temperature-programmed desorption of ammonia (NH_3-TPD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies. Furthermore, changes in the activities of several selected catalysts with time on stream were examined from a practical viewpoint, and the amount of carbonaceous deposits on the catalysts during the dehydration was measured.

2. Experimental

The solid acid catalysts used in the present study were H-mordenites (JRC-Z-HM20(4) and JRC-Z-HM90(2)), H-ZSM5 zeolites (JRC-Z5-25H and JRC-Z5-90H), H-beta-zeolite (JRC-Z-HB25(1)), H-Y zeolite (JRC-Z-HY5.5), and silica–alumina (JRC-SAL-2), which were the reference catalysts supplied by Catalysis Society of Japan. In the present paper, the symbols HM20, HM90, HZSM5-25, HZSM5-90, HB25, HY5.5, and SA represent JRC-Z-HM20(4), JRC-Z-HM90(2), JRC-Z5-25H, JRC-Z5-90H, JRC-Z-HB25(1), JRC-Z-HY5.5, and JRC-SAL-2, respectively. The molar ratios of SiO_2 to Al_2O_3 in HM20, HM90, HZSM5-25, HZSM5-90, HB25, HY5.5, and SA were 18.9, 90, 25, 90, 25, 5.6, and 9.2, respectively. The solid acid catalysts were used as received for the dehydration process.

The dehydration was carried out in a fixed-bed flow reactor under atmospheric pressure. Pure ethanol (99.5%) obtained from Nacalai Tesque Inc. was used as received. The temperature of the catalyst fixed in the reactor was raised to the reaction temperature in a flow of He. Ethanol was then fed into the reactor along with He. The reaction products were analyzed by FID gas chromatographs that were directly connected to the reactor. The products of the dehydration were ethylene, diethyl ether, small amounts of ethane, acetaldehyde, propene, and butenes. The yield of each product was defined as the conversion of ethanol to the products, and the selectivity to each product was defined as its yield divided by the total conversion of ethanol.

The amount of carbonaceous deposits on the post-reaction catalyst was measured by TG/DTA.

In order to characterize the acid sites on the solid acid catalysts, NH_3-TPD measurements of the catalysts and DRIFTS studies on pyridine adsorbed on their acid sites were carried out.

The NH_3-TPD measurements were carried out under atmospheric pressure using a TPD apparatus connected to a mass spectrometer (Microvision from Leda-Mass

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Ltd.). Approximately 150 mg of the catalyst sample was treated in a sample tube at 773 K for 1 h in a flow of He. The temperature was reduced to 373 K, and the sample was placed in a flow of a gas mixture of NH_3(10)/He(90) for 1 h and then in the flow of He (30 ml/min) for 1.5 h. The effluent gas at the outlet of the sample tube was analyzed with the mass spectrometer while the sample was heated to 773 K at a rate of 10 K/min. The signals of $m/e=$ 16, 17, 18, and 28 were simultaneously monitored. Since the signal of $m/e=$ 17 might originate from both NH_3 and H_2O, the signal of $m/e=16$ was considered to indicate the presence of NH_3 in the effluent gas.

The DRIFTS studies on pyridine adsorbed on the acid sites of the catalyst were carried out using an FT-IR spectrometer (JIR-6500 from JEOL Ltd.) equipped with an MCT detector and a diffuse reflectance cell (Catalytic DRIFT Chamber from Spectra-Tech Inc.); the cell was used to obtain the diffuse reflectance spectra at a resolution of 4 cm^{-1}. The powder catalyst sample placed in the cell was treated in a flow of Ar at 623 K for 30 min. Pyridine was then adsorbed on it by passing Ar through a pyridine container at room temperature and the sample cell at 423 K for 30 min. The sample on which pyridine was adsorbed was treated at 623 K in a flow of Ar for 1 h to remove the pyridine that was weakly adsorbed on the sample. The diffuse reflectance spectra of the adsorbed pyridine were recorded at 623 K in a flow of Ar.

3. Results and discussion

Figure 1 shows the conversion of ethanol and the selectivity to products such as ethylene and diethyl ether as a function of W/F during the dehydration over HM90. The result clearly indicates that ethylene is produced via diethyl ether. In the present study, the yield of ethylene was considered as a measure of the catalyst activity during the dehydration.

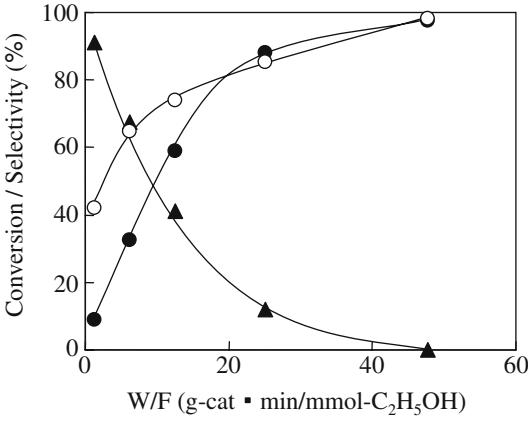

Figure 1. Conversion of ethanol (○) and the selectivities to ethylene (●) and to diethyl ether (▲) in the dehydration of ethanol over the HM90 catalyst as a function of W/F. Reaction conditions: 453 K; 0.1 MPa; ethanol concentration in the feed (C_2H_5OH/He) = 0.04

Table 1
Activities of various solid acid catalysts for dehydration of ethanol into ethylene

Solid acid	Temperature (K)	W/F (g-cat min/ mmol-C_2H_5OH)	Yield of ethylene (%)
HM20	453	12.5	93.9
	453	25.1	99.8
HM90	453	12.5	52.8
	453	25.1	99.9
HZSM5-25	453	12.5	40.8
	453	25.1	95.9
HZSM5-90	453	12.5	7.6
	453	25.1	23.3
	473	12.5	31.9
HB25	453	12.5	34.4
	453	25.1	57.5
HY5.5	473	12.5	3.4
	523	12.5	71.3
SA	523	12.5	15.3
	573	12.5	76.7

Table 1 shows the activities of various solid acid catalysts for the dehydration of ethanol into ethylene. It can be observed that the catalyst activity decreases in the following order: HM20 > HM90 > ZSM5-25 > HB25 > ZSM5-90 > HY5.5 > SA.

NH_3-TPD measurements and DRIFTS studies were carried out in order to clarify the relationship between the catalyst activity and the number of acid sites on the solid acid catalysts.

Figure 2 shows the NH_3-TPD profiles of several solid acid catalysts. The profile and amount of NH_3 desorbed from the catalyst can be considered as the acid strength distribution and the number of acid sites on the catalyst,

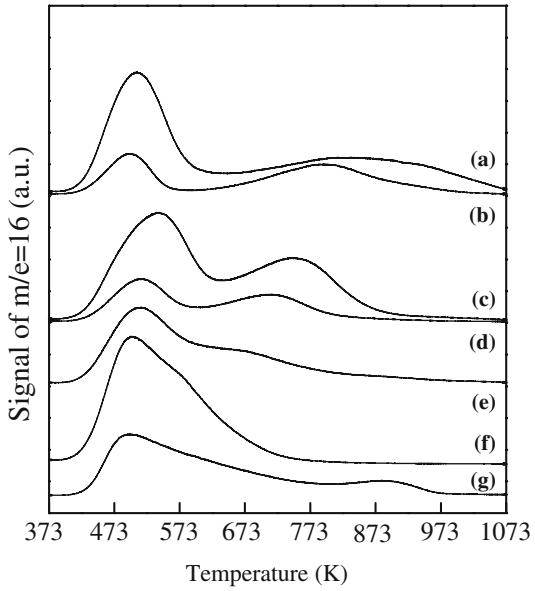

Figure 2. NH_3-TPD profiles of HM20 (a), HM90 (b), HZSM5-25 (c), HZSM5-90 (d), HB25 (e), HY (f) and SA (g). Operating conditions: 0.1 MPa; flow rate of He = 60 ml/min; heating rate = 10 K/min.

including both the Brønsted and Lewis acid sites, respectively. The amount of NH_3 desorbed from all the catalysts with the exception of SA at temperatures greater than 823 K reduces in the same order as the catalyst activity, as shown above. Therefore, it is suggested that the strong acid sites from which NH_3 could be desorbed at temperatures greater than 823 K should be necessary for the dehydration of ethanol into ethylene.

Figure 3 shows the DRIFTS profiles of pyridine adsorbed at 473 K on several solid acid catalysts. It is well known that the absorption bands at 1545 and 1455 cm^{-1} are assigned to the adsorbed pyridinium ions and pyridine coordinated to the Lewis acid sites, respectively. The percentage of Brønsted acid sites in the total number of acid sites (Brønsted acid sites + Lewis acid sites) on each solid acid catalyst was estimated from the integrated peak areas of the two absorption bands of the catalyst [8]. The percentage of Brønsted acid sites on HM20, HM90, ZSM5-25, ZSM5-90, HB25, HY5.5, and SA were estimated to be 83%, 95%, 94%, 92%, 33%, 83%, and 50%, respectively. As described above, the amount of NH_3 desorbed from SA at temperatures greater than 823 K was higher than that from HY, whereas the catalytic activity of SA was lower than that of HY. Since the percentage of the Brønsted acid sites on HY was higher than that on SA by 65%, it is suggested that the Brønsted acid sites are active sites for the dehydration of ethanol into ethylene. Accordingly, the results strongly suggest that the catalyst activity during the dehydration process should be correlated with the number of strong Brønsted acid sites where NH_3 could be desorbed at temperatures greater than 823 K in the present TPD experiments. In other words, the strong Brønsted acid sites should be the active sites for the dehydration of ethanol into ethylene.

The H-mordenites were more active than the other solid acid catalysts tested, as shown in Table 1. The changes in the activities of HM20 and HM90 with time on stream during the dehydration of ethanol at 453 K were examined from a practical viewpoint, as shown in figure 4. Although the conversion of ethanol was almost constant during its dehydration over HM20 for 40 h, the selectivity to ethylene gradually decreased, while that to diethyl ether gradually increased with time on stream 20 h after the reaction began. On the other hand, both the conversion of ethanol and the selectivities to ethylene and diethyl ether were almost constant during the dehydration over HM90 for 40 h. Since the accumulation of carbonaceous deposits on the catalyst is considered to be one of the causes of catalyst deactivation, as suggested by previous studies [6,7], the amount of carbonaceous deposits on the post-reaction catalysts was measured. The amount of carbonaceous deposits on HM20 was 6 mg-C/g-cat, while that on HM90 was too low to be measured. These findings suggest that, in practice, HM90 is more suitable than HM20 for the dehydration of ethanol into ethylene.

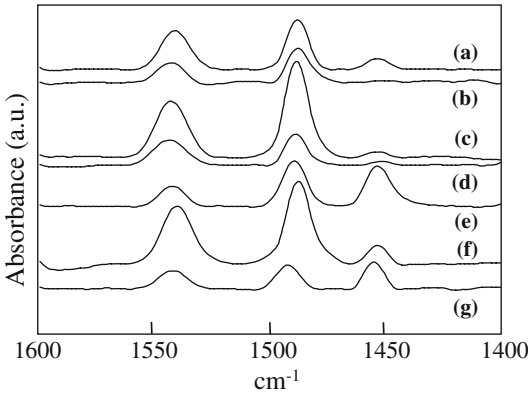

Figure 3. DRIFTS profiles of pyridine adsorbed at 623 K over HM20 (a), HM90 (b), HZSM5-25 (c), HZSM5-90 (d), HB25 (e), HY (f) and SA (g).

4. Conclusions

(1) The dehydration of ethanol into ethylene was investigated over various solid acid catalysts such as zeolites and silica–alumina at temperatures ranging from 453 to 573 K under atmospheric pressure. Ethylene was produced via diethyl ether during the dehydration process. H-mordenites were the most active for the dehydration.

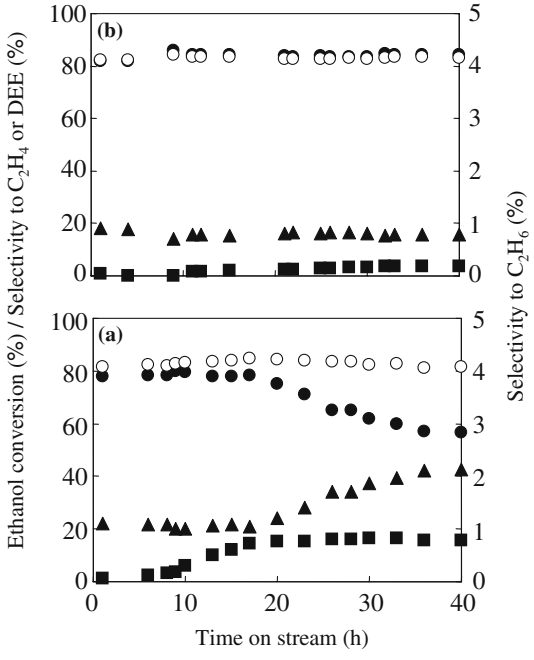

Figure 4. Conversion of ethanol (○) and the selectivities to ethylene (●), diethyl ether (DEE,▲) and ethane (■) in the dehydration of ethanol over the HM20 (a) and the HM90 (b) catalysts as a function of time on stream. Reaction conditions: 453 K; 0.1 MPa; ethanol concentration in the feed (C_2H_5OH/He) = 0.04; W/F = 26.6 g-cat min/mmol- C_2H_5OH.

(2) The catalyst activity during the dehydration could be correlated with the number of strong Brønsted acid sites.
(3) The H-mordenite was more stable with a SiO_2/Al_2O_3 ratio of 90 than with a SiO_2/Al_2O_3 ratio of 20.

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