# TPD of Ethanol and Acetaldehyde Adsorbed on a Zinc Oxide - Calcium Carbonate Catalyst in the Presence or Absence of Water Vapor

Tsuyoshi NAKAJIMA[*], Takehisa YAMAMOTO[**], and Shozi MISHIMA[***]

The Temperature Programmed Desorption (TPD) spectra of ethanol and acetaldehyde adsorbed on a $ZnO\text{-}CaCO_3$ (molar ratio = 9:1) catalyst were investigated in the presence or absence of water vapor. It was found that compared with the TPD in the absence of water vapor, most of the desorption products vanished and the desorption rates of acetone and methane increased markedly in the presence of water vapor. These results strongly suggest that water promotes the conversion of adsorbed acetaldehyde to surface acetate.

## 1. Introduction

As a non-petrochemical process, the synthesis of acetone by the reaction

$$2C_2H_5OH + H_2O \rightarrow CH_3COCH_3 + 4H_2 + CO_2 \tag{1}$$
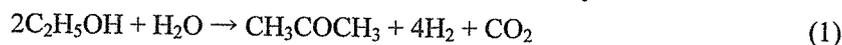
is very important to diversify its raw materials. For Reaction (1), catalysts based on zinc oxide, such as $ZnO$[1], $Fe_2O_3\text{-}ZnO$[2,3] and $ZnO\text{-}CaCO_3$[4], are known to be highly active. It is also known that the reaction follows the steps: ethanol $\rightarrow$ acetaldehyde $\rightarrow$ acetic acid $\rightarrow$ acetone[1]. Acetaldehyde, an intermediate compound, is formed by the dehydrogenation of ethanol, while acetone, the objective compound, is made by the ketonation of acetic acid[1,5]. The details of the reaction from acetaldehyde to acetic acid, however, have not yet been elucidated.

There are chiefly two theories for the route from acetaldehyde to acetic acid.   One is Kagan's theory[1] where ethyl acetate, formed by Tishchenko Reaction (2), is hydrolyzed by Reaction (3) to produce acetic acid:

$$2CH_3CHO \rightarrow CH_3COOC_2H_5 \tag{2}$$

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH \tag{3}$$
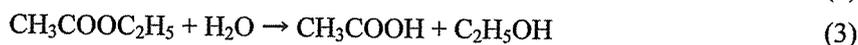
The other theory[6] is that adsorbed acetaldehyde is directly converted to surface acetate, i.e., adsorbed acetic acid, by a nucleophilic attack of a surface hydroxy group:

$$CH_3CHO(a) + HO^-(a) \rightarrow CH_3COO^-(a) + H_2 \tag{4}$$
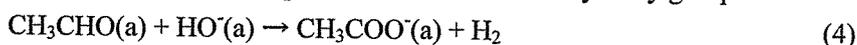
where the species followed by "(a)" denote adsorbed ones and a "-" (or "+") superscript denotes some negative (or positive) partial charge.

The third theory to be considered may result from the temperature programmed desorption

[*] Professor, Department of Chemistry and Material Engineering

[**] Ex-student of Master's Program (Synthetic Chemistry)

Present address: Sumitomo Electric Industries, LTD., Itami Works; 1-1-1 Koya-kita, Itami 664-0016, Japan

[***] Associate Professor, Department of Chemistry and Material Engineering

(hereafter, abbreviated as TPD) of acetaldehyde adsorbed on zinc oxide[7]. This theory is described by the reactions:

$$CH_3CHO + O(s) \rightarrow CH_3CHOO(a) \qquad (5)$$

$$CH_3CHOO(a) \rightarrow CH_3COO(a) + H(a) \qquad (6)$$
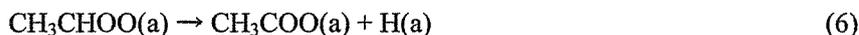
where O(s) denotes a lattice oxygen atom. Since the main component of the active catalysts is zinc oxide, there is a possibility that Reactions (5) and (6) are a valid route for the conversion of acetaldehyde to acetic acid.

In this paper, the TPD of ethanol and acetaldehyde adsorbed on $ZnO-CaCO_3$ was studied in the presence or absence of water vapor in order to elucidate the route followed during the production of acetone from ethanol in the presence of water vapor.

## 2. Experimental

### 2.1 Catalyst and reagent

The preparation method of the catalyst (molar ratio of $ZnO:CaCO_3$ = 9:1) has been reported elsewhere[4)6)]. An X-ray diffraction spectrum of the catalyst showed that it was a mixture of zinc oxide, calcium carbonate (Calcite) and a small amount of basic zinc nitrate, and that the composition of the mixture did not change, except for a slight increase in the amount of carbonate, after the TPD experiment in the presence of water vapor[8].

Ethanol and acetaldehyde were supplied by Wako Pure Chemicals Co. Ltd. Reagent grade ethanol was dried over Molecular Sieves 4A and the first grade acetaldehyde was purified by distillation.

### 2.2 TPD experiments

The TPD experiments were carried out using a conventional flow system with GC as stated in a previous paper[8]. The elution gas was nitrogen (100 mL/min) dried by a molecular sieve 13X column or moistened by passing it through a bubbler containing water at 273 K or 313 K. Stainless steel tubing and a sampling unit were kept above a temperature of 400 K in an oven.

A 0.3 g sample of the catalyst was fixed in a 10 mm$\phi$ Pyrex glass reactor with a coaxial well for a thermocouple and heated at 773 K for 2 h in a dry nitrogen stream. After cool down to room temperature, a 5 $\mu L$ sample of ethanol or acetaldehyde was thrice injected into the dry nitrogen stream, which was passed through the catalyst for the adsorption. The catalyst was washed with a neat nitrogen stream for 30 min to eliminate any physically adsorbed species, followed by heating the catalyst from room temperature to 823 K at 3 K/min. The eluting gas was repeatedly analyzed using a GC with an FID (Shimadzu Co., GC-8AIF) and the TPD spectra were recorded.

The GC analyses were carried out using 2-m glass columns packed with PEG-6000/Terephthalic acid (Shimalite TPA) as the separation columns. In case of analyzing the permanent gas mixtures, 6-m stainless steel columns packed with VZ-7 (GL Science Co. Ltd.) or 1-m glass columns packed with Active Carbon (GL Science Co. Ltd.) were used. Peak areas were determined by the data recorder using relative molar sensitivities determined by analyzing standard mixtures. The sensitivities reported in the literature[9] were also applied for a few compounds.

## 3. Results and discussion

### 3.1 TPD spectra of ethanol in the absence of water vapor

Fig. 1(a) shows the TPD spectra of ethanol adsorbed on the catalyst at room temperature in the absence of water vapor. The horizontal axis indicates the temperature of the catalyst and the vertical axis indicates the desorption rate (arbitrary unit). Since desorbed amounts are generally very small, we used FID as a detector. Thus, desorption products sensitive to the FID, generally organic compounds, are recorded in TPD.

A large desorption peak for ethanol was observed at 363 K. The rest of the adsorbed ethanol was desorbed as acetaldehyde at 513 K, butadiene at 523 K, ethylene at 533 K, acetone at 643 K, propylene at 653 K and methane at 703 K. This variety of desorption species probably indicates the formation of a reactive compound, acetaldehyde, from the adsorbed ethanol on the surface. It is important to note that no ethyl acetate was desorbed. Bowker et al.[7] reported that the desorptions of ethylene and acetaldehyde occurred at the same temperature, 510 K, in their paper on the TPD of ethanol adsorbed on polycrystalline ZnO. In the present study of ethanol on a ZnO-CaCO$_3$ catalyst, however, ethanol and acetaldehyde were desorbed at different temperatures, indicating that their precursors were different.

Takezawa et al.[10] concluded that acetaldehyde was formed via the following Reactions (7) and (8) from their study on the dehydration mechanism of ethanol on MgO by IR, TPD and kinetic measurements.

$$C_2H_5OH \rightarrow C_2H_5O^-(a) + H^+(a) \tag{7}$$

$$C_2H_5O^-(a) + H^+(a) \rightarrow CH_3CHO(a) + H_2 \tag{8}$$
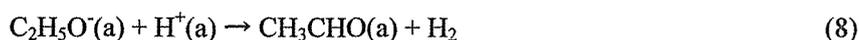
Iwasawa et al.[11], however, hypothesized on the basis of their recent study that the dehydration proceeded by Reaction (9), not Reaction (8).

$$C_2H_5O^-(a) \rightarrow CH_3CHO(a) + H^-(a) \tag{9}$$

We have confirmed their hypothesis by a theoretical study[12].

Tench et al.[13] studied adsorption of methanol on a silica gel surface and concluded that the surface species $CH_3^+(a)$ and $CH_3O^-(a)$ were formed. Thus, ethanol will probably produce the surface species $C_2H_5^+(a)$ by Reaction (10).

$$C_2H_5OH + H^+(a) \rightarrow C_2H_5OH_2^+(a) \rightarrow C_2H_5^+(a) + H_2O \tag{10}$$
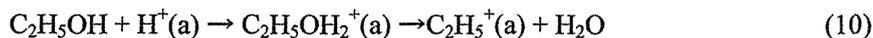
Noller et al. deduced the same surface species in their TPD study of ethanol adsorbed on silica, MgO and MgO-SiO$_2$ and concluded that $C_2H_5^+(a)$ is more stable than $C_2H_5O^-(a)$ and is desorbed at a higher temperature[14]. Therefore, the fact that acetaldehyde and ethylene were desorbed at 513 K and 533 K, respectively, can be explained by the concept that the former was formed by Reactions (7) and (9) and the latter was formed by Reactions (10) and (11).

$$C_2H_5^+(a) \rightarrow C_2H_4 + H^+(a) \tag{11}$$

$H^+(a)$ formed by Reaction (11) will readily react with $H^-(a)$ formed by Reaction (9) and this explains the fact, found out by Bowker et al. in their study of the TPD of ethanol on ZnO[15], that olefin and hydrogen are desorbed at the same temperature.
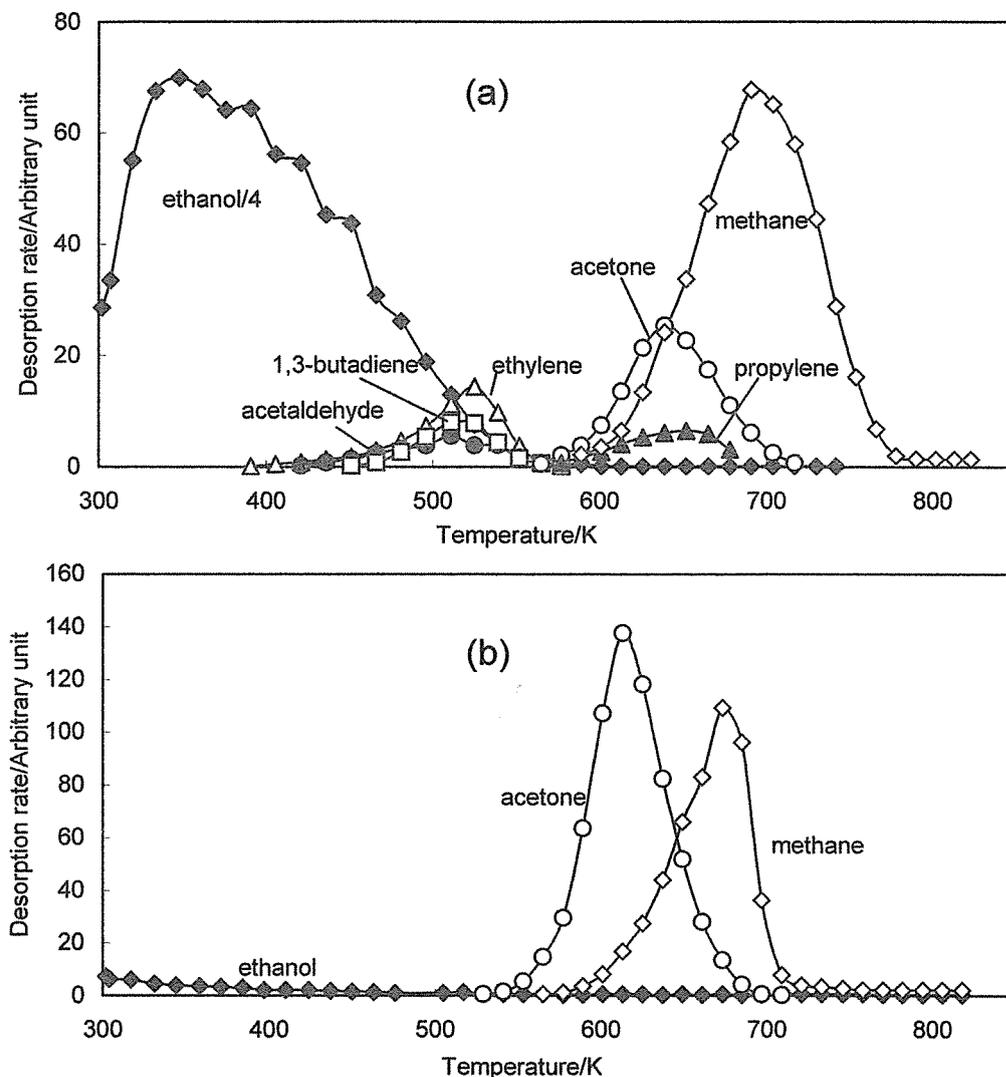
Fig. 1 TPD profiles of ethanol adsorbed on the ZnO-CaCO3 catalyst in the absence or presence of water vapor. N2 flow rate : 100 mL/min., Heating rate : 3 K/min. (a) in the absence of water vapor, catalyst : 0.301 g, (b) in the presence of water vapor (0.61 kPa), catalyst : 0.302 g.

It is well known that surface acetate is formed from ethoxide and that the acetate changes into acetone[10)16)]. The desorption temperatures of acetone (643 K) and methane (703 K) were nearly the same as those in the TPD of acetic acid[8)]. This fact strengthens the theory that ethanol is converted via surface acetate to acetone and methane. The decomposition of acetic acid into methane and $CO_2$ is a well-known reaction. Detailed comparison with those in the TPD of acetic acid[8)], however, revealed that the desorption temperature of acetone in the TPD is 15 K higher than that in the TPD of acetic acid, indicating the acetate formed from ethoxide is more stable than that formed from acetic acid. These two acetate species may be different in each adsorbed state. Further details are going to be studied.
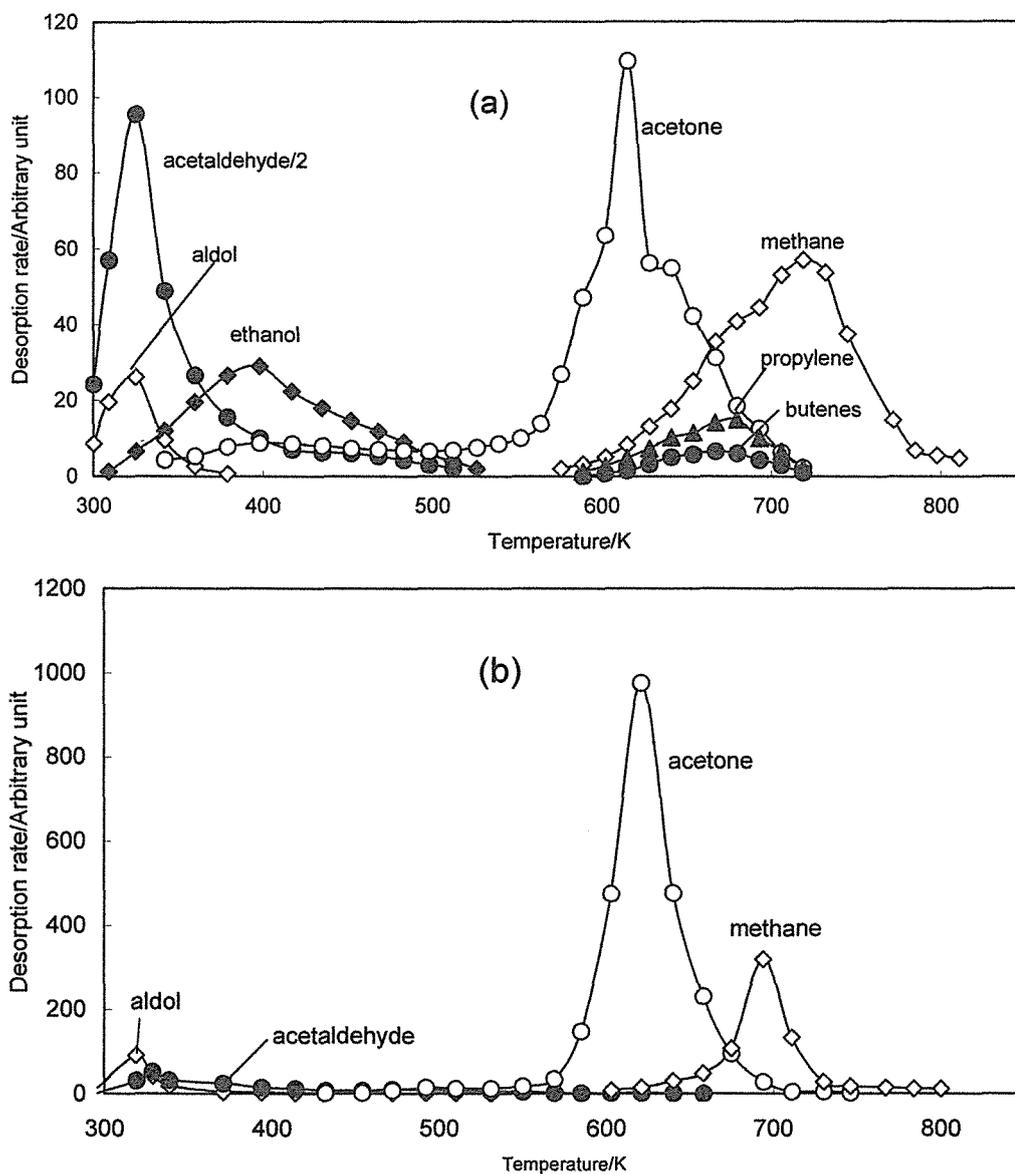
Fig. 2  TPD profiles of ethanol adsorbed on the ZnO-CaCO3 catalyst in the absence or presence of water vapor.  N2 flow rate : 100 mL/min., Heating rate : 3 K/min.  (a) in the absence of water vapor, catalyst : 0.303 g,   (b) in the presence of water vapor (7.4 kPa), catalyst : 0.310 g.

3.2 TPD spectra of ethanol in the presence of water vapor

Fig. 1(b) shows the TPD spectra of ethanol in the presence of water vapor (vapor pressure = 0.61 kPa). The main differences from the curves in the absence of water vapor were a great decrease in the amount of the adsorbed ethanol and the disappearance of all peaks except for those for acetone and methane. The desorption temperatures of the latter two decreased 20~30 K. These shifts likely present a new example for controlled reactivity of adsorbates by molecules in the gas phase via weak interactions.

TPD spectral peaks of ethylene, acetaldehyde, etc. observed in the absence of water vapor completely disappeared in the presence of water vapor. On the other hand, the height of the acetone peak increased three times compared to that in the absence of water vapor.

The decrease in the amount of adsorbed ethanol can be explained by the replacement of non-dissociatively adsorbed ethanol for water vapor, and by the elution of ethoxide by the reverse reaction of Reaction (7) where $H^+(a)$ is produced by the adsorption of water:

$$H_2O \rightarrow H^+(a) + OH^-(a) \tag{12}$$

The disappearance of the ethylene peak agrees with the expected inhibition of Reaction (10) due to the presence of water vapor. The increase in the height of the acetone peak strongly suggests that the water vapor promotes the conversion of adsorbed acetaldehyde to the surface acetate by Reaction (4).

### 3.3 TPD spectra of the adsorbed acetaldehyde in the absence of water vapor

The TPD spectra of acetaldehyde in the absence of water vapor are shown in Fig. 2(a). Since acetaldehyde is very reactive, many desorption peaks were observed. Acetaldehyde and aldol were desorbed at 320 K and ethanol at 400 K. Acetone was desorbed at 403 K and 623 K. Desorption of propylene and butanes were observed at about 673 K and methane at 713 K. Ethyl acetate, however, was not desorbed in TPD.

According to Kagan's hypothesis, acetaldehyde is converted to ethyl acetate. Since adsorbed ethyl acetate is desorbed at about 373 K[17], its desorption peak should be observed when ethyl acetate is formed from the adsorbed acetaldehyde at temperatures above 373 K. However, this was not the case. Thus, Kagan's hypothesis must be rejected.

In TPD, acetaldehyde and aldol desorbed at temperatures as low as 320 K are likely to be physically adsorbed species, while acetaldehyde desorbed at higher temperatures (up to 520 K) are likely to be chemically adsorbed species.

Desorption of ethanol at 400 K indicates that there are reverse reactions of Reactions (9) and (7). It is well known that aldol is formed by the aldol condensation of acetaldehyde:

$$2CH_3CHO(a) \rightarrow CH_3CH(OH)CH_2CHO(a) \tag{13}$$

Acetone desorbed at 403 K is thought to be formed from this aldol by Komarewsky's scheme[18].

### 3.4 TPD spectra of the adsorbed acetaldehyde in the presence of water vapor

The TPD spectra of acetaldehyde in the presence of water vapor are shown in Fig. 2(b). Adsorption of acetaldehyde was so strong that we had to increase vapor pressure of water to 7.4 kPa in order to observe clear changes in the spectra. During the measurement of the spectra, no desorption peaks of ethanol, propylene or butenes were observed. Although the peak height for acetaldehyde greatly decreased, that for acetone increased 10 times compared to the peak found in TPD in the absence of water vapor. Again, no peak for ethyl acetate was observed.

In the presence of water vapor, the concentration of $H^-(a)$ remains low because it can react with the $H^+(a)$ supplied by Reaction (12) and be desorbed as hydrogen. Therefore, there seems to be no ethoxide formation from acetaldehyde by the reverse of Reaction (9) and thus, no formation of ethanol.

In the presence of water vapor, the desorption rate of acetone and methane greatly increased, indicating that water promotes the conversion of acetaldehyde to acetate. No production of butanes and propylene probably indicates that the dimerization of acetaldehyde is inhibited by its decrease in concentration due to its swift conversion to acetate.

As stated in the introduction, Bowker et al. theorized that acetate was formed from adsorbed acetaldehyde via Reactions (5) and (6)[7]. (We call this route Bowker's theory.) Reaction (5) needs lattice oxygen atoms, which are converted to surface hydroxyls in the presence of water vapor[19]. Therefore, if acetaldehyde is converted to acetate by Bowker's theory, the conversion should be inhibited by the presence of water vapor. This was not the case since the conversion was promoted by water vapor. These facts clearly contradict Bowker's theory.

### 3.5 Theory for the conversion of acetaldehyde to acetic acid

In this paper, the TPD of ethanol and acetaldehyde was explained by several surface reactions and adsorption and desorption reactions involving several surface species. These results can be compiled into a theory for the conversion of acetaldehyde to acetic acid. It is shown as follows:

$$C_2H_5OH(g) \xrightarrow{(7)} \left\{ \begin{array}{l} H^+(a) \\ C_2H_5O^-(a) \end{array} \right. \xrightarrow{(9)} \left\{ \begin{array}{l} CH_3CHO(a) \\ H^-(a) \end{array} \right.$$

$$H_2O(g) \xrightarrow{(12)} \left\{ \begin{array}{l} H^+(a) \\ HO^-(a) \end{array} \right.$$

$$\left. \begin{array}{l} HO^-(a) \\ CH_3CHO(a) \end{array} \right\} \xrightarrow{(4)} \left\{ \begin{array}{l} H_2(g) \\ CH_3COO^-(a) \end{array} \right.$$
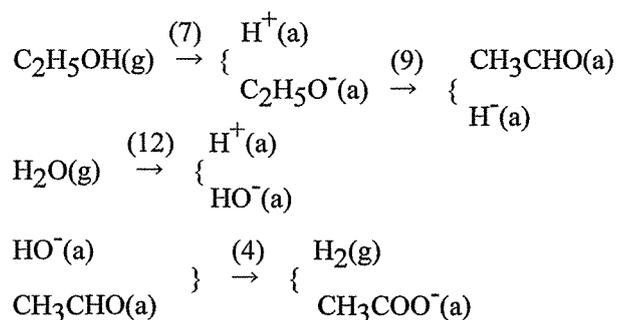
A perturbation study[20] on Reaction (1) showed that the rate-determining step is the conversion of acetaldehyde to acetic acid and that the conversions of ethanol to acetaldehyde and of acetic acid to acetone are rapid. Therefore, from the above theory, the rate-determining step for Reaction (1) should be Reaction (4) by the process of elimination. Reaction (4) is probably started by a nucleophilic attack of a basic hydroxy group on the positively charged carbonyl carbon of acetaldehyde adsorbed on an acidic surface metal ion. It is known that the active catalyst for Reaction (1) needs both acidic and basic sites on its surface[3]. Thus, the conclusion that Reaction (4) is the rate-determining one agrees well with this experimental fact.

### 4. Summary

TPD spectra of ethanol and acetaldehyde adsorbed on a ZnO-CaCO$_3$ (molar ratio = 9:1) catalyst were investigated in the presence or absence of water vapor.

We found that compared with the TPD in the absence of water vapor, most of the desorption products vanished and the desorption rates of acetone and methane increased markedly in the presence of water vapor. These results strongly suggest that water promotes the conversion of adsorbed acetaldehyde to surface acetate.

On the other hand, the desorption peak of ethyl acetate was not observed even in the absence of water vapor. Thus, Kagan's theory for Reaction (1) was rejected in the presence of water vapor. Further, production of surface acetate was promoted by the presence of water vapor despite the fact that the concentration of lattice oxygen decreased. This fact contradicts Bowker's theory.

## References

1)  M. Ya. Kagan, I. A. Sobolev and G. D. Lyubarskii, Chem. Ber., **68B**, 1140 (1935).

2)  R. Sreerama Murthy, P. Patnaik, P. Sidheswaran and M. Jayamani, J. Catal., **109**, 298 (1988).

3)  T. Nakajima, H. Nameta, S. Mishima and I. Matsuzaki, J. Mater. Chem., **4**, 853 (1994).

4)  T. Nakajima, T. Yamaguchi and K. Tanabe, J. Chem. Soc., Chem. Commun., 394 (1987).

5)  M. Ya. Kagan and V. C. Klimenkov, Zh. Fiz. Khim., **3**, 244 (1932).

6)  T. Nakajima, K. Tanabe, T. Yamaguchi, I. Matsuzaki and S. Mishima, Appl. Catal., **52**, 237 (1989); N. Takezawa, N. Iwasa, Catal. Today, **36**, 45 (1997).

7)  M. Bowker, H. Houghton, K. C. Waugh, J. Chem. Soc., Faraday Trans. I, **78**, 2573 (1982).

8)  Submitted to J. Fac. Engin., Shinshu Univ.

9)  S. Araki, in *Gas Chromatography* (Jikken Kagaku Koza, Vol. Zoku-9), edited by H. Hara (Maruzen, Tokyo, 1965), p.146.

10)  N. Takezawa, C. Hanamaki, H. Kobayashi, J. Catal., **38**, 101 (1975).

11)  Y. Iwasawa, Accounts Chem. Res., **30**, 103 (1997); M. Nishimura, K. Asakura, Y. Iwasawa, Proc. 9th Intern. Congr. Catal., 1842 (1988).

12)  Y. Shinohara, T. Nakajima, S. Suzuki, S. Mishima, H. Ishikawa, J. Chem. Software, **4**, 89 (1998).

13)  A. J. Tench, D. Giles, J. F. J. Kibblewhite, Trans. Faraday Soc.,**67**, 854 (1971).

14)  H. Noller, G. Ritter, J. Chem. Soc., Faraday Trans. I, **80**, 275 (1984).

15)  M. Bowker, R. W. Petts, K. C. Waugh, J. Catal., **99**, 53 (1986).

16)  R. G. Greenler, J. Chem. Phys., **37**, 2094 (1962).

17)  Unpublished data.

18)  Komarewsky et al. proposed the following scheme to the conversion of acetaldehyde to acetone in the absence of water vapor:

$$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$$

$$CH_3CH(OH)CH_2CHO \rightarrow CH_3CH(OH)CH_3 + CO$$

$$CH_3CH(OH)CH_3 \rightarrow CH_3COCH_3 + H_2$$

cf. V. I. Komarewsky and J. R. Coley, J. Am. Chem. Soc., **63**, 700 (1941), ibid., **63**, 3269 (1941), V. I. Komarewsky and L. G. Smith, J. Am. Chem. Soc., **66**, 1116 (1944).

19)  H. P. Boehm, Disc. Faraday Soc., **52**, 264 (1971).

20)  T. Nakajima, H. Nameta, S. Mishima, I. Matsuzaki, Nippon Kagaku Kaishi, 121 (1994).