One-step formation of ethyl methyl ketone from 1-butene and water on ultrastable Y-type zeolite catalyst

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Proton exchanged ultrastable Y-type zeolite with silica/alumina = 40 showed a pronounced catalytic activity for the formation of ethyl methyl ketone directly from 1-butene and water. The formation rate of ethyl methyl ketone was much higher than those on MoO_3-based catalysts in the oxidation of 1-butene by oxygen. It was suggested that the basic site necessary for the formation of ethyl ketone directly from 1-butene and water would be the pentacoordinated Al.

Keywords: Ethyl methyl ketone; ultrastable Y-type zeolite; pentacoordinated aluminum; acid-base catalysis

1. Introduction

Ethyl methyl ketone is commercially important and has been industrially made by the dehydrogenation of 2-butanol [1]. Since the alcohols are usually obtained through the direct or indirect hydration of the olefin with the same carbon number, it would be much more desirable to avoid the alcohol and synthesize the ethyl methyl ketone by a direct reaction between olefin and water. Here, we wish to report that the proton-exchanged ultrastable Y-type zeolite having silica/alumina = 40 efficiently catalyzes the formation of ethyl methyl ketone from 1-butene and water without oxygen.

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2. Experimental

The parent zeolites, ZSM-5, ferrierite (denoted as MFI and FER, respectively), and ultrastable Y-type (dealuminated by steaming, USY) zeolites were supplied by Tosoh Corporation and mordenite (MOR) and Y-type were obtained from the Catalysis Society of Japan. Proton exchanged zeolites were prepared as described previously [2] and abbreviated as H-USY-40 (cation-zeolite structure-silica/alumina). The reaction of 1-butene and water was carried out in a conventional flow reactor at 373–573 K at 1.5 atm using 1 g of catalysts. The each flow rate of 1-butene or water vapor was 15 $cm^3 \cdot min^{-1}$. The reactants and products were analyzed by gas chromatography using PEG 1000, Porapak Q, and Molecular Sieve 5 A columns.

The ^{27}Al MASNMR spectra were measured using a Bruker MSL-400 spectrometer, working at 104.26 MHz with a spinning frequency at 4.0 kHz. All measurements were carried out at room temperature with $Al(H_2O)_6^{3+}$ as a standard reference.

3. Results and discussion

Fig. 1 shows the time courses of the conversions into ethyl methyl ketone and 2-butanol from 1-butene and water on H-USY-40. Ethyl methyl ketone and 2-butanol were the main products except for the isomerization products, trans-2-butene and cis-2-butene. Approximately steady formation of ethyl methyl ketone was attained after 6 h and the conversion of 1-butene into 2-butanol

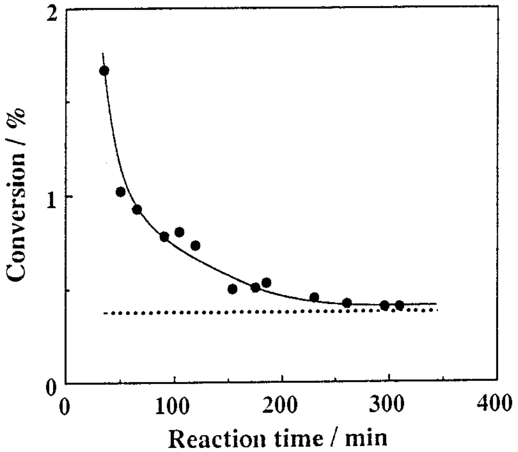

Fig. 1. Time courses of the conversions into ethyl methyl ketone and 2-butanol. Solid and broken lines indicate the conversions into ethyl methyl ketone and 2-butanol, respectively. Catalyst, H-USY-40. Reaction temperature, 443 K.

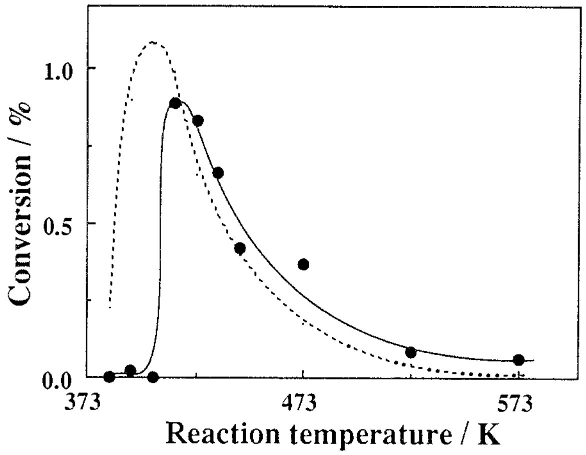

Fig. 2. Temperature dependence of the conversions into ethyl methyl ketone and 2-butanol. Solid and broken lines indicate the conversions into ethyl methyl ketone and 2-butanol, respectively. Catalyst, H-USY-40.

changed little with time. Hereafter, the selectivity was evaluated except for the isomerization products.

The temperature dependence of the conversions into ethyl methyl ketone and 2-butanol on H-USY-40 is shown in fig. 2. The conversion into ethyl methyl ketone was very low below 403 K, sharply increased at 413 K, and then decreased at higher temperatures. Above 423 K ethyl methyl ketone was the major product. The conversion into 2-butanol increased with increment of reaction temperature, reached maximum at 403 K, and then decreased. The reason for the decline in conversions into ethyl methyl ketone and 2-butanol at higher temperatures is the reduction in the equilibrium conversion into 2-butanol and/or the polymerization of 1-butene, as was discussed previously for the hydration of ethene into ethyl alcohol [2].

The formation rates of ethyl methyl ketone on various proton zeolites and mixed metal oxide catalysts are summarized in fig. 3. H-USY-40 showed the highest activity among the catalysts listed in fig. 3. The activities of H-MOR and H-FER zeolites were very low, though they were reported to be very active for the hydration of lower olefins [2–5]. In addition, it should be noted that H-Y-5.6, the mother zeolite of H-USY-40, showed little catalytic activity for the ketonization, indicating the generation of active sites for the reaction upon the dealumination treatment.

The H_2 evolution was qualitatively confirmed by gas chromatography in the reaction of 1-butene and water. It is widely accepted that the dehydrogenation of alcohol to yield ketone (or aldehyde) and hydrogen is well catalyzed on basic active sites [6]. Fig. 3 and the H_2 evolution strongly suggest the presence of basic sites on the USY zeolites. The formation of basic Al anion on zeolite by steaming has indeed been reported [7], supporting the idea.

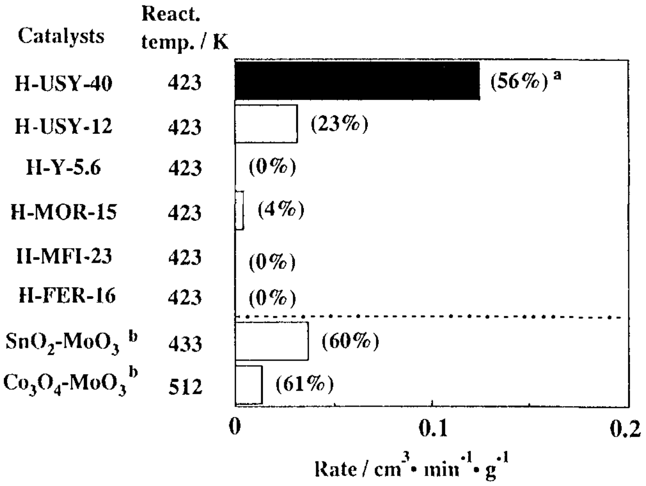

Fig. 3. Rates of ethyl methyl ketone formation over various catalysts. a) Figures in parentheses were selectivities to ethyl methyl ketone. b) Cited from ref. [10]. The partial pressures of 1-butene and water on SnO_2-MoO_3 and Co_3O_4-MoO_3 were similar to those in the present work. Reactions on SnO_2-MoO_3 and Co_3O_4-MoO_3 were carried out with oxygen.

The ^{27}Al MASNMR spectra of H-USY-40 were measured to clarify the active sites and are depicted in fig. 4. Fig. 4a shows that H-USY-40 without evacuation contains octahedrally coordinated non-framework Al (−1 ppm) and tetrahedrally coordinated framework Al (60 ppm). The former ^{27}Al signal is due to free

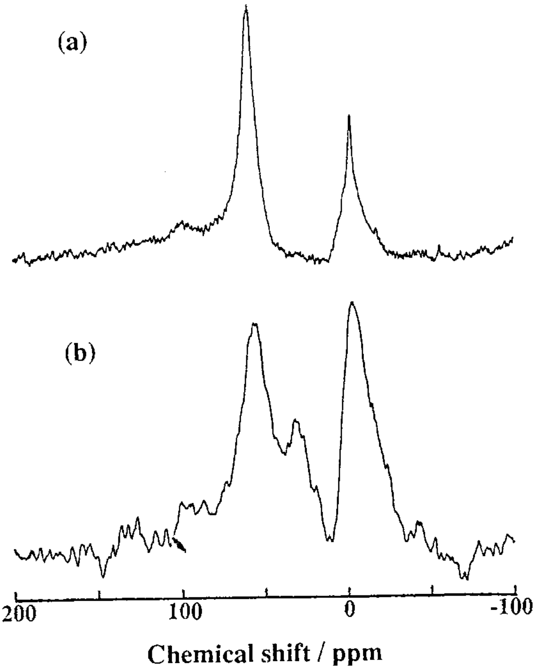

Fig. 4. ^{27}Al MASNMR spectra of H-USY-40 without evacuation (a) and evacuated at 423 K for 30 min (b).

$Al(H_2O)_6^{3+}$ in the cationic positions [8]. After H-USY-40 was evacuated at 423 K, the third peak appeared at 33 ppm (fig. 4b). This peak was assigned to the pentacoordinated Al based on the report of Gilson et al. [9]. The signal intensity of pentacoordinated Al on H-USY-40 decreased with the decrement of the conversion into ethyl methyl ketone. Further, H-Y-5.6 contains no peak at 33 ppm. These facts suggest that the basic site on H-USY-40 is probably due to the pentacoordinated Al. Further studies on the active centers with solid state MASNMR are in progress.

Moro-oka et al. [10] have reported that MoO_3-based catalysts such as SnO_2-MoO_3 and Co_3O_4-MoO_3 were active for the oxidation of 1-butene by oxygen to produce ethyl methyl ketone. Fig. 3 reveals that H-USY-40 has the higher activity for the formation of ethyl methyl ketone than the MoO_3-based catalysts even in the absence of oxygen and the selectivity to ethyl methyl ketone was nearly equal to those on the MoO_3-based catalysts.

In conclusion, it was found that the new type of formation reaction of ethyl methyl ketone directly from 1-butene and water, which is different from the oxidation of 1-butene by oxygen on MoO_3-based catalysts, was efficiently catalyzed by H-USY-40.

Acknowledgments

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