Kinetic Study on Disproportionations of C1 Aldehydes in Supercritical Water: Methanol from Formaldehyde and Formic Acid

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The reaction pathways and kinetics of C1 aldehydes, formaldehyde (HCHO) and formic acid (HCOOH═HOCHO), are studied at 400 °C in neat condition and in supercritical water over a wide range of water density, 0.1−0.6 g/cm^3. Formaldehyde exhibits four reactions: (i) the self-disproportionation of formaldehyde generating methanol and formic acid, (ii) the cross-disproportionation between formaldehyde and formic acid generating methanol and carbon dioxide, (iii) the water-independent self-disproportionation of formaldehyde generating methanol and carbon monoxide, and (iv) the decarbonylation of formaldehyde generating hydrogen and carbon monoxide. The self- and cross-disproportionations overwhelm the water-independent self-disproportionation and the formaldehyde decarbonylation. The rate constants of the self- and cross-disproportionations are determined in the water density range of 0.1−0.6 g/cm^3. The rate constant of the cross-disproportionation is 2−3 orders of magnitude larger than that of the self-disproportionation, which indicates that formic acid is a stronger reductant than formaldehyde. Combining the kinetic results with our former computational study on the equilibrium constants of the self- and cross-disproportionations, the reaction mechanisms of these disproportionations are discussed within the framework of transition-state theory. The reaction path for methanol production can be controlled by tuning the water density and reactant concentrations. The methanol yield of ∼80% is achieved by mixing formaldehyde with formic acid in the ratio of 1:2 at the water density of 0.4 g/cm^3.

1. Introduction

C1 chemistry is the chemistry of simplest organic compounds with single carbon atom. Coupled with energy issues, one of the most important targets of C1 chemistry is the production of such compounds as alcohols or olefins.[1−9] To obtain a desired product, reaction path control is indispensable, and it is often done by using hazardous organic solvents and catalysts. Organic reactions in supercritical water, in contrast, can be controlled through solvation by tuning the reaction temperature and the water (solvent) density.[3,4,10] In the present work, we thus develop the C1 chemistry in supercritical water and provide a clean C1 chemistry without any catalysts. Here we focus on the noncatalytic reactions of C1 aldehydes, formaldehyde and formic acid, and develop a clean process of methanol formation in supercritical water on the basis of kinetic analysis with the water density variation at 400 °C.

Methanol is an alternative energy source to fossil fuels and is commercially produced by the gas-phase reaction of carbon monoxide and hydrogen (synthesis gas) in the presence of catalysts.[11] The reaction of C1 aldehydes in supercritical water can serve as a new and clean way of methanol production. In hot water, aldehyde is a source of the corresponding alcohol through the noncatalytic self- and cross-disproportionations.[1,2,12] The former is a redox reaction of two aldehyde molecules of the same kind to produce alcohol and carboxylic acid, and the latter is a redox reaction of aldehyde and formic acid (hydroxyl formaldehyde) to produce alcohol and carbon dioxide. Both proceed without base catalyst in sub- and supercritical water, which sharply differentiates the hydrothermal disproportionations from the base-catalyzed Cannizzaro reaction in ambient condition.[13] Here we use supercritical water as a clean reaction medium and optimize the methanol yield by tuning the water density.

Hydration strongly influences the hydrothermal reactivity of organic molecules. The variation of the water density allows us to control hydration and to clarify the reaction mechanisms. However, there are a limited number of studies which focus on the water density effect on aldehyde disproportionations in supercritical water[14] despite the intensive studies of hydrothermal aldehyde disproportionations with a wide range of pH variation from basic to acidic conditions.[15−22] In the present work, we study the water density effect on the self- and cross-disproportionations of formaldehyde through the determination of the rate constants at 400 °C in the water density range of 0.1−0.6 g/cm^3. Previously, we computationally examined the equilibrium constants of the self- and cross-disproportionations and the formaldehyde hydration in a wide range of temperature and water density.[3,4] Combining the experimental and theoretical results, here, we elucidate the reaction mechanisms of the self- and cross-disproportionations by proposing a key role of methanediol ($CH_2(OH)_2$), the hydrated form of formaldehyde, as a reactant in the self-disproportionation.

In the former experimental work on the hydrothermal reactions of C1 aldehydes in subcritical water, we focused on the clean C−C bond formation without organic solvent or metal catalyst.[1,2] In the present work, we expand the formaldehyde reaction into supercritical conditions and focus on the clean methanol formation, which serves as a model for various alcohol productions from corresponding aldehydes in hydrothermal conditions.[14,23−25] On the basis of the kinetic analysis, we control

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the reaction path for methanol production by the water density and reactant concentrations and show that supercritical water is more suitable for selective methanol formation than subcritical water. Our kinetic analysis is performed using ^{1}H and ^{13}C NMR spectroscopy to detect all of the products in the gas and the liquid phases and monitor the minute-scale production of methanol.

The experimental procedure is in section 2. In section 3.1, we discuss the reaction scheme on the basis of the product distribution at a fixed reaction time. In section 3.2, the time evolutions of reactants and products are examined in both neat and hydrothermal consitions. In section 3.3, the reaction mechanisms of the self- and cross-disproportionations are examined on the basis of the rate constants and the former computational studies.[3,4] In section 3.4, path weight control for methanol formation is demonstrated as a clean method for methanol production. Conclusions are given in section 4.

2. Experimental Section

1,3,5-Trioxane (a formaldehyde trimer, called *s*-trioxane hereafter) was obtained from Nacalai and used without further purification. ^{13}C-enriched formalin (99 at. % and 20% in H_2O) was obtained from ISOTEC and was used as received. As a solvent, water (H_2O) was purified using a Milli-Q Labo (Millipore) filter system.

^{13}C-enriched formalin was sealed in a quartz tube with water under argon atmosphere. The tube was 2.5 mm i.d. and 4.0 mm o.d. The reaction temperature was fixed at 400 °C. The sample filling factor, defined as the volume ratio of the solution to the total sample tube at room temperature, determines the water density in supercritical conditions and was varied from 0.1 to 0.6. The filling factor corresponds to the water density in the range of 0.1−0.6 g/cm^3. While the water density was varied, the concentration of formaldehyde in supercritical conditions was fixed at 0.1 M (mol dm^{-3}). To clarify the effect of water, the neat reaction was also studied at 400 °C. In the neat reaction, *s*-trioxane was used as a formaldehyde producer and was sealed in a Pyrex NMR tube of 7.0 mm i.d. and 8.0 mm o.d. under argon atmosphere without water. The initial formaldehyde concentration was set to 0.1 M, which corresponds to the *s*-trioxane concentration of 0.1/3 M.

Each sample tube was heated in a programmable electric furnace kept at the reaction temperature of 400 ± 1 °C. In the hydrothermal reaction, the sample was removed from the furnace after a desired reaction time and cooled to room temperature by a water bath. The sample was then put in a Pyrex NMR tube, and the ^{1}H and proton-decoupled ^{13}C NMR spectra were measured at room temperature with 400- and 500-MHz NMR (ECA, JEOL). In the reaction tube, the liquid and gas phases coexist, and the both phases are measured to identify all the products. The liquid and gas phases were separately measured as described elsewhere.[14] In the neat reaction, the sample was cooled with air within a minute and the ^{1}H and proton-decoupled ^{13}C NMR spectra were measured with 400- and 600-MHz NMR. In this case, the NMR spectra were taken at 130 °C so that the sample may be in the homogeneous gas phase.

In the neat experiment, we used a Pyrex tube with a thickness of 0.5 mm as a reactor. The time evolution was observed for the reactant and products at time intervals of 5−15 min by the repetition of heating, cooling, and measuring of a single sample. Because of the thinness of the used tube, the sample reaches the reaction temperature in less than 30 s. We have confirmed that the neat reaction of formaldehyde does not proceed at all within 60 min at the reaction temperature lower than 300 °C. The essential dead time is therefore the time needed for a sample to reach 400 °C from ∼300 °C and is much shorter than 30 s. Thus, the effect of the time needed for the sample to reach the reaction temperature was not taken into account due to the separation of the time scales of the reaction monitoring and the essential dead time. The hydrothermal reaction was studied at a time step of 1 min since the reaction is rather rapid. A series of samples were used to obtain the time evolution of the spectra instead of repeating the heating, cooling, and measuring of a single sample. A number of samples were prepared for each reaction mixture, and every sample was assigned to a different reaction time as described in the previous paper.[1] This is because it takes about 1 min until the sample attains the desired reaction temperature due to the low thermal conductivity of quartz[26] and because this "dead time" brings an artifact to the time evolution. The reaction time was set to 2 min or longer. This treatment reduces the error of reaction time to less than 1 min, while with a single sample, the error increases as the number of repetition time of the reaction and measurement increases.

3. Results and Discussion

The reaction scheme and kinetics of formaldehyde in supercritical water are studied by analyzing the neat and hydrothermal reactions of formaldehyde at 400 °C. To establish the kinetics, all the chemical species need to be analyzed quantitatively in both liquid and gas phases. We have applied powerful ^{1}H and ^{13}C NMR spectroscopy to quantify the time evolution of all the reaction products with and without protons.

3.1. Products and Reaction Pathways.

3.1.1. Neat Reaction. First we examine what products are generated and how they are distributed in the reaction of formaldehyde in the absence of water at 400 °C. The initial concentration of *s*-trioxane is set so that it may provide 0.1 M formaldehyde after immeasurably fast monomerization. Figure 1a shows the ^{1}H NMR spectrum after 60 min of reaction. More than 91% of the proton-based mass balance is maintained through the reaction; all of the main reaction pathways are covered by the present study.

Formaldehyde, carbon monoxide, and methanol are observed as major products. Products are generated in the decreasing order:[27]

$$\mathrm{HCHO}\ (0.32) > \mathrm{CO}\ (0.20) > \mathrm{CH_3OH}\ (0.14) > \mathrm{H_2}\ (0.05)$$

The numbers in the parentheses are the yields, the product concentrations divided by the initial concentration of formaldehyde. The yield of carbon monoxide is nearly equal to the sum of methanol and hydrogen yields. The equality can be explained by the following reactions:

$$\mathrm{2HCHO} \rightarrow \mathrm{CH_3OH} + \mathrm{CO} \qquad (1)$$

$$\mathrm{HCHO} \rightarrow \mathrm{CO} + \mathrm{H_2} \qquad (2)$$

Equation 1 is the water-independent self-disproportionation of formaldehyde, in which one formaldehyde molecule reduces the other into alcohol and oxidizes itself to carbon monoxide in the absence of water.[24] It is striking that formaldehyde disproportionates without any solvents or catalysts. The water-independent bimolecular self-disproportionation is found only for formaldehyde.[14] Equation 2 is the proton-transferred decarbonylation of formaldehyde.[24] In this reaction, one proton is intramolecularly transferred to the other proton attached to the same carbonyl group to form a hydrogen−hydrogen bond, followed by the carbonyl group elimination through a breakage of two hydrogen−carbon bonds. The proton-transferred bi-

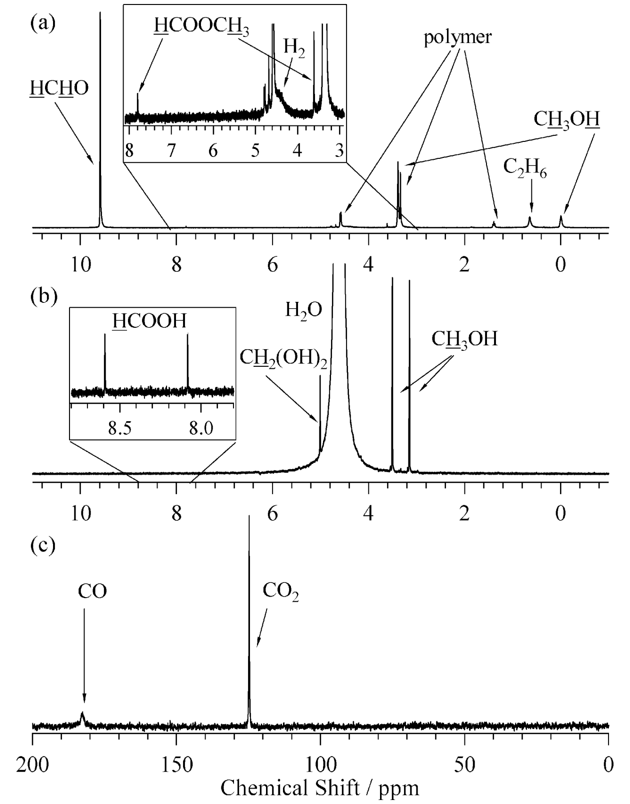

Figure 1. (a) ^{1}H NMR spectrum for the reaction of 0.1 M formaldehyde (*s*-trioxnae) after 60 min at 400 °C without solvent. Since H_2 shows a broad signal, it overlaps with other peaks. (b) ^{1}H NMR spectrum of the liquid phase for the reaction of 0.1 M formaldehyde (^{13}C-enriched formalin) after 4 min with water density of 0.4 g/cm^3 at 400 °C. Though the signal of methanediol is a doublet due to ^{13}C−H coupling, one of the signals is hidden by the peak of H_2O. (c) ^{13}C NMR spectrum of the gas phase. Neat spectrum a is measured at 130 °C to make the sample homogeneous. Spectra b and c of the hydrothermal reaction are measured at 40 °C. Since the NMR measurement is performed at room temperature, formaldehyde is hydrated and is observed as methanediol in spectrum b.

molecular decarbonylation found here for the C1 aldehydes is common to other aldehydes.[14,23,25]

3.1.2. Hydrothermal Reaction. Here we examine how the reaction of formaldehyde is modified by the presence of water. The reaction is studied for 0.1 M formaldehyde at a water density of 0.4 g/cm^3 at 400 °C. Parts b and c of Figure 1 show, respectively, the liquid-phase ^{1}H NMR and gas-phase ^{13}C NMR spectra after 4 min of reaction. It is to be noted that the mass balance is maintained through the reaction within an error of 2% based on carbon atom. As seen in Figure 1b, methanol is the primary product. Products generated are in the decreasing order as follows:

$$CH_3OH\ (0.38) > CO_2\ (0.28) > CH_2(OH)_2\ (0.24) > H_2\ (0.09) > CO\ (0.07) > CH_3OCH_2OH\ (0.01) > HCOOH\ (<0.01)$$

It is of great interest that the methanol yield is ~3 times larger than that in the neat gas and that the reaction is much faster in supercritical water. A trace amount of formic acid is detected in supercritical water, in contrast to the neat condition. Unlike the neat condition, neither ethane nor methyl formate is observed.[27] Importantly, the yields of byproducts including formaldehyde polymers are less than 2%. Thus hot water strongly enhances the methanol formation and suppresses side reactions of formaldehyde such as polymerization.

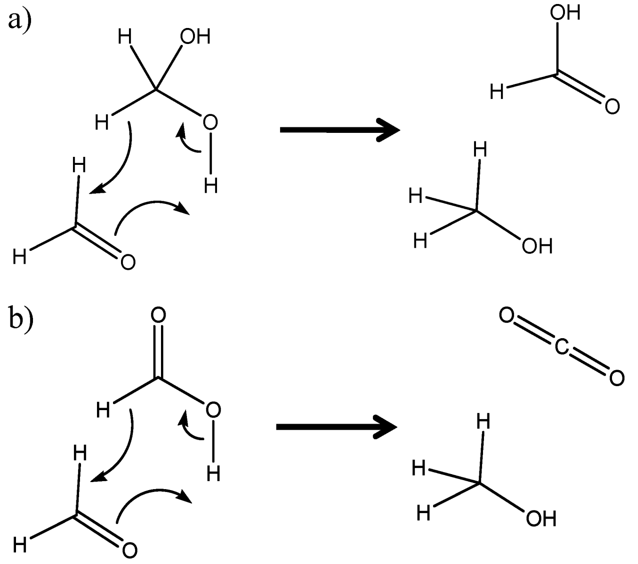

Figure 2. Proposed reaction mechanisms of (a) the self-disproportionation and (b) the cross-disproportionation.

As mentioned above, the methanol formation is significantly enhanced by the presence of water. A new reaction path is opened by the presence of water. It is proposed as the following:

$$2HCHO + H_2O \rightarrow HCHO + CH_2(OH)_2 \rightarrow CH_3OH + HCOOH \quad (3)$$

Equation 3 is the self-disproportionation of formaldehyde, in which two molecules of formaldehyde react to reduce one formaldehyde and oxidize the other.[1,2,12] We propose a mechanism as shown in Figure 2a. One formaldehyde is first hydrated into methanediol and then disproportionates with unhydrated formaldehyde. In supercritical water, no base catalyst is needed to reduce formaldehyde, in sharp contrast to the usual base-catalyzed Cannizzaro reaction in ambient condition.[13]

The self-disproportionation is to generate methanol and formic acid in an equal amount with each of their yields not exceeding 50%; see eq 3. There is, however, a marked difference in the yield between methanol and formic acid. Some other reaction path must exist that can generate methanol besides eqs 1 and 3. Methanol can be produced additionally by

$$HCHO + HCOOH \rightarrow CH_3OH + CO_2 \quad (4)$$

Equation 4 is the cross-disproportionation, a redox reaction between aldehydes of different kinds. Here, formic acid, a member of C1 aldehyde, reduces formaldehyde into methanol and oxidizes itself into carbon dioxide.[28] The mechanism is proposed in Figure 2b. Similar to the self-disproportionation (eq 3), the cross-disproportionation in supercritical water proceeds without base catalysts. The extremely low concentration of formic acid indicates that formic acid is a reactive intermediate and that as soon as formic acid forms, it is consumed by the cross-disproportionation. It is of interest that, practically, formic acid, the oxidized formaldehyde, has a stronger reducing ability than formaldehyde. In the case of other aldehydes, the cross-disproportionation with formic acid also proceeds faster than the self-disproportionation.[14,25] Hot water makes base catalyst unnecessary that is needed in the ambient condition. Thus, the hydrothermal disproportionations illustrate the potential of sub- and supercritical water as a new solvent for green organic chemical reactions.

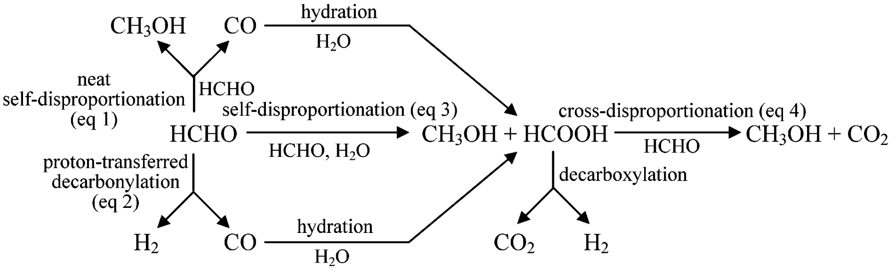

Figure 3. Proposed reaction pathways of C1 aldehydes in supercritical water at 400 °C.

Figure 3 shows the proposed reaction scheme of formaldehyde in supercritical water at 400 °C. The reactions which require water as a reactant or solvent are written with horizontal arrows, and the reactions which proceed in both neat and hydrothermal conditions are written with vertical arrows. The self-disproportionation and the hydration of carbon monoxide give rise to formic acid,[5,6] which is consumed immediately by the cross-disproportionation. The formation and consumption of formic acid are the core of the hydrothermal reaction of formaldehyde. It is thus significant that formic acid is observed in this study, which strongly supports the reaction scheme shown in Figure 3.

3.2. Time Evolution of Reactants and Products. In supercritical water, methanol is produced from the water-independent self-, hydrothermal self-, and cross-disproportionations. To determine each reaction path weight, it is thus indispensable to divide the observed time evolution of methanol into components of each disproportionation. In supercritical water, every product is provided by multiple reactions, as seen in Figure 3, and it is impossible to discuss the path weight based on the product distribution in supercritical water alone. In this section, we first determine the rate constants of the water-independent self-disproportionation (eq 1) and the decarbonylation of formaldehyde (eq 2) in the absence of water. Then we clarify the path weights of other reactions in supercritical water, assuming that the solvent water has little effect on the rate constants of the water-independent self-disproportionation and the formaldehyde decarbonylation.

3.2.1. Water-Independent Self-Disproportionation and Decarbonylation of Formaldehyde. Here, we determine the rate constants of the water-independent self-disproportionation $k_{\mathrm{wi-self}}$ and the decarbonylation of formaldehyde k_{deCO} based on the time evolution of formaldehyde, methanol, and hydrogen. Figure 4a shows the time evolution of the reactants and products in the reaction of 0.1 M formaldehyde (0.1/3 M *s*-trioxane) in the absence of solvent at 400 °C. According to eqs 1 and 2, the rate equations for methanol and hydrogen are expressed as

$$\frac{\mathrm{d[CH_3OH]}}{\mathrm{d}t} = k_{\mathrm{wi-self}}[\mathrm{HCHO}]^2 \tag{5}$$

$$\frac{\mathrm{d[H_2]}}{\mathrm{d}t} = k_{\mathrm{deCO}}[\mathrm{HCHO}] \tag{6}$$

The reactions of formaldehyde are considered to be second order in the water-independent self-disproportionation and first order in the decarbonylation. Since the concentration of formaldehyde [HCHO] can be considered as constant at the early stage of reaction (<15 min), $k_{\mathrm{wi-self}}$ and k_{deCO} are respectively obtained by expressing the concentrations of methanol [CH_3OH] or hydrogen [H_2] as a linear function of the reaction time. The values of $k_{\mathrm{wi-self}}$ and k_{deCO} are determined as $(8 \pm 4) \times 10^{-4}$ M^{-1} s^{-1} and $(4.4 \pm 0.3) \times 10^{-5}$ s^{-1}, respectively.

Here, we compare the decarbonylation rate of formaldehyde and acetaldehyde. The value of k_{deCO} for formaldehyde is ∼0.2 of that for acetaldehyde at 400 °C obtained in the previous study.[14] This result corresponds to the orbital size of the proton-accepting atom. In the decarbonylation of formaldehyde, the orbital of transferred proton must overlap with another proton orbital to form a proton−proton bond, while in the decarbonylation of acetaldehyde, the transferred proton's orbital overlaps with a carbon orbital of a methyl group to form a proton−carbon bond. Because the size of the proton orbital is small, the formation of a proton−proton bond in a single formaldehyde molecule is more difficult than that of a proton−carbon bond in an acetaldehyde molecule.

3.2.2. Time Evolution of Reactant and Products in Supercritical Water. Here we examine how the time evolution of the products varies with the water density. Parts b and c of Figure 4 show how the reactant is depleted and products are evolved in the hydrothermal reaction of 0.1 M formaldehyde at 400 °C and water densities of 0.1 and 0.4 g/cm^3, respectively. The time evolution of formic acid is expanded in Figure 4d because of its low concentration. As seen in Figure 4a,b, the methanol formation is markedly accelerated by the presence of water (note the time scales of Figure 4a,b). The methanol yield of ∼30% is achieved within 10 min in supercritical water at the water density of 0.1 g/cm^3, whereas in the neat condition, it attains only ∼3% within the same reaction time. The methanol formation in the hydrothermal condition is clearly governed by the reactions unique to the hydrothermal condition and not by the water-independent self-disproportionation (eq 1). The self- (eq 3) and the cross-disproportionations (eq 4) are to be the major reactions in supercritical water. It is of interest that the reaction scheme is changed so drastically by the presence of water even when the water density is so low as 0.1 g/cm^3.

When the water density is increased from 0.1 to 0.4 g/cm^3, the product distribution varies notably indicating the path weight variation. As seen in Figure 4b−d, the methanol formation is accelerated and the formic acid concentration decreases as the water density increases. This implies the acceleration of the cross-disproportionation, as discussed in detail below. Also it should be noted that the yield of carbon monoxide is ∼20% and is almost constant at 0.1 g/cm^3, while at 0.4 g/cm^3, it attains only ∼10% and disappears after 9 min of reaction. It is suggested that, at the high water density of 0.4 g/cm^3, water is plenty enough to convert all carbon monoxide into formic acid through the hydration, while at 0.1 g/cm^3, this process does not proceed appreciably for lack of water. This corresponds well to the reaction scheme in Figure 3, in which formic acid is provided from both self-disproportionation (eq 3) and hydration of carbon monoxide. The hydrothermal disproportionations (eqs 3 and 4) and the formation of formic acid through the hydration of carbon monoxide are common to other aldehydes.[14,23−25]

To see the path weights of the methanol formations, we divide the observed methanol yield into the partial yields of the water-

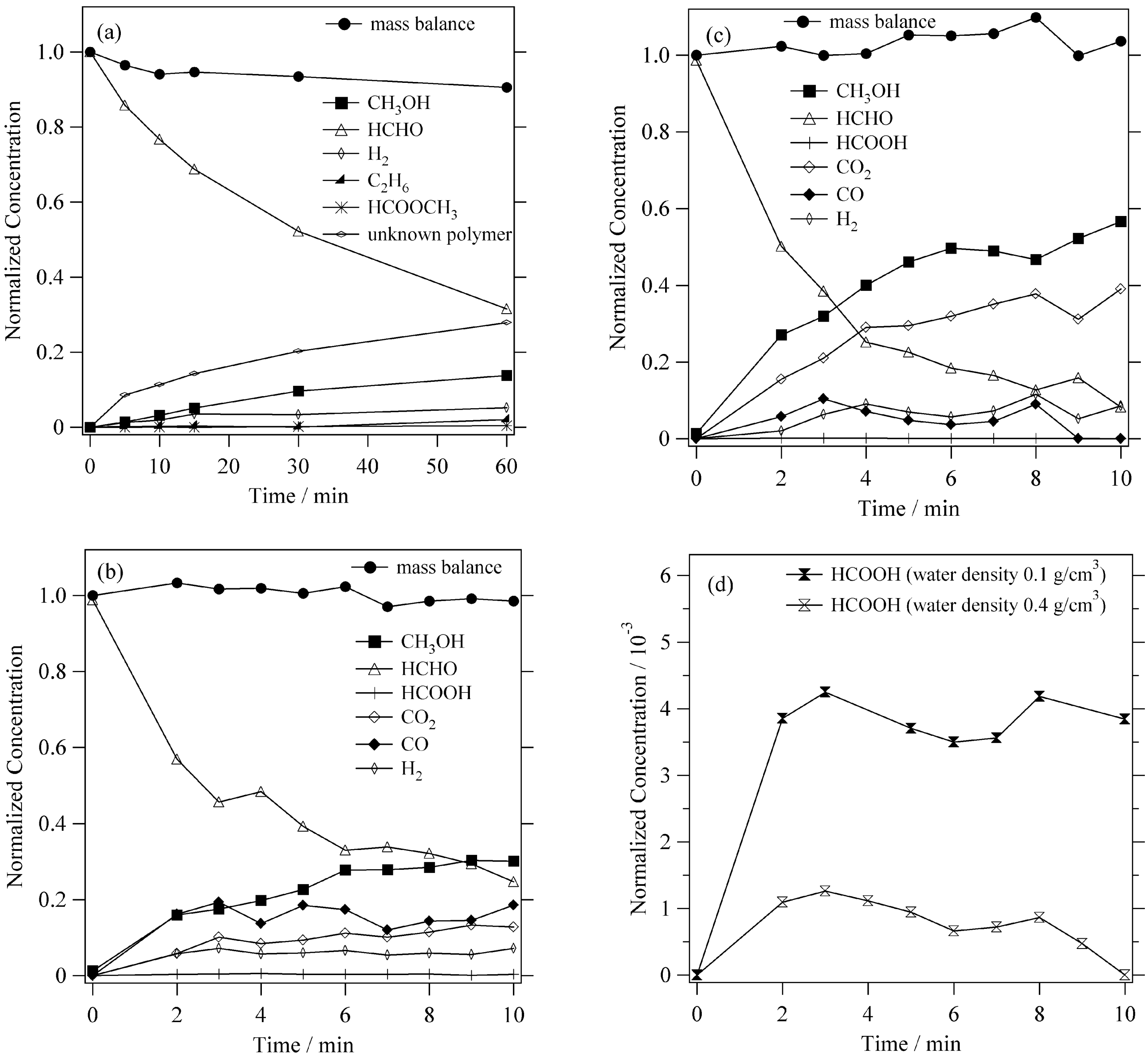

Figure 4. Time evolutions of the formaldehyde and product concentrations at 400 °C. (a) Neat reaction with the initial concentration of 0.1 M. (b and c) Hydrothermal reactions with the initial concentration of 0.1 M at water densities of 0.1 (b) and 0.4 g/cm^3 (c). The time scale in the supercritical condition (b and c) is one-sixth of that in the neat condition (a). (d) Time evolution of formic acid at the water densities of 0.1 and 0.4 g/cm^3. Note that the ordinate scale in panel d is smaller by three orders than those in panels a−c. The normalized concentration denotes the ratio of the product concentration against the initial concentration of formaldehyde except for unknown polymers: the normalized polymer concentration is the ratio of the proton concentration carried by the unknown species against the initial proton concentration due to formaldehyde. The mass balance in panel a is proton-based, and in panels b and c, the mass balance is carbon-based. Since the NMR measurement is performed at room temperature, formaldehyde is hydrated and is observed as methanediol in the NMR spectra for panels b and c.

independent self-, the hydrothermal self-, and the cross-disproportionations. Since the reaction scheme in supercritical water is too complicated to solve, we estimate the weight of the water-independent self-disproportionation (eq 1) and the decarbonylation of formaldehyde (eq 2) in hydrothermal conditions using the rate constants obtained in the neat condition. See Appendix A for details of methanol yield partitioning. Figure 5 shows the methanol yields from the hydrothermal self-$[CH_3OH]_{self}$ and the cross-disproportionations $[CH_3OH]_{cross}$, respectively, after 5 min of reaction at the water densities of 0.1−0.6 g/cm^3. The water density dependence of $[CH_3OH]_{self}$ and $[CH_3OH]_{cross}$ are not monotonic. Both $[CH_3OH]_{self}$ and $[CH_3OH]_{cross}$ increase as the water density increases from 0.1 to 0.4 g/cm^3, and at higher densities, the methanol yields slightly decrease.[29] $[CH_3OH]_{cross}$ is comparable to $[CH_3OH]_{self}$ despite the extremely low concentration of formic acid compared to that of formaldehyde (cf. Figure 4b−d and eqs 3 and 4). The cross-disproportionation is to be much faster than the self-disproportionation.

3.3. Water Density Effect and Reaction Mechanisms. To see the effect of water density in more detail, we determine the rate constants of the self- and cross-disproportionations, k_{self} and k_{cross}, in the water density range of 0.1−0.6 g/cm^3. The rate equations for the self- and the cross-disproportionations are expressed, respectively, as[30]

$$\frac{d[CH_3OH]_{self}}{dt} = k_{self}[HCHO]^2 \tag{7}$$

$$\frac{d[CH_3OH]_{cross}}{dt} = k_{cross}[HCHO][HCOOH] \tag{8}$$

The order of [HCHO] in the self-disproportionation is taken to be 2. See Appendix B for the rate determination. The values of

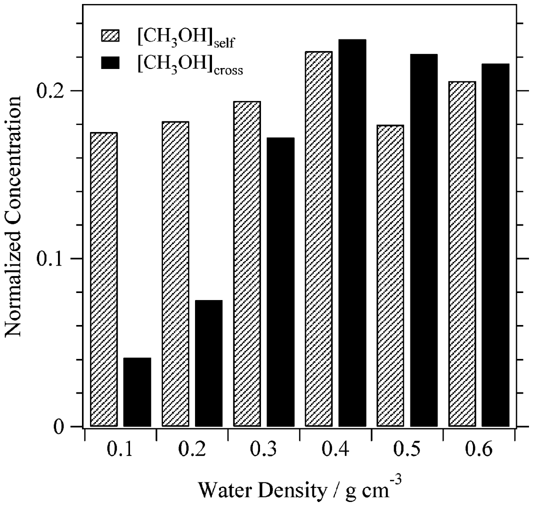

Figure 5. Methanol yields of the self- and the cross-disproportionations, $[CH_3OH]_{self}$ and $[CH_3OH]_{cross}$, respectively, after 5 min of reaction at the water densities of 0.1−0.6 g/cm^3 and 400 °C.

TABLE 1: Rate Constants of the Self- and Cross-Disproportionations at 400 °C

	rate constants/(M^{-1} s^{-1})	
water density/(g cm^{-3})	k_{self}	k_{cross}
0.1	$(1.3 \pm 0.1) \times 10^{-2}$	$(8 \pm 2) \times 10^{-1}$
0.2	$(1.6 \pm 0.2) \times 10^{-2}$	9 ± 2
0.3	$(2.0 \pm 0.1) \times 10^{-2}$	18 ± 4
0.4	$(2.3 \pm 0.3) \times 10^{-2}$	25 ± 2
0.5	$(1.9 \pm 0.4) \times 10^{-2}$	11 ± 3
0.6	$(2.6 \pm 0.4) \times 10^{-2}$	13 ± 1

k_{self} and k_{cross} are shown in Table 1 and Figure 6. Figure 6 shows that the water density dependence of the rate constants k_{self} and k_{cross} is not monotonic. As the water density increases to 0.4 g/cm^3, k_{self} weakly increases but does not vary significantly at higher densities. On the other hand, k_{cross} shows a steep increase with the density increase, has a maximum at the density of 0.4 g/cm^3, and slightly decreases as the density further increases. In neutral supercritical water, the main reaction paths of the two disproportionations are neither base-catalyzed nor acid-induced because the water density dependence of k_{self} and k_{cross} cannot be explained in terms of hydroxide ion [OH$^-$] and proton [H$^+$] concentrations generated by the autoprotolysis of water. When the water density is varied from 0.1 to 0.6 g/cm^3, [OH$^-$] and [H$^+$] increase by 5−6 orders of magnitude (from 1×10^{-11} to 9×10^{-6} M), which is too large compared to the variation of k_{self} and k_{cross}.[31]

Here we propose methanediol ($CH_2(OH)_2$) as a reactant in the hydrothermal self-disproportionation (cf. eq 3). To discuss the methanediol-participating self-disproportionation, we introduce the equilibrium constants of the self- K_{self} and cross-disproportionations K_{cross}, and the equilibrium constant K_r of the formaldehyde hydration. K_r is the ratio of the methanediol concentration to the formaldehyde concentration. K_{self} and K_{cross} are expressed as[32]

$$K_{self} = \frac{[CH_3OH][HCOOH]}{[HCHO]^2} \tag{9}$$

$$K_{cross} = \frac{[CH_3OH][CO_2]}{[HCHO][HCOOH]} \tag{10}$$

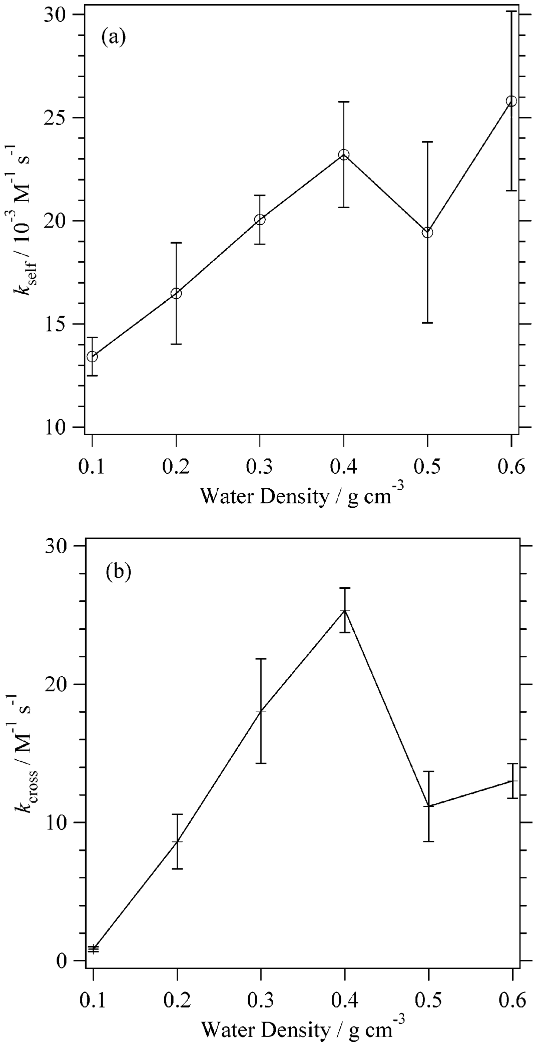

Figure 6. Rate constants of (a) the self-disproportionation and (b) the cross-disproportionation at the water densities of 0.1−0.6 g/cm^3 and 400 °C.

K_{self} corresponds to the equilibrium between the far left- and far right-hand sides of eq 3, and K_{cross} corresponds to eq 4. K_{self}, K_{cross}, and K_r were examined computationally in previous works.[3,4,32] Figure 7 shows K_{self} and K_{cross} with the water density variation from 0.1 to 1.2 g/cm^3 at 400 °C. In aqueous solution, formaldehyde is in part hydrated into methanediol. The rate constant k'_{self} and the equilibrium constant K'_{self} of the methanediol-participating self-disproportionation are introduced, respectively, as

$$\frac{d[CH_3OH]_{self}}{dt} = k'_{self}[HCHO][CH_2(OH)_2] \tag{11}$$

$$K'_{self} = \frac{[CH_3OH][HCOOH]}{[HCHO][CH_2(OH)_2]} \tag{12}$$

Thus we obtain $k_{self} = k'_{self}K_r$ and $K_{self} = K'_{self}K_r$ (cf. eqs 7 and 9), considering that the formaldehyde hydration is much faster than the self-disproportionation. Note that K'_{self} corresponds to the equilibrium between the middle and the right-hand side of eq 3. The water density dependence of K'_{self} is shown in Figure 7. According to k_{self} shown in Table 1 and K_r from ref 3, k_{self} increases by ~70% and, correspondingly, K_r increases by ~60% by the water density change from 0.1 to 0.4 g/cm^3. The variation of k_{self} is close to that of K_r. The methanediol population change can be the main cause of the water density dependence of k_{self}. In the water density range of interest, the value of k'_{self} is

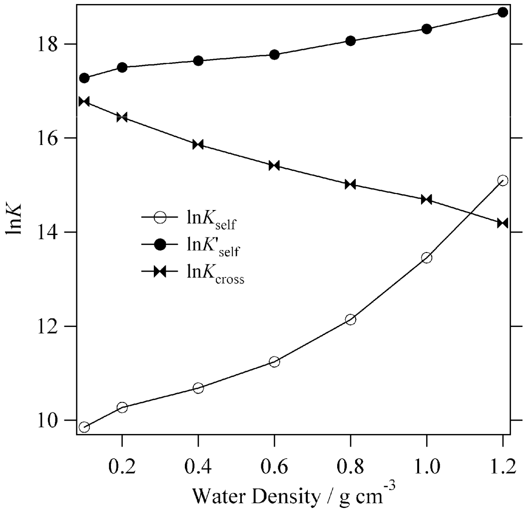

Figure 7. Equilibrium constants of the self-disproportionation (K_{self} and K'_{self}) and the cross-disproportionation K_{cross} at 400 °C. The values of K_{cross} are from ref 4. K_{self} is obtained by multiplying the concentration of water to the equilibrium constant in ref 4 so that the dimensions of K_{self} and K_{cross} are made the same.

determined as ~20 $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$, which is comparable to the value of k_{cross}. Thus the population of methanediol can be the cause of the apparent difference in the reducing ability between formic acid and formaldehyde (cf. Table 1). As seen in Table 1, the increase of the water density from 0.4 to 0.6 g/cm^3 has little effect on k_{self} while it slightly decreases k_{cross}. We consider that although the transition states of the self- and cross-disproportionations are both destabilized in this water density region,[33] the increase of K_{r} compensates for the destabilization of the transition state in the self-disproportionation.

To discuss the reaction mechanisms of the self- and cross-disproportionations, here we compare free energy changes of the cross- and methanediol-participating self-disproportionations. According to the transition-state theory and the rate constants k'_{self} and k_{cross}, it is found that the activation free energies of the methanediol-participating self- and cross-disproportionations at 400 °C differ only by ~4 kcal/mol, which is ~10% of their own activation free energies.[34] Also, K'_{self} and K_{cross} shown in Figure 7 indicate that the total free energy changes of these disproportionations differ by ~3 kcal/mol, which is also ~10% of their total free energy changes.[3,4] The parallelism between the activation free energies and the total free energy changes of the cross- and methanediol-participating self-disproportionations supports the mechanisms proposed in Figure 2a,b. In both disproportionations, two hydrogens attached to carbon and oxygen of the reducing molecule are transferred to formaldehyde through the formation of 6-membered ring. The reaction mechanisms of the methanediol-participating self- and cross-disproportionations are thus considered to be similar.[35]

3.4. Methanol Formation. With the aim of efficient methanol production, we compare the reduction of formaldehyde in supercritical water with that in subcritical water and show that supercritical conditions are preferable to subcritical in terms of reaction time and efficiency of formic acid as a formaldehyde reducer.

The supercritical water dramatically shortens the reaction time for the reduction of formaldehyde into methanol, without the loss of the final yield. As seen in Figure 4c, supercritical water reduces ~60% of formaldehyde into methanol without any catalysts within 10−20 min, while it takes a few dozens of hours to give the same yield in subcritical condition.[1] The methanol yield of 60% is close to the maximum (67%), which is achieved only when the cross-disproportionation is dominant. The supercritical water can serve as the effective solvent for the aldehyde reduction into alcohol.

We show that we can achieve even higher methanol yields than ~60% by adding formic acid or carbon monoxide[36] to accelerate the cross-disproportionation. As a formaldehyde reducer, the excessively added formic acid works more efficiently in the supercritical water than in the subcritical water. The amount of formic acid needed to attain a desired methanol yield depends on the ratio of the rate constants of the self- and cross-disproportionations, $k_{\mathrm{cross}}/k_{\mathrm{self}}$. As $k_{\mathrm{cross}}/k_{\mathrm{self}}$ gets larger, a less amount of formic acid is needed to suppress the self-disproportionation. At 400 °C, $k_{\mathrm{cross}}/k_{\mathrm{self}}$ is maximized when the water density is 0.4 g/cm^3. In this case, the value of $k_{\mathrm{cross}}/k_{\mathrm{self}}$ is more than 2 orders of magnitude larger than that at 225 °C. Thus added formic acid or carbon monoxide should work more efficiently in the supercritical water than in the subcritical water. At 0.4 g/cm^3 and 400 °C, the reaction of 0.1 M formaldehyde and 0.2 M formic acid resulted in the methanol yield of ~80% with the reaction time of 15 min. Only 2-fold of formic acid against formaldehyde is needed to attain such a high methanol yield. At 225 °C on the saturation curve, however, about 7-fold of formic acid is needed to achieve the same methanol yield with the reaction time of 2 h.[1,37] The reduction of aldehydes using formic acid or carbon monoxide in supercritical water serves as a new way of alcohol production which is a clean process without any catalysts and fast enough for practical use.

4. Conclusions

For the reaction of formaldehyde in supercritical water, we have established the reaction kinetics including the effect of the water density. Formaldehyde is found to produce methanol through the water-independent self-, the hydrothermal self-, and the cross-disproportionations in supercritical water at 400 °C. The water-independent self-disproportionation is found only for formaldehyde. On the basis of the product distribution and the time evolution of reactant and products, the methanol yields of the water-independent self-, the hydrothermal self-, and the cross-disproportionations are determined, respectively. The noncatalytic hydrothermal disproportionations are found to be dominant.

To clarify the reaction path weight and the reaction mechanism, the water density dependence of the rate constants of the self- and cross-disproportionations are studied in the range of 0.1−0.6 g/cm^3. The rate constant of the cross-disproportionation is found to be 2−3 orders of magnitude larger than that of the hydrothermal self-disproportionation in the supercritical condition at 400 °C. Combining the result of kinetic analysis with the equilibrium constants of C1 aldehyde reactions from the former computational studies,[3,4] we have elucidated the role of methanediol as a reactant in the self-disproportionation. The reaction mechanisms of the cross- and the methanediol-participating self-disproportionations are similar to each other. By adding 2-fold of formic acid to formaldehyde from outside, we can enhance the reaction path weight for methanol production. The methanol yield of ~80% is achieved within 15 min at the water density of 0.4 g/cm^3 and 400 °C. Added formic acid is found to reduce formaldehyde more efficiently in supercritical water than in subcritical.

Appendix A: Determination of Methanol Yields of Three Disproportionations

According to Figure 3, the total yield of methanol $[\mathrm{CH_3OH}]_{\mathrm{total}}$ can be expressed as

$$[\mathrm{CH_3OH}]_{\mathrm{total}} = [\mathrm{CH_3OH}]_{\mathrm{wi-self}} + [\mathrm{CH_3OH}]_{\mathrm{self}} + [\mathrm{CH_3OH}]_{\mathrm{cross}} \quad (13)$$

where $[\mathrm{CH_3OH}]_{\mathrm{wi-self}}$, $[\mathrm{CH_3OH}]_{\mathrm{self}}$, and $[\mathrm{CH_3OH}]_{\mathrm{cross}}$ denote the methanol yields from the water-independent self- (eq 1), the hydrothermal self- (eq 3), and the cross-disproportionations (eq 4), respectively. For $[\mathrm{CH_3OH}]_{\mathrm{wi-self}}$, we adopt the methanol yield that we estimate from the rate constant $k_{\mathrm{wi-self}}$ obtained in section 3.2.1. The determination of $[\mathrm{CH_3OH}]_{\mathrm{wi-self}}$ in supercritical water is described in Appendix B. The values of $[\mathrm{CH_3OH}]_{\mathrm{self}}$ and $[\mathrm{CH_3OH}]_{\mathrm{cross}}$ are obtained in the following way. Since carbon dioxide is provided from the cross-disproportionation (eq 4) and the decarboxylation of formic acid, the methanol yield from the cross-disproportionation $[\mathrm{CH_3OH}]_{\mathrm{cross}}$ can be expressed as

$$[\mathrm{CH_3OH}]_{\mathrm{cross}} = [\mathrm{CO_2}]_{\mathrm{total}} - [\mathrm{CO_2}]_{\mathrm{deCO_2}} \quad (14)$$

where $[\mathrm{CO_2}]_{\mathrm{total}}$ and $[\mathrm{CO_2}]_{\mathrm{deCO_2}}$ are the total yield of carbon dioxide and the carbon dioxide yield from decarboxylation of formic acid, respectively. We obtained $[\mathrm{CO_2}]_{\mathrm{deCO_2}}$ by determining the hydrogen yield from the decarboxylation of formic acid $[\mathrm{H_2}]_{\mathrm{deCO_2}}$, since $[\mathrm{CO_2}]_{\mathrm{deCO_2}} = [\mathrm{H_2}]_{\mathrm{deCO_2}}$ (cf. Figure 3). Using the total hydrogen concentration $[\mathrm{H_2}]_{\mathrm{total}}$ and the hydrogen yield from the decarbonylation of formaldehyde (eq 2) $[\mathrm{H_2}]_{\mathrm{deCO}}$, $[\mathrm{CO_2}]_{\mathrm{deCO_2}}$ can be written as

$$[\mathrm{CO_2}]_{\mathrm{deCO_2}} = [\mathrm{H_2}]_{\mathrm{deCO_2}} = [\mathrm{H_2}]_{\mathrm{total}} - [\mathrm{H_2}]_{\mathrm{deCO}} \quad (15)$$

The value of $[\mathrm{H_2}]_{\mathrm{deCO}}$ can be estimated from the rate constant k_{deCO}; see section 3.2.1. The determination of $[\mathrm{H_2}]_{\mathrm{deCO}}$ in supercritical water is described in Appendix B. Then we can obtain the methanol yield from the self-disproportionation $[\mathrm{CH_3OH}]_{\mathrm{self}}$ through

$$[\mathrm{CH_3OH}]_{\mathrm{self}} = [\mathrm{CH_3OH}]_{\mathrm{total}} - [\mathrm{CH_3OH}]_{\mathrm{cross}} - [\mathrm{CH_3OH}]_{\mathrm{wi-self}} \quad (16)$$

Here, we assume that that the solvent water has little effect on the rate constants of the water-independent self-disproportionation $k_{\mathrm{wi-self}}$ and the decarbonylation of formaldehyde k_{deCO}. According to our former experiment, the solvent water has little effect on the decarbonylation (∼30%).[14] Further, both water-independent self-disproportionation and decarbonylation of formaldehyde are very slow compared to the hydrothermal self- and cross-disproportionations (cf. Figure 4a−c). We can thus adopt the assumption safely.

Appendix B: Rate Equations

The methanol yield $[\mathrm{CH_3OH}]_{\mathrm{wi-self}}$ of the water-independent self-disproportionation and the hydrogen yield $[\mathrm{H_2}]_{\mathrm{deCO}}$ of formaldehyde decarbonylation in supercritical conditions are estimated by the following equations:

$$[\mathrm{CH_3OH}]_{\mathrm{wi-self}} = k_{\mathrm{wi-self}} \sum_{i=0}^{t} [\mathrm{HCHO}]_{(i)}^{2} \times \Delta \quad (17)$$

$$[\mathrm{H_2}]_{\mathrm{deCO}} = k_{\mathrm{deCO}} \sum_{i=0}^{t} [\mathrm{HCHO}]_{(i)} \times \Delta \quad (18)$$

where Δ denotes the sampling interval, which is 1 min in the present study. $[\mathrm{HCHO}]_{(i)}$ indicates the yield of formaldehyde at a time of i. The values of $[\mathrm{CH_3OH}]_{\mathrm{wi-self}}$ and $[\mathrm{H_2}]_{\mathrm{deCO}}$ are obtained using $[\mathrm{HCHO}]_{(i)}$ at each reaction time and the rate constants of the water-independent self-disproportionation $k_{\mathrm{wi-self}}$ and the formaldehyde decarbonylation k_{deCO} determined in section 3.2.1.

To obtain the rate constants of the self- and cross-disproportionations, k_{self} and k_{cross}, the integrations of eqs 7 and 8 are approximated, respectively, by the summation of reactants concentrations with short time interval as

$$[\mathrm{CH_3OH}]_{\mathrm{self}} = k_{\mathrm{self}} \sum_{i=0}^{t} [\mathrm{HCHO}]_{(i)}^{2} \times \Delta \quad (19)$$

$$[\mathrm{CH_3OH}]_{\mathrm{cross}} = k_{\mathrm{cross}} \sum_{i=0}^{t} [\mathrm{HCHO}]_{(i)}[\mathrm{HCOOH}]_{(i)} \times \Delta \quad (20)$$

The values of k_{self} and k_{cross} are determined by calculating their values in every minute until formic acid becomes undetectable and by averaging them respectively.

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(26) To estimate the time needed for a quartz sample to attain the reaction temperature, a thermocouple was twisted around the sample and the time evolution of the sample temperature in an electric furnace kept at 400 °C was monitored. It took ~1 min for the sample to reach 400 °C.

(27) In this measurement, ~20% (proton-based percentage) of products are not determined precisely. Since formaldehyde monomers tend to polymerize, they are presumed to be derivatives of formaldehyde polymers. As minor products, ethane and methyl formate are detected and their total yield is ~3%

(28) Since the yield of hydrogen is low, the decarboxylation of formic acid is a minor path and most of formic acid is consumed by the cross-disproportionation in the present reaction condition. Further, as shown in refs 5 and 6, the decarboxylation of formic acid is a slow reaction and has a minor contribution to the hydrothermal reactions in the time scale of ~10 min.

(29) The water dependence of $[CH_3OH]_{self}$ and $[CH_3OH]_{cross}$ seen in Figure 5 is common to reaction times other than 5 min.

(30) The rate constant k_{self} is introduced by eq 7 without explicitly separating $[H_2O]$. Water is the solvent, and its concentration does not change in the course of reaction. In the hydrothermal self-disproportionation, water participates both as a solvent and as a reactant. The water density $[H_2O]$ affects the rate constant k_{self} through solvation and concentration itself. However, Table 1 shows that the water density dependence of k_{self} is not monotonic, and even when the water concentration is removed from the rate constant k_{self} by $k = k_{self}/[H_2O]$, k is still dependent on $[H_2O]$. k thus does not give clearer information on the water density dependency, and we adopt the rate equation in the form of eq 7 where $[H_2O]$ is not explicitly separated.

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(32) By multiplying the concentration of water $[H_2O]$ to the equilibrium constant K_{self} of the self-disproportionation in ref 4, the dimensions of the equilibrium constants of the self- K_{self} and cross-disproportionations K_{cross} are made the same so that they can be compared.

(33) The strong and anisotropic fluctuations in the local electric field of solvent water may play a key role in the noncatalytic disproportionations in supercritical conditions. We speculate that the transition states of the disproportionations are destabilized at high water density because of the partial charge shielding by hydrogen bonds and/or the packing effect.

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(35) We confirmed that the differences in the activation free energies and in the total free energy changes are small between the cross- and methanediol-participating self-disproportionations in subcritical conditions at 225 and 300 °C. The reaction mechanisms of the self- and cross-disproportionations are thus common to the sub- and supercritical conditions. k_{self} and k_{cross} at 225 °C are taken from ref 1, and k_{self} and k_{cross} at 300 °C ($(3 \pm 1) \times 10^{-3}$ and $(4 \pm 1) \times 10^{-2}$ M^{-1} s^{-1}, respectively) are determined from additional runs. K_{self}, K_{cross}, and K_r are from refs 3 and 4.

(36) Carbon monoxide reacts with water to produce formic acid in hydrothermal conditions.[5,6]

(37) Methanol yield can be enhanced by the formic acid addition as long as the cross-disproportionation proceeds much faster than the self-disproportionation and the formic acid decompositions.