

TPD of Acetic Acid Adsorbed on Zinc Oxide - Calcium Carbonate Catalyst in the Presence or Absence of Water Vapor

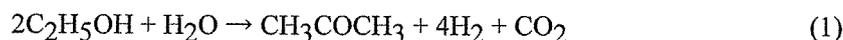
Tsuyoshi NAKAJIMA*, Takehisa YAMAMOTO**, and Shozi MISHIMA***

(Received July 15, 1999; revised January 11, 2000; accepted January 17, 2000)

The Temperature Programmed Desorption (TPD) spectra of acetic acid adsorbed on a ZnO-CaCO₃ (molar ratio = 9:1) catalyst in the presence or absence of water vapor have been studied. It was found that the desorption behavior of acetic acid from the catalyst is well explained by Imanaka's mechanism. The TPD of acetic acid was only slightly influenced by the presence of water vapor except for the decrease in the desorption as 1-butene. This fact suggests that the surface reaction between acetate and acyl groups is the rate-determining step for the conversion of acetic acid into acetone.

1. Introduction

It has been known that ZnO-CaCO₃ catalyst¹⁾²⁾ and Fe₂O₃-ZnO catalyst³⁾⁴⁾ are highly active for the conversion of ethanol to acetone in the presence of water vapor:



It has also been known that the conversion proceeds through the scheme, ethanol → acetaldehyde → acetic acid → acetone^{5)~7)}. However, details of this scheme have not yet been established.

In order to improve these ZnO-based catalysts, it is necessary to elucidate the mechanistic details of the conversion on the catalysts. As a part of the study, we investigated the TPD of acetic acid in the presence or absence of water vapor to obtain information on the conversion of acetic acid to acetone on the ZnO-CaCO₃ catalyst. For the conversion in the absence of water vapor, two reaction mechanisms, which involve the reaction of surface hydroxy groups with acyl groups⁸⁾⁹⁾ or the reaction of acetyl groups with each other¹⁰⁾ as the key step, have already been proposed. The conversion in the presence of water vapor, however, has not yet been studied.

2. Experimental

2.1 Catalyst and reagent

The preparation method of the catalyst has been stated elsewhere¹⁾²⁾. An X-ray diffraction spectrum of the catalyst was obtained using a Gaiger-Flex (Rigaku Denki Co., RAD-1A, CuK α filtered through a graphite monochrometer). Reagent grade acetic acid was used as received from Wako Pure Chemicals Co., Ltd.

2.2 TPD experiment

The TPD experiments were carried out using a conventional vacuum apparatus with a mass filter

* 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

or using a flow system with a GC. When the former apparatus was used, ca. 0.3 g of the catalyst was fixed in a 12 mm ϕ quartz container with a coaxial well for a thermocouple and evacuated for 2 h at 773 K. After cool down to room temperature, the catalyst was equilibrated with acetic acid vapor (the final pressure = 0.13 kPa) for 30 min, followed by evacuation for 1 h. During heating of the catalyst to 1123 K at 13 K/min, we repeatedly analyzed the desorbing compounds to obtain the TPD spectra.

During the analyses using a mass filter (Shinku-Riko Co., NAG-515), ca. 0.09 Pa of Ar gas was added as an internal standard. The mass spectra were recorded by a data analyzer (Shimadzu Co., C-R3A) and analyzed by the least square method using fragmentation coefficients determined by the same conditions for the neat compounds.

This method may sometimes carry large errors when desorbed gas contains several compounds. In this case or in the TPD in the presence of water vapor, the flow system with the GC was used. 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 (vapor pressure = 6.1×10^2 Pa). Stainless steel tubing and a sampling unit were packed in an oven and its temperature was kept over 400 K.

A 0.3 g sample of the catalyst was fixed in a 10 mm ϕ 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 μ L sample of acetic acid was thrice injected into the dry nitrogen stream, which was passed through the catalyst for the adsorption of acetic acid. The catalyst was washed with a neat nitrogen stream for 30 min to eliminate any physically adsorbed acetic acid, 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 literature¹¹⁾ were also applied for a few compounds.

3. Results and discussion

Fig. 1 shows the X-ray diffraction of the catalyst calcined at 773 K for 3 h in air. The peaks were all assigned to zinc oxide, calcium carbonate (Calcite) and basic zinc nitrate, and thus the catalyst was found to be a mixture of these compounds.

The TPD in the presence of water vapor may change the structure of the catalyst. To check this possibility, we heated the sample at 803 K for 2 h in a dry nitrogen stream, then cooled it to room temperature and again heated the catalyst to 803 K in a moistened nitrogen stream (vapor pressure of water = 1.6 kPa). We observed the evolution of carbon dioxide from 773 K, which means the thermal decomposition of the carbonate. In the XRD taken after the experiment, there was no change except for a slight increase in the height of the peaks assigned to the carbonate. Therefore, the TPD in the presence of water vapor made no change in the catalyst except for a slight increase in the degree of crystallization of the carbonate.

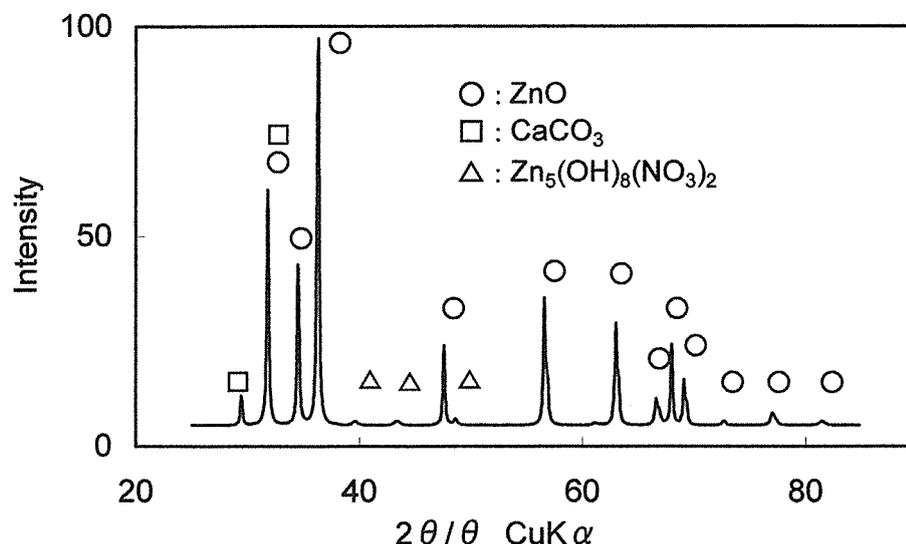


Fig. 1 X-ray powder diffraction profile of the ZnO-CaCO₃ (9:1) catalyst

Fig. 2 shows the TPD spectrum of acetic acid adsorbed on the catalyst. The horizontal axis indicates the temperature of the catalyst and the vertical axis indicates the desorption rate (arbitrary unit). We observed a peak of water at 598 K and peaks of acetone, carbon dioxide and monoxide, i.e., decomposition products of acetic acid, at 600 K. We also observed small peaks of butene and methane near 700 K while we could not find a peak of acetic acid, which means the acetic acid strongly adsorbs on the catalyst. The rapid increase in the evolution of carbon dioxide over 700 K is explained by the decomposition of the carbonate. The existence of peaks for carbon monoxide and hydrogen suggest that the evolution is accompanied by the water gas shift reaction.

Bowker et al.¹²⁾ studied the TPD of acetic acid on ZnO with defects caused by the partial reduction and reported that they observed peaks of acetic acid, ketene, carbon dioxide, hydrogen and water at 600 K. While their results mostly agreed with ours, we could not detect the desorption of acetic acid and ketene. We certainly observed fragment peaks at $m/e = 14$ and 42 in the MS of the evolved gas at about 600 K, but these were attributed to methane and acetone desorbed in the same temperature range on the basis of the quantitative relations between the other fragment ions. We can not completely deny the desorption of ketene but we can say that its production was, if any, very small. In the TPD of acetic acid on TiO₂, the desorptions of acetone and ketene were reported¹⁰⁾. The fact that the desorption products differed from one catalyst to another suggests that the relative rates of the reactions involved in the mechanism of the acetic acid conversion changes with catalysts.

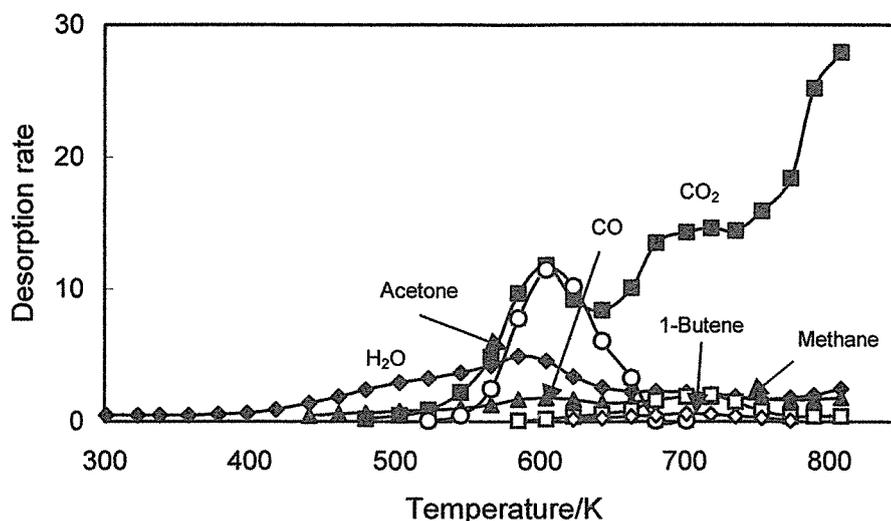
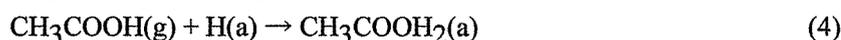
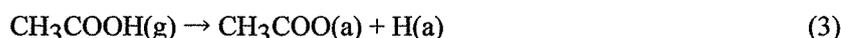


Fig. 2 TPD profiles of acetic acid adsorbed on the ZnO-CaCO₃ catalyst. The sample temperature was raised at a rate of 13 K/min in a vacuum.

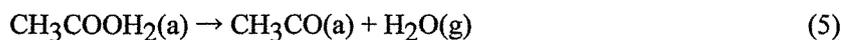
Oxide surfaces are generally hydroxylated by the moisture in air according to the following equation¹³⁾



where H₂O(g) is the moisture in air, HO(a) is a surface hydroxyl group and H(a) is an adsorbed hydrogen (hereafter, species having (g) and (a) denote the gaseous and adsorbed species, respectively). The hydroxy groups desorb as water when heated, but some remain, e.g., after heating and evacuating at 773 K, ca. 1 nm⁻² remained on the ZnO surfaces¹⁴⁾. Acetic acid adsorbs on the hydroxylated surface to produce HO(a), H(a), CH₃COO(a) and CH₃COOH₂(a) as follows⁸⁾:



Water desorbed at 580 K. The temperatures were so high that water was not likely formed from the physically adsorbed water. The water was probably partly formed from the surface hydroxyl groups by the reverse reaction of (2) and partly from CH₃COOH₂(a) by reaction (5). The formed acetyl group probably reacts with the methyl group of the acetate group to form acetone and carbon dioxide according to reaction (6).



These reactions explain the reason why the water desorption (580 K) was accompanied by the desorptions of acetone and carbon dioxide (600 K) in the TPD (Fig. 2). The fact that water, acetone and carbon dioxide desorb at about the same temperature indicates that reaction (5) is more difficult than reaction (6). The same fact cannot be explained by the mechanism proposed by Kim et al.¹⁰⁾, where acetone is produced by the mutual reaction of two acetate groups. Kim's mechanism may not be applied to the reaction on the ZnO-CaCO₃ catalyst.

The desorption of methane observed at 713 K is accompanied by the desorption of carbon dioxide. This fact suggests that acetic acid decomposed through reactions (7) and (8). Since the desorption of methane and carbon dioxide simultaneously occur, the common reaction (7) is rate-determining.



Thus, acetone and methane are probably produced from the acetate group. Acetone, however, desorbs at a 115 K lower temperature than methane. This fact indicates that reaction (7) is more difficult than reaction (5).

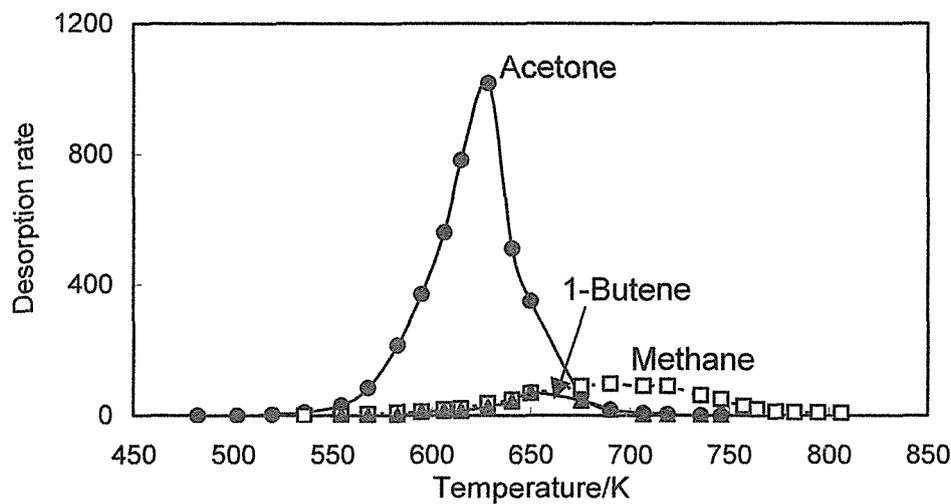
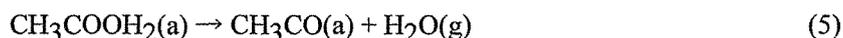
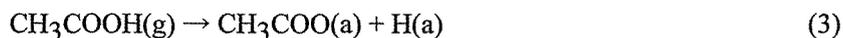


Fig. 3 TPD profiles of acetic acid adsorbed on the ZnO-CaCO₃ catalyst. The sample temperature was raised at a rate of 3 K/min in the absence of water vapor.

From the above TPD results, acetic acid is reasonably thought to convert to acetone through the following mechanism:



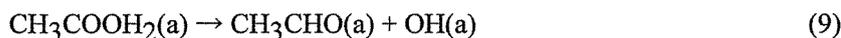
The mechanism agrees well to that proposed by Imanaka et al.⁸⁾ for the conversion on ZnO and MnO, thus their mechanism is found to be valid for the conversion on the ZnO-CaCO₃ catalyst. Since reaction (5) proceeds at the highest temperature among the reactions constituting the mechanism, it is thought to be rate-determining.

Since water is one of the reactants and acetic acid is the intermediate compound in the ethanol conversion to acetone, we studied the effect of water on the acetic acid conversion. The TPD of adsorbed acetic acid was recorded in the absence or presence of water vapor (the pressure = 6.1×10^2 Pa) in the eluting gas stream.

Fig. 3 shows the TPD recorded in the absence of water vapor. Analyzed by the FID, the

desorptions of water, hydrogen, carbon monoxide and dioxide were not measured, but the desorption quantities of the other compounds such as acetone, 1-butene and methane were accurately determined.

The TPD shows that the desorption of acetone (ca. 628 K), 1-butene (ca. 650 K) and methane (ca. 690 K) agreed well with that measured using the mass filter (Fig. 2) except for the slight difference in peak temperature. 1-Butene is reasonably thought to be produced by the hydrogenation of 1,3-butadiene produced by the Lebedev reaction of acetaldehyde which is a product of reaction (9),



The Lebedev reaction is a relatively easy reaction and is promoted by mixed oxides on the basis of silica, alumina, zinc oxide, etc.^{15)~18)} It is also known that the acetaldehyde adsorbed on MgO desorbs as 1,3-butadiene¹⁹⁾.

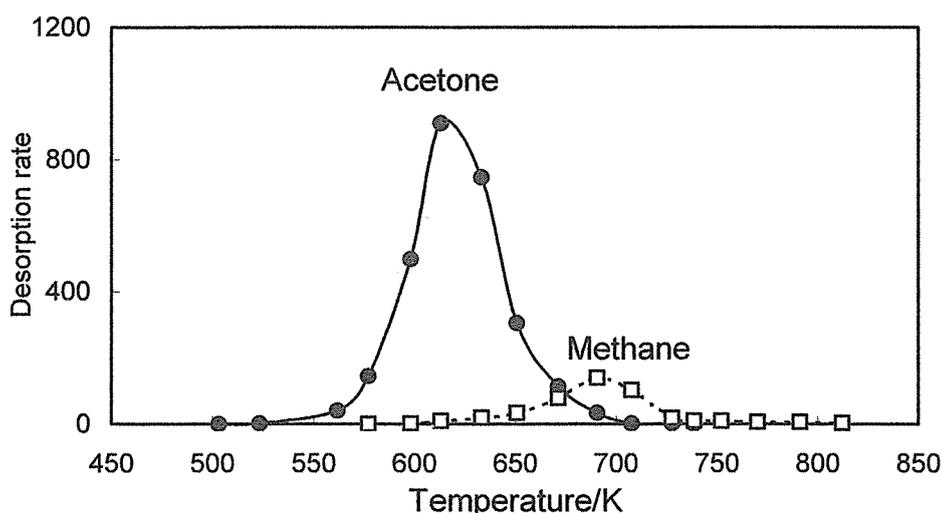


Fig. 4 TPD profiles of acetic acid adsorbed on the ZnO-CaCO₃ catalyst. The sample temperature was raised at a rate of 3 K/min in the presence of water vapor (6.1×10^2 Pa).

Fig. 4 shows the TPD of acetic acid in the presence of water vapor (the pressure = 6.1×10^2 Pa). Acetic acid desorbed as acetone (ca. 620 K) and methane (ca. 690 K). When compared with the TPD in the absence of water vapor, the peak of 1-butene disappeared in Fig. 4. The suppression of 1-butene by water vapor is probably the result of a decrease in the surface concentration of acetaldehyde, the precursor of 1-butene. The conversion of acetaldehyde to acetic acid seems to be promoted by the presence of water vapor. Except for the 1-butene result, the TPD determined in the presence of water vapor agrees well with that determined in the absence of water vapor, indicating that the presence of water vapor have no substantial effect on the conversion mechanism of acetic acid to acetone.

4. Summary

The TPD spectra of acetic acid, an intermediate compound in the conversion of ethanol to acetone,

adsorbed on ZnO-CaCO₃ (molar ratio = 9:1), an effective catalyst for the conversion, have been measured in the presence or absence of water vapor. The X-ray diffraction data indicated that the catalyst was a mixture of zinc oxide, calcium carbonate (calcite) and a small amount of zinc nitrate hydroxide and that the composition is hardly changed during the TPD measurement in the presence of water vapor.

It was found that the desorption behavior of acetic acid from the catalyst as acetone and methane was hardly influenced by the presence of the water vapor (6.1×10^2 Pa) except that 1-butene did not form in the presence of the vapor. The results for the 1-butene desorption were likely explained by the effect of the vapor on the concentration of acetaldehyde, a precursor of acetic acid.

Thus, the conversion of acetic acid to acetone in the presence of water vapor was concluded to proceed through the same mechanism so far proposed for the absence of the vapor, involving the surface reaction of acetate with acyl groups as the rate-determining step.

References

- 1) T. Nakajima, T. Yamaguchi and K. Tanabe: J. Chem. Soc., Chem. Commun., 394 (1987)
- 2) T. Nakajima, K. Tanabe, T. Yamaguchi, I. Matsuzaki and S. Mishima: Appl. Catal., **52**, 237 (1989)
- 3) T. Nakajima, H. Nameta, S. Mishima and I. Matsuzaki: J. Mater. Chem., **4**, 853 (1994)
- 4) R. Sreerama Murthy, P. Patnaik, P. Sidheswaran and M. Jayamani: J. Catal., **109**, 298 (1988)
- 5) T. Nakajima, H. Nameta, S. Mishima and I. Matsuzaki: Nippon Kagaku Kaishi, 121 (1994)
- 6) M. Ya. Kagan, I. A. Sobolev and G. D. Lyubarskii: Chem. Ber., **68B**, 1140 (1935)
- 7) M. Ya. Kagan and V. C. Klimenkov: Zh. Fiz. Khim., **3**, 244 (1932)
- 8) T. Imanaka, T. Tanemoto and S. Teranishi, Preprints of Papers, No.4 in *7th Intern. Congr. Catalysis* (Tokyo, Japan, 1980)
- 9) R. Swaminathan and J. C. Kuriacose: J. Catal., **16**, 357 (1970)
- 10) K. S. Kim and M. A. Barteau: Langmuir, **4**, 945 (1988)
- 11) S. Araki, in *Gas Chromatography* (Jikken Kagaku Koza, Vol. Zoku-9), edited by H. Hara (Maruzen, Tokyo, 1965), p.146.
- 12) M. Bowker, H. Houghton and K. C. Waugh: J. Catal., **79**, 431 (1983)
- 13) H. P. Boehm: Disc. Faraday Soc., **52**, 264 (1971)
- 14) T. Morimoto and H. Naono: Bull. Chem. Soc. Jpn., **46**, 2000 (1973)
- 15) S. V. Lebedev: Zhur. Obschei Khim., **3**, 698 (1933) (Chem. Abstr., **28**, 3050 (1935))
- 16) G. Egloff and G. Hulla: Chem. Revs., **36**, 67 (1945)
- 17) Yu. A. Gorin: Zhur. Obschei Khim., **20**, 1596 (1950) (Chem. Abstr., **45**, 1948g (1951))
- 18) R. Ohnishi, T. Akimoto and K. Tanabe: J. Chem. Soc., Chem. Commun., 1613 (1985)
- 19) N. Takezawa, C. Hanamaki and H. Kobayashi: J. Catal., **38**, 101 (1975)