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Hydrogen generation from ethanol in supercritical water without catalyst

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Abstract—Without oxidizing reagents or catalysts, ethanol was smoothly converted to CH_3CHO and H_2 in supercritical water at 450–500°C. CH_3CHO was further decomposed into CH_4 and CO instead of being oxidized into acetic acid. These features suggest the direct participation of water molecules in the ethanol dehydrogenation. © 2003 Elsevier Science Ltd. All rights reserved.

Supercritical (SC) water is a promising new medium for chemical reactions in both laboratory and industrial scales because of its environmentally benign nature and feasibility in the adjustment of solvent characters. A variety of reactions, including bond fission and oxidation in SC water, have been reported in this decade.[1] The main interest has been focused on the supercritical water oxidation (SCWO) to decompose hazardous chemicals such as PCB, dioxins and chlorinated freons with the aid of oxygen.[2] In these years, however, novel features of reactions in SC water such as organic synthesis[3] or fuel production by waste gasification have been recognized,[4] which encourages our expectation for a new SC water technology to produce useful chemicals.

Recently, we have found that hydrogen and acetaldehyde are formed from ethanol as major products in SC water at 400–500°C *without any oxidizing reagents or catalysts*.[5] The present finding is quite surprising since it is believed, to our best knowledge, that alcohol oxidation to aldehyde needs an oxidizing reagent and that a simple acid–base catalyst does not oxidize alcohol to aldehyde but lead to dehydration to produce alkene or ether.[6] To generate H_2 from ethanol in SC water below 500°C, oxygen is usually added to SC water for the partial oxidation[7] or catalysts is used as in steam reformation.[8] The formation of H_2 and acetaldehyde from ethanol implies the removal of two hydrogen atoms, α-hydrogen and hydroxyl hydrogen in alcohol. Since the activation energy of the process is considered to be quite high, the detachment of hydrogen from alcohol without catalysts has been overlooked in the past. Further experiments have revealed that a similar reaction occurred for isopropyl alcohol to produce H_2 and acetone without any by-products.[5]

In the present paper, we report the main features of the H_2 formation in pure SC water and discuss a possible mechanism for the H_2 formation at the temperature 500°C. We propose the possibility of 'water-catalyzed mechanism' including the participation of some water molecules in its transition state, which will provide a key concept to understand novel features of reactions in SC water.

A flame-sealed small quartz tube was used as a reactor. The quartz reactor was selected to avoid the possible catalytic activity of the reactor wall. The effects of metal walls on reactions were separately examined by placing stainless steel (SUS 316) or copper wires in the quartz capillary together with the reactants and solvent. Special attention was paid to thoroughly eliminate oxygen from water because the partial oxidation of alcohol by dissolved O_2 gas also generates H_2. Water was completely degassed by the freeze-and-thaw procedure and the quartz reactor was sealed under vacuum. The water density and temperatures used for the experiments were 0.20 g/cm^3 and 500°C, respectively. From the amount of the reaction products and the survived reactant, the time-dependent yields of respective products were calculated.[10]

Keywords: supercritical water; ethanol; decomposition; dehydroxylation; wall effect; oxidation.

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Ethanol in water was decomposed at the density of 0.20 g cm^{-3} and at 500°C. Acetaldehyde was the only detectable component in the liquid phase, while hydrogen, methane, carbon monoxide, carbon dioxide and small amounts of ethylene and ethane were detected in the gas phase. The amount of hydrogen was stoichiometrically equal to the sum of acetaldehyde, carbon monoxide and twice amounts of carbon dioxide. Such stoichiometry suggests the following successive reactions.

The initial step is the dehydrogenation from ethanol, which is followed by the decomposition of CH_3CHO into CH_4 and CO, and finally CO is converted into H_2 by the water–gas shift reaction. All these processes can proceed smoothly without any catalyst. The yield of CH_3CHO increases with time at a initial rate of 3.52×10^{-5} s^{-1}.

To confirm the absence of further oxidation of acetaldehyde to acetic acid, an aqueous acetaldehyde solution was heated above the critical temperature. No acetic acid was detected even after 60 min heating at 450°C; instead, the decomposition to CH_4 and CO was observed.[11] The generated CO was then suffered from the water–gas shift reaction to produce H_2 and CO_2.

The production of ethylene in the present reaction suggests an additional reaction pathway, i.e. the elimination of a water molecule from ethanol. This process occurred with a smaller branching ratio relative to the dehydrogenation. A part of resulting ethylene could be converted to ethane by the hydrogen addition.[13] As apparent from Figure 1, the yield of ethylene starts decreasing after 30 min while the ethane yield still increases. If this is the case, the sum of ethylene and ethane yields should corresponds to the amount of ethylene generated by the dehydration. Figure 2 shows that the sum of ethylene and ethane yields obeys the 1st order fit with respect to time. The evaluated rate constant was 1.29×10^{-5} s^{-1}, which is about one-thirds of the decomposition rate.

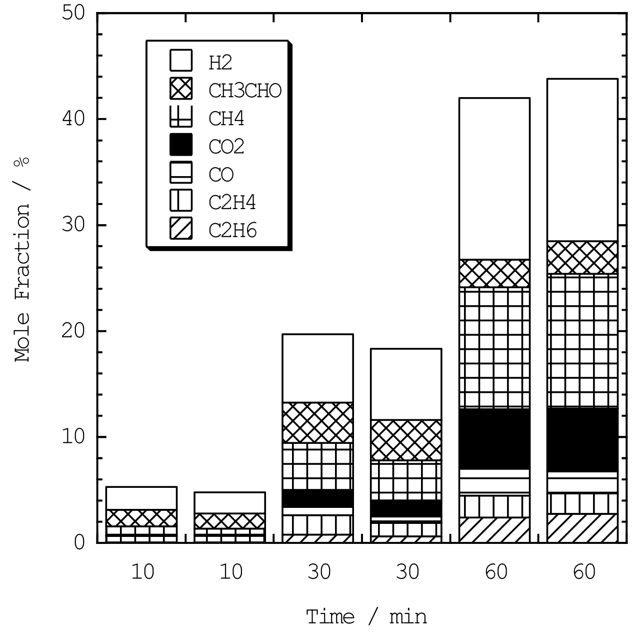


Figure 1. Time dependence of the yields of all products for ethanol reaction at the density of 0.20 g cm^{-3} at 500°C. The experiments at a given condition have been carried out twice as presented above.

The decomposition of ethanol in SC water thus proceeds in parallel two pathways, Schemes 1 and 2 with the major contribution of the dehydrogenation pathway 1. In the course of this study, we noticed that the effects of metallic reactor wall and the residual oxygen are quite significant. The wall effect to the decomposition was examined by introducing the SUS 316 and copper wires into the quartz reactor. The effect of residual

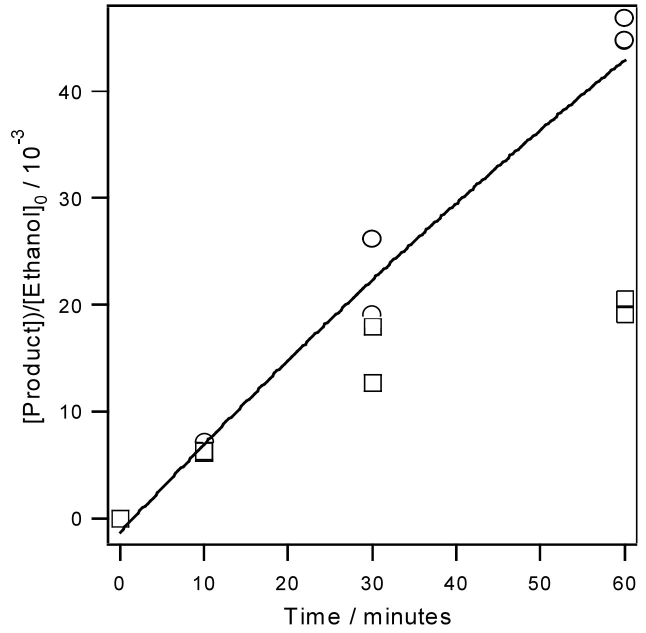
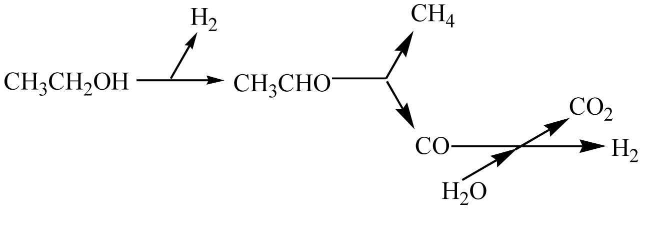
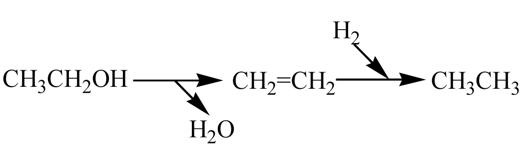


Figure 2. Time dependence of C_2H_4 and C_2H_6 production. Keys are as follows: ○, $CH_2{=}CH_2{+}CH_3CH_3$; □, $CH_2{=}CH_2$. The solid line shows the fitting curve of the initial rate of C_2H_4 generation by first order rate law.



Scheme 1.



Scheme 2.

oxygen was also examined by comparing the product yields between degassed and non-degassed samples.

As listed in Table 1, the copper wire accelerated the whole reaction considerably at the density of 0.34 g cm^{-3} at 450°C, whereas SUS 316 showed little catalytic effect. Also shown in Figure 3 is the effect of residual oxygen in water. At 450°C and at the density of 0.34 g cm^{-3}, the acetaldehyde yields for the non-degassed samples are always larger than those of degassed samples. Thus, residual oxygen must be eliminated to obtain the accurate mechanism for the ethanol decomposition in SC water.

Regarding the mechanism of the ethanol decomposition in SC water without catalytic reagents, three possibilities are considered, that is, ion, radical and water-catalyzed mechanisms. The first possibility involves the participation of ionic species in supercritical water, i.e. H^+ or/and OH^-. However, aqueous ethanol is never oxidized to acetaldehyde in the presence of acidic or alkaline reagent under the ambient condition. Instead, ethanol is dehydrated to ethylene or ether. In fact, the enhancement of the dehydration by acid catalyst in SC water was reported.[12] From this fact, H^+/OH^- in SC water is considered to facilitate only the minor ethylene formation process in the present reaction system. In the second possibility, two radical species should be considered, OH and H radicals. At high temperatures in the presence of oxygen molecules, OH radicals are recognized to play an essential role in the oxidation of organic compounds.[14,15] If the OH radical mechanism is applicable to the present system, acetaldehyde should be further oxidized to acetic acid as was observed in SCWO.[15] Thus, the absence of acetic acid production in the present system negates the oxidation by OH radicals. Another free radical H, if present in the system, may abstract hydrogen from the α-C–H bond which is weaker than the C–H bonds of alkanes.

$$H+CH_3CH_2OH \rightarrow H_2+CH_3CHOH \tag{1}$$

$$CH_3CHOH \rightarrow CH_3CHO+H \tag{2}$$

Above two radical reactions were reported in the radiolysis of alcohol in the vapor phase[16] and the stoichiometry and the side products are similar to the present result. However, without a high-energy source for the bond fission, this process can hardly be initiated even in high temperature SCW system because of its high activation energy.[9]

The third possibility is the direct participation of water molecules through a multicenter transition state including an ethanol molecule and several water molecules bridging the oxygen atom of ethanol and the α-hydrogen. Takahashi et al.[17] suggested the occurrence of such reaction based on the theoretical calculations. They proposed a transition state consisting of an ethanol molecule and two water molecules as shown in Scheme 3. The transfer of hydrogen atoms among three molecules produces a hydrogen molecule, two water molecules and resulted in an oxidized molecule, acetaldehyde.

Similar proton-transferring mechanisms in SCW involving one or two water molecules were proposed so far

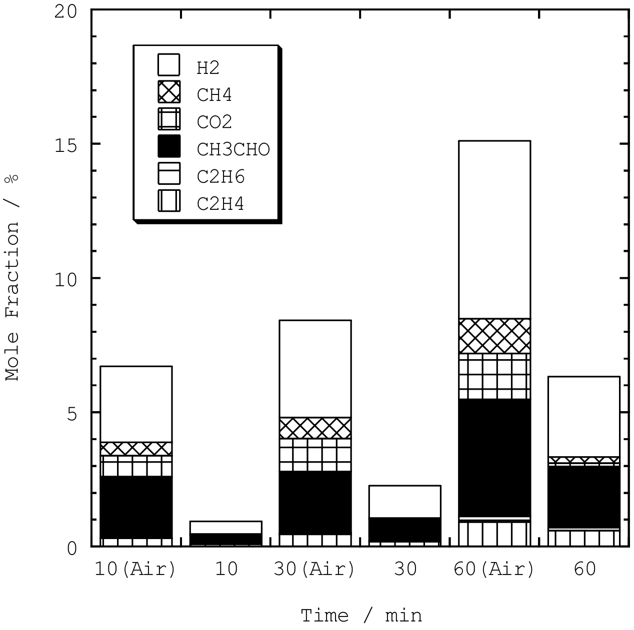
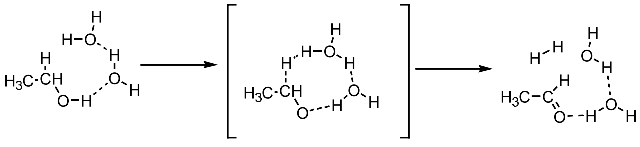


Figure 3. Oxygen effect on the ethanol decomposition reaction. (Air) indicates the yields of the typical reaction products in the non-degassed experiments. Details are described in text.



Scheme 3.

Table 1. The wall effects on the yields of the major products in ethanol decomposition in SCW at 450°C, $\rho = 0.34$ g cm^{-3}, 30 min

Entry	Conc. (M)	Metal catalyst	H_2 (mol%)	CH_4 (mol%)	CH_3CHO (mol%)
1	1.0	–	1.19	0.0358	0.798
2	1.0	–	1.20	0.0581	0.862
3	1.0	SUS 316	1.00	ND	0.759
4	1.0	SUS 316	1.26	0.0243	0.673
5	1.0	Cu	2.75	0.0568	1.73
6	1.0	Cu	1.90	0.0790	1.36

ND: Detected, but could not be determined quantitatively.

for the water–gas shift reaction[18] and the formic acid decomposition in subcritical water.[19] In addition, proton transfer through the water wire is considered to play a critical role in catalytic processes of enzyme reactions.[20] Considerable number of organic reactions in SCW might proceed through the water-bridged transition state.

Although the reaction mechanism of ethanol decomposition in SCW is not well identified, the water-catalyzed mechanism seems to be the most reasonable at present. We are planning to collect another evidence for the above mechanism.

Acknowledgements

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