Chemical Reactions of C$_1$ Compounds in Near-Critical and Supercritical Water

Masaru Watanabe,*,† Takafumi Sato,‡ Hiroshi Inomata,*,† Richard Lee Smith, Jr.,† Kunio Arai,†
Andrea Kruse,*,§ and Eckhard Dinjus§

Research Center of Supercritical Fluid Technology, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan, Department of Applied Chemistry, Utsunomiya University, 7-1-2 Yoto, Utsunomiya 321-8585, Japan, and Institut für Technische Chemie (ITC-CPV), Forschungszentrum Karlsruhe GmbH, P.O. Box 3640, 76021 Karlsruhe, Germany

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* Corresponding authors. M.W.: email, meijin@scf.che.tohoku.ac.jp; telephone and fax, +81-22-217-7282. H.I.: e-mail, inomata@scf.che.tohoku.ac.jp; telephone, +81-22-217-7283; fax, +81-22-217-7282. A.K.: e-mail, andrea.kruse@itc-cpv.fzk.de; telephone, +49 7247/82-3388; fax, +49 7247/82-2244.
† Tohoku University.
‡ Utsunomiya University.
§ Institut für Technische Chemie (ITC-CPV).

1. Introduction

1.1. Near-Critical Water (NCW) and Supercritical Water (SCW) as Reaction Media

Water is an ecologically safe substance widespread throughout nature.[1] Liquid water at standard conditions (25 °C and 0.1 MPa) is an excellent solvent for many compounds and electrolytes because of its high dielectric constant, but it is poorly miscible with hydrocarbons and gases. Temperature and pressure have a great effect on the properties of water. As the temperature of water is increased, the dielectric constant decreases, and it has a value of 10 in the range of conditions (400 °C and 20 MPa)[2] of interest in this review. The vapor pressure of water terminates at the critical point (T_c = 373.946 °C, P_c = 22.064 MPa, ρ_c = 322 kg/m^3), and beyond this state, the density of supercritical water (SCW) can be varied continuously to have liquidlike to gaslike values without abrupt changes associated with a phase transition over a wide range of conditions.[2] In the supercritical region, water becomes completely miscible with many hydrocarbons and gases[3] but becomes a poor solvent for many inorganics,[4] and this is one reason that SCW has high technological potential.

The absence of phase boundaries at supercritical conditions allows many reactions to proceed homogeneously with few mass transfer limitations. The complete miscibility of SCW with gases and organic compounds makes SCW an excellent solvent for oxidations, hydrogenations, and hydroformylations. To exploit these property characteristics, SCW applications, such as SCWO (supercritical water oxidation), have been developed for treatment of organic wastes such as transformer oils. For example, a commercial-scale reactor was recently brought online for solid waste handling including toxic organic chemicals such as polychlorinated biphenyls (PCBs) by the Organo company in Japan.[5] Fundamental studies for SCWO processes have been conducted using many simple compounds such as CO, CH$_3$OH, or CH$_4$.[6-24] Mainly, SCWO studies for these compounds have been performed with the objective to elucidate reaction mechanisms so that the chemistry of SCW reaction media can be better understood.
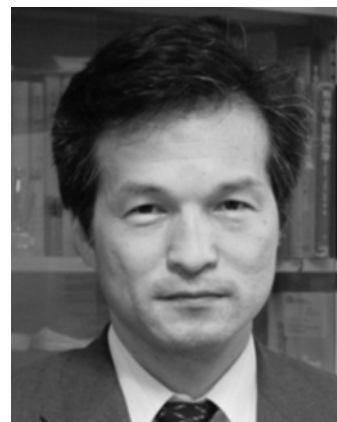
Masaru Watanabe was born in 1969 in Fukushima (Japan). He received his B.S. degree in 1993 and M.S. degree in 1995 from Meiji University. These degrees are in Applied Chemistry. He received his Ph.D. degree from Tohoku University in 1999. The Ph.D degree is in Chemical Engineering. His study for the Ph.D. degree, conducted under the direction of Professor Kunio Arai, was focused on investigation of the role of water in hydrocarbon pyrolysis. He was a Research Associate at the Department of Chemical Engineering, Tohoku University, in 1999. From 2000 to the present, he has been a Research Associate at the Research Center of Supercritical Fluid Technology, Tohoku University.

Takafumi Sato was born in 1974 in Fukushima (Japan). He received his B.S. degree in 1996, M.S. degree in 1998, and Ph.D. degree in 2001 from Tohoku University. All of his degrees are in Chemical Engineering. His graduate study, conducted under the direction of Professor Kunio Arai, focused on evaluation of the role of water in water-gas shift reaction and Friedel–Crafts alkylation without catalyst in supercritical water. He worked as a research fellow at the Research Center of Supercritical Fluid Technology, Tohoku University, from 2001 to 2003. During this term, he performed his study as a visiting scholar for 3 months at the Department of Chemical Engineering, University of Waterloo, Canada. In 2003, he was a research fellow at the Supercritical Fluid Research Center, National Institute of Advanced Industrial Science and Technology (AIST). Since 2004, he has been a Research Associate of the Department of Applied Chemistry at Utsunomiya University.

Hiroshi Inomata was born in 1956 in Sendai (Japan). He received his Ph.D. degree in Chemical Engineering from Tohoku University in 1984. He became a Professor of the Faculty of Engineering, Tohoku University, in 1997. He is now at Tohoku University, Research Center of Supercritical Fluid Technology in Sendai, Japan, where he has been a Professor since 2002. His research fields are separation, reaction, plastics processing using supercritical fluid, and molecular dynamics of supercritical solution.

Richard Smith was born in 1956 in Atlanta, Georgia (USA). He received his Ph.D. degree in Chemical Engineering from the Georgia Institute of Technology in 1985. He is at Tohoku University, Research Center of Supercritical Fluid Technology in Sendai, Japan, where he has been a Professor since 2002. His research interests include high pressure phase equilibria and phenomena, especially water and carbon dioxide systems as applied to systems development. Richard is the Asian Regional Editor for the *Journal of Supercritical Fluids*. Further information on his group may be found at http://www.che.tohoku.ac.jp/~smith/Lab.htm.

Much effort has been expended for making detailed numerical models for systems of interest to SCWO, as discussed in refs 6−24 and in some of the sections below.

Green chemistry and sustainability have drawn interest to applications of biomass gasification and organic reforming with near-critical water (NCW) and SCW[25−49] because H_2 or CH_4 is expected to be our future source of energy through fuel cell technologies. The VERENA pilot scale plant has been constructed in Karlsruhe[50] to explore supercritical water gasification (SCWG); however, there is still much ongoing research to understand the chemistry of biomass conversion for specific product requirements. Depending on the reaction conditions for SCWG, H_2 and CH_4 can be identified as the chief products of interest. For example, H_2 formation is dominant at higher temperatures and lower pressures, whereas CH_4 product is favored at lower temperatures.[30] However, using alkali hydroxide,[33,36,39] Ni catalyst,[27−29,32−34] Pt catalyst,[27,40] Ru catalyst,[27−29,48] and some metal oxides,[39,44] the formation of H_2 can be enhanced in NCW, sometimes through the use of phase separation.[32−34,40] These results show that another characteristic of the NCW and SCW reaction media is the controllable product distribution by changing conditions and catalyst selection. Membrane processes in NCW and SCW are being considered to enhance H_2 production because chemical equilibria, such as in the water-gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$), can be shifted to products by removing H_2 from the system, thus driving the reaction to the right.[51]

Kunio Arai was born in 1942 in Saitama (Japan). He worked at Nippon Kokan (NKK) from 1967 to 1969. He received his Ph.D. degree in Chemical Engineering from Tohoku University in 1972. He has been a Professor at the Faculty of Engineering, Tohoku University, since 1986 and a Professor at the Department of Engineering, Graduate School of Tohoku University, since 1997. He has directed the Research Center of Supercritical Fluid Technology, Tohoku University, since 1995. Also, he has directed the Supercritical Fluid Research Center, Tohoku Center, National Institute of Advanced Industrial Science and Technology (AIST), since 2001.

Eckhard Dinjus was born in 1944 in Saalfeld/Thüringen (Germany). He studied chemistry at the Friedrich-Schiller-University Jena (Ph.D. 1972, habilitation 1988). Then, he spent 1.5 years in industry. In 1990–1991 he worked as a Guest Scientist at the Max Planck Institute for coal research in Mühlheim/Ruhr. From 1991 to 1996 he headed the working group "CO$_2$-Chemistry" of the Max Planck Society at the University of Jena. In 1996 he was appointed to a Professorship for Technical Chemistry at the University of Heidelberg and as the Head of the Institut für Technische Chemie, Chemisch Physikalische Prozesse at the Forschungszentrum Karlsruhe GmbH. He is interested in metal–organically catalyzed syntheses, syntheses in supercritical fluids, supercritical fluid chemistry and technology, and fuel-from-biomass processes.

Andrea Kruse was born in 1964 in Brunswick (Germany). She studied chemistry at the University of Heidelberg (diploma 1991). From 1991 to 1994 she did her Ph.D. thesis on pyrolysis in supercritical water at the Institut für Technische Chemie of the Forschungszentrum Karlsruhe GmbH, receiving her Ph.D. from the University of Heidelberg. Today, she is a Senior Scientist at the Institut für Technische Chemie, responsible for and contributing to fundamental aspects of chemical reactions in supercritical water. Her current activities comprise conversion of biomass in hot compressed water, total and partial oxidation in supercritical water and CO$_2$, and process analytics.
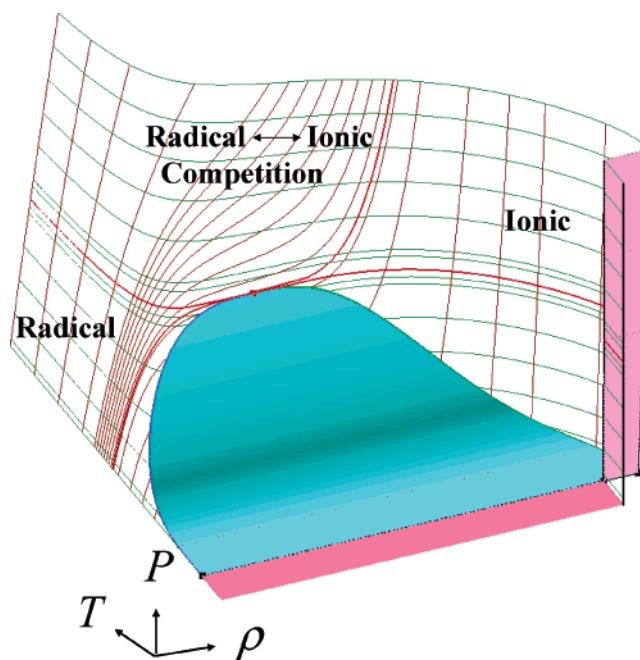
NCW and SCW are being recognized as essential for green chemical environments in organic syntheses, such as acylations,[52] alkylations,[53−56] amidations,[57,58] Cannizzaro type reactions,[59−63] hydrogenations,[64,65] partial oxidations,[10,66−76] rearrangements,[77,78] and retro-aldol condensations.[79] Among these reactions, the possibility to produce CH$_3$OH directly from CH$_4$ is very attractive in SCW, since the selectivities have been favorable,[10,66−69,75,76,80−97] although the yields that have been reported thus far have been too low.[66] Nevertheless, there seems to be ample opportunities, since the solvent conditions and catalysts can affect the chemistry considerably.

1.2. Important Roles and Properties of NCW and SCW in Chemical Reactions

Many possible chemical reaction pathways exist, as viewed by the $P-\rho-T$ surface of water. As shown

Figure 1. $P-\rho-T$ surface of water showing the main reaction regimes.

in Figure 1, the main reaction pathways that have been identified in SCW are those with an ionic or radical character. Reactions seem to proceed via ionic pathways in liquid water, high pressure SCW, and probably the dense gas phase. In contrast, radical reactions seem to be the main reaction pathways in steam and less dense SCW. Both reactions proceed competitively around the critical point of water.[98] Therefore, the contribution of the nonideality of water is probably large for all the reactions around the critical point of water, and many experimental and computational studies are needed to resolve the contributions. Molecular reactions, which refers to reactions that are through neither ionic nor radical

intermediates, are molecular rearrangements enhanced by coordination with water, and these possibly proceed around the critical region of water.[55]

Development of NCW and SCW industrial processes requires an understanding of how to apply current state-of-the-art chemistry in SCW reaction media as well as identification of new chemistries specific to SCW reaction media. The properties of the SCW media can greatly affect reaction chemistries. To understand reaction mechanisms in NCW and SCW, the chemistry of water for many types of reactions will need to be studied. Akiya and Savage overviewed and reported on the role of high temperature water (HTW) for various chemical reactions in a highly significant review.[99] In this section, some of the roles and properties of NCW and SCW in chemical reactions will be described.

1.2.1. Solvent

The large diffusion coefficients and low viscosities of NCW and SCW, along with the complete miscibility of NCW and SCW with many substances, can accelerate chemical reactions and can improve reaction efficiency. For example, the rate of cellulose decomposition above 350 °C increases greatly because of the miscibility of cellulose with NCW and SCW.[100] On the other hand, for reactions in SCW, a cage effect originating from long-range correlation of water molecules surrounding a solute has been discussed in some studies[99] that could reduce solute–solute interactions, and this has been suggested as the reason to explain the unexpected low pyrolysis reaction rate of *tert*-butylbenzene.[101] These findings are in accordance with the findings of Ferry and Fox that solvent cages leads to an inhibition of the decay of reactive intermediates formed by the reaction of OH free radical with benzene and pentabromophenolate anions, respectively.[102] Furthermore, in heterogeneous catalysis, NCW and SCW properties can help reduce mass transfer limitations and avoid coke formation or catalyst poisoning.[103]

1.2.2. Pressure

Water becomes a collision partner in many chemical reactions, which means that reactions in the critical region can have a large density dependence due to the influence of solvent density on free radicals. Experimental and theoretical studies show that the rates of free radical reactions exhibit pressure dependence. The reaction rate constant for free radical reactions typically increases with pressure up to a certain plateau value. This behavior has been called the high pressure falloff curve, and the plateau value has been called the limiting high pressure rate coefficient (k_{HP})[104] due to frequent collision of the reactant with the surrounding molecules.[105,106] A further increase in pressure leads to no change in the reaction rate until the falloff pressure is reached, at which diffusion control occurs and the reaction rate decreases with pressure.[105] These effects are, to a first approximation, independent of the nature of the reaction media, since they are simply a consequence of the increase in collision frequency that establishes a nearly equilibrium population of excited metastable

vibrational energy states known as RRKM theory or the Lindemann–Hinshelwood model. Especially at higher pressures, additional effects due to solvent–reactant interactions can change the shape of the falloff curve. These solvent effects are usually dependent on the nature of the surrounding gas or fluid.[106] In reactions of small free radicals such as H or OH in gases such as argon or nitrogen, the k_{HP} reaches a plateau at pressures around 10 MPa.[104] In studies of SCWO modeling, this was considered in modifying the gas-phase kinetics used (see sections 3.2, 6.3, and 7.3). Larger molecule free radicals have many degrees of freedom and reach their k_{HP} plateau near ambient conditions[107] and generally are diffusion controlled.

1.2.3. Dielectric Constant

One of the important parameters for the solvent effects of water in reactions is the dielectric constant. The polarity of the solvent influences the rates of chemical reactions via the Kirkwood relation.[99] During a reaction, the transition state may be of higher or lower polarity than the initial state. A high relative dielectric constant lowers the activation energy of a reaction for a transition state of higher polarity than the initial state. As a consequence, many reactions have a high activation volume. By variation of the relative dielectric constant with temperature and pressure, reaction rates can be controlled.

1.2.4. Molecule

Water is a molecule with a permanent dipole, and therefore, it is reactive in a variety of cases. In some key reaction steps in total oxidation, SCW is assumed to take part in the activation complex.[108,109] By forming a complex, the activation energy is lowered, which means that water acts as a catalyst in these reactions. As discussed later in more detail (section 5), HCOOH decomposition into CO_2 and H_2 via molecular elimination is enhanced by water molecules that form activated complexes according to simulation results. In this review, we would like to denote "molecular reactions" as those reactions that are "water molecule catalyzed" reactions. Such water bridge complexes have been reported to be important for S_N2 type hydrolysis and H_2 elimination from an alcohol. Molecular reactions are important for understanding reaction mechanisms around the critical point of water, where ionic and radical reactions also competitively occur. As a solvent, water can most likely affect chemical reactions for cases where the activated complex has a polarity that is different from that of the initial compounds.

1.2.5. Ion Product

The ion product of water (K_w) has a strong influence on reactions. The ion product increases slightly with temperature up to around 10^{-11} in the range between 200 and 300 °C. Above the critical temperature, K_w decreases drastically with temperature but increases with pressure. The K_w in SCW at high pressures can be some orders of magnitude higher than that in ambient water. In this region, water may play the role of an acid or base catalyst[61–63,77,78,110–115]

because of the high concentration of H_3O^+ and OH^- ions. Acid- or base-catalyzed reactions in water at high pressures and high temperatures show a characteristic non-Arrhenius kinetic behavior near the critical point of water.[116−118] Below the critical temperature of water, the reaction rates usually increase with temperature until the critical temperature is reached. At the critical point, reaction rates can decrease or increase drastically depending on the chemistry and properties, as discussed in this review.

## 1.3. Previous Reviews on Organic Reactions in NCW and SCW

The property effects just discussed influence reactions competitively rather than independently. Comparison of reactions over a wide range of temperature and pressure conditions is useful for trying to elucidate the role that water plays in the chemistry, and for this purpose, many reviews of organic reactions in NCW and SCW have been published.[99,119−125] Organic reactions have been examined over the years and classified by the kind of reaction[119−121,125] or by the type of species.[122−124] For example, Katritzky et al. summarized reactions of aromatic hydrocarbons and their derivatives in SCW.[124] In that review, they suggested that many reactions proceed via radical or ionic reactions in SCW and that the competition between these two reaction pathways depends on both the compound and the conditions.[124] Akiya and Savage[99] summarized the role of water in many reactions. According to their review,[99] water can act as a proton donor, a catalyst, or hydration agent for many kinds of organic reactions. Simple compounds, such as C_1 molecules (CO, HCHO, HCOOH, CH_3OH, CH_4, and chlorinated methanes) are suitable reactants for the analyses of the role of water on the reaction because the number of products is probably smaller than that for larger molecules and experimental complications such as phase separations are likely to be reduced. Moreover, C_1 compounds occur as intermediates in SCWO and SCWG and represent the target compounds for these processes.

1.4. Objective of This Review

The focus of this review is on the chemistry of C_1 compounds in NCW and SCW with respect to the present state of research activity in this field. In this review, the C_1 compounds discussed are carbon dioxide, carbon monoxide, formaldehyde, formic acid, methanol, methane, and chlorinated methanes. All of the reactions treated in this review are those that have been conducted over a temperature range from 250 to 660 °C and a pressure range from 4 to 40 MPa.

In NCW and SCW, CO_2 becomes readily soluble in water and some portions of soluble CO_2 become carbonic acid (CO_3^{2-}).[126,127] Therefore, the catalytic properties of CO_2 in water can probably be controlled with temperature or pressure, which can be used advantageously in some chemistries and for cases where the use of a supported catalyst is undesirable. CH_4 is an important fuel and source of syngas, that can be obtained from mixtures of CO and hydrogen. CO is mainly used as syngas for the synthesis of
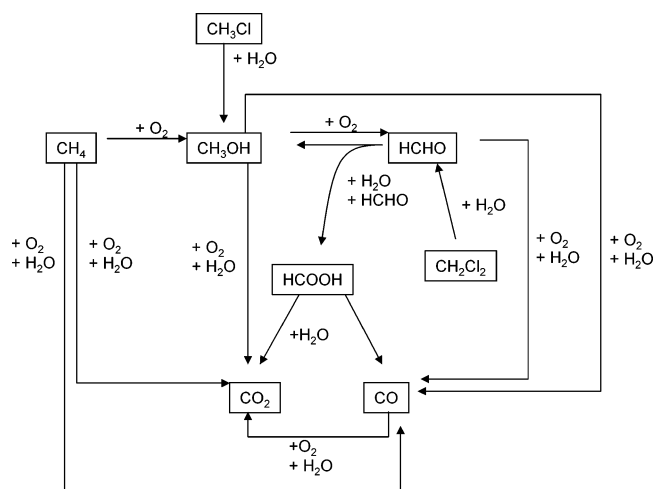
Figure 2. Interrelationship between C_1 compounds and their reaction pathways in near-critical and supercritical water.

methanol and hydrocarbons through Fischer−Tropsch reaction, but it is also used for the carbonylation as the source of phosgene with Cl_2. CH_3OH has been mainly used as the source of formaldehyde and dimethylterephthalate, but it is expected to be used as a fuel, energy, and chemical source, since combustion of CH_3OH is cleaner than that of petroleum. Formaldehyde is commonly used as the source of various resins, such as phenolic and urea resins, and is partly used for synthesis of polyatomic alcohols. HCOOH is an intermediate for various reactions. Chlorinated methanes have been used as solvents and chemical intermediates. Therefore, there seems to be considerable industrial interest in C_1 chemistry and the motivation for using NCW and SCW as reaction media in these applications is the motivation for this review.

Figure 2 shows the reaction pathways for C_1 compounds in NCW and SCW considered in this review. For all reactions in Figure 2, water acts as a polar or weakly polar solvent. In the Cannizzaro, hydrolysis, reforming, and water-gas shift reactions, water is a reactant. For HCOOH decomposition, decarboxylation is probably catalyzed initially by water and subsequently by both water and carbonic acid. Water is also a precursor of active oxidants such as OH and HO_2 radicals. Decarboxylation is catalyzed by water, but it is also further catalyzed by carbonic acid formed by CO_2 that evolves and then dissolves into water. Reactions for each component can be placed into the categories of oxidation, partial oxidation, water-gas shift, decomposition, reforming, and Cannizzaro reaction, showing the numerous C_1 conversions that are possible.

This review is arranged as follows. In section 2, acid catalytic effects of CO_2 on dehydration in NCW and SCW are treated. In section 3, CO reactions are summarized, that is, water-gas shift and oxidations. For the water-gas shift reaction (section 3.1), reported data are compared and the kinetics are discussed. For CO oxidation (section 3.2), the kinetics are mainly discussed. Formaldehyde (HCHO) reactions are treated in section 4. For HCHO reactions, Cannizzaro type reactions are described. For formic acid

(HCOOH), self-decomposition yields $CO + H_2O$ and $CO_2 + H_2$, which also brings into play the water-gas shift reaction. The predominance of these two reaction pathways depends on reaction conditions such as water density that also affects properties. The relationship between the HCOOH reaction and the water-gas shift reaction is discussed in section 5. For the CH_3OH and CH_4 reactions, reforming, partial oxidation, and total oxidation are summarized in sections 6 and 7. In reforming, H_2 recovery from CH_4 and CH_3OH in SCW is described in sections 6.1 and 7.1. Partial oxidation of CH_3OH and CH_4 yields important chemicals such as HCHO and CH_3OH. The possibility of new synthetic chemical techniques, that is, partial oxidation in NCW and SCW, is considered in sections 6.2 and 7.2. The main reaction pathways for total oxidation of CH_3OH and CH_4 can be obtained by comparison of literature results (sections 6.3 and 7.3). The reactions of chlorinated methanes (CH_3Cl and CH_2Cl_2) are covered in section 8. In section 9, we consider reactor wall effects in which some detailed studies have been reported for HCOOH reactions. The relationship between the various C_1 reactions is described in section 10, and finally, the authors' outlook on this field is provided in section 11.

2. Carbon Dioxide (CO₂)

Hunter et al.[127] examined aspects of the catalytic properties of CO_2 in NCW using a batch reactor. They used cyclohexanol dehydrations to form cyclohexene in the presence of CO_2 in NCW at 250 and 275 °C (15−180 min reaction time). The yield of cyclohexane without CO_2 was 10 mol % at 250 °C and 30 min, while that with 10 mg of CO_2 was 22 mol % under the same conditions.[127] They concluded that the cylcohexanol dehydration was promoted by CO_2 and that CO_2 worked as an acid catalyst, since CO_2 can ionize to form carbonic acid and a proton[128,129] for these reactions, because Akiya et al.[130] found that dehydration of cyclohexanol was catalyzed by protons via an E2 mechanism in NCW and SCW (250−380 °C and 0.08−0.81 g/cm³ water density). Minami et al.[131] also examined the catalytic effect of CO_2 as acid catalyst on cyclohexanol dehydration in SCW (380 °C, 0.34−0.55 g/cm³ water density, 5−25 min reaction time), by use of a batch reactor. The yield of cyclohexene reached up to about 33 mol % at 7 min, 0.5 g/cm³ water density, and 0.6 g of CO_2 loaded, whereas the yield was 5 mol % without CO_2 under the same conditions. The above results demonstrate that CO_2 can act as an acid catalyst in NCW and SCW. This means that that reactions that generate CO_2 might be affected by the catalytic effect of CO_2 and thus may require consideration of CO_2 dissociation in detailed reaction mechanisms.

3. Carbon Monoxide (CO)

3.1. Water-gas Shift Reaction

The catalytic water-gas shift reaction has been studied for reactants in NCW. Elliott and Sealock[132] conducted the water-gas shift reaction with several alkali, alkaline earth, and transition metal carbonates at 200−400 °C and 500 kg/m³ of water density using an autoclave reactor. They reported that various alkali compounds act as catalyst with activities in the order alkali metals > transition metals > alkaline earth metals. Catalytic water-gas shift reactions were found to be faster than noncatalytic reactions. The conversion of CO achieved was about 50% for a 10 min reaction time at 300 °C with alkali metal carbonate catalyst, while the conversion under noncatalytic conditions was only 3%. They studied the reaction mechanism for basic aqueous solutions and proposed a cyclic system that used three intermediate anions:[133] carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and hydroxide ion (OH^-). They found that catalysts that generate these anions are effective for promoting the water-gas shift reaction. Ross et al.[134] studied the hydrogenation of bituminous coal with CO through a water-gas shift reaction in SCW (400 °C). They reported that alkali (KOH) was effective for promoting the rate of the water-gas shift reaction. Thus, alkali seems to have good potential for enhancement of the water-gas shift reaction rate in both NCW and SCW.

Melius and Bergan[135] conducted a theoretical investigation of the homogeneous water-gas shift reaction. They proposed that the transition state of the water-gas shift reaction consisted of CO and several water molecules. They calculated the activation energy of the reaction and showed that the activation energy decreases with increasing number of water molecules in the transition state complex, which means that increased water density should enhance the water-gas shift reaction rate.

Hirth and Franck[10] measured the equilibrium of the water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) at 500 and 600 °C and 40 MPa. They reported an equilibrium constant K_x (molar fraction basis) of 1.83 at 500 °C and of 0.49 at 600 °C. The equilibrium constants at normal pressure (0.1 MPa), K_a, are 4.91 at 500 °C and 2.55 at 600 °C. If K_a (0.1 MPa) is the chemical equilibrium constant based on an ideal gas, K_x can be expressed as $K_x = K_a\phi$ at each temperature, where ϕ is the ratio of fugacity coefficients. For this case, ϕ was 0.37 and 0.19 at 500 and 600 °C, respectively. The fugacity coefficients are far removed from unity, which indicates that the contribution of fugacity to the equilibrium constant can be considerable for NCW and SCW.

There are several reports on the kinetics of the noncatalytic water-gas shift reaction in supercritical water.[8,136−138] Holgate et al.[8] measured the reaction rate of the water-gas shift reaction from 446 to 593 °C at 24.6 MPa with a flow type apparatus. Those authors summarized their data with a global rate expression:

$$-d[CO]/dt = 10^{3.3} \exp[(-95 \times 10^3)/RT][CO]^{0.71} \tag{1}$$

where reaction rate is given in mol/L·s, concentration is in mol/L, and activation energy is in J/mol.

Rice et al.[136] measured the reaction rate of the water-gas shift reaction at lower temperatures and evaluated the effect of water density. They conducted

an in-situ analysis of the water-gas shift reaction with Raman spectroscopy at 410–520 °C and 2.0–60 MPa. They found the disappearance rate of CO increased with increasing pressure. A first-order rate constant for CO concentration k was determined from

$$-d[CO]/dt = k[CO] \qquad (2)$$

The initial decay curve of CO was not used for determination of the rate constant k because the reliability of the initial rate was considered to be low due to the batch apparatus used. Thus, they determined the rate constant k for the water-gas shift reaction from the disappearance rate of CO at under chemical equilibrium by suggesting that only the forward reaction occurs. At a water concentration of 20 mol/L, k was found to be

$$k\ (\text{s}^{-1}) = 10^{7.22}\exp\{(-145 \times 10^3\ (\text{J/mol})]/RT\} \quad (3)$$

The reaction rate constant k increased with increasing water density, which led those authors to propose an extended expression that included the effect of water density as

$$-d[CO]/dt = k'[CO][H_2O]^a \qquad (4)$$

At densities above 10 mol/L, the empirical reaction orders, a, were determined to be 6.1, 4.5, and 4.6 at 410, 450, and 480 °C, respectively. The high reaction order of water concentration was used to justify experimental findings that an increase in water concentration or water density accelerated the disappearance of CO. The water-gas shift reaction is clearly promoted at high water densities above 410 °C.

Rice et al.[136] proposed evidence for CO transition states through calculation of thermochemical constants of the transition state from experimental data with methods discussed previously. They showed that the water-gas shift reaction near the critical point of water could not proceed through a simple bimolecular reaction.

The water-gas shift reaction rate was also determined around the critical point of water by Sato et al.,[137,138] who measured the reaction rate from 380 to 420 °C and at pressures from 10 to 30 MPa with a flow type apparatus. CO conversion was about 6% for 5 min reaction time at 400 °C. The reaction rate was remarkably low and almost independent of CO and water concentration. The global rate expression proposed by those authors was

$$-d[CO]/dt = 10^{3.9}\ (\text{s}^{-1}) \times$$
$$\exp\{[-98 \times 10^3\ (\text{J/mol})]/RT\}[CO] \quad (5)$$

An Arrhenius plot of the rate constants obtained in these studies is shown in Figure 3. The slope of the curve, namely activation energy, is similar for eqs 1 and 5. The studies of Holgate et al.[8] and Sato et al.[137,138] were conducted with a flow apparatus, and the rate constant was determined from the initial decay curve of CO disappearance. Thus, the forward reaction of the water-gas shift could be evaluated in these studies. On the other hand, Rice et al. used a
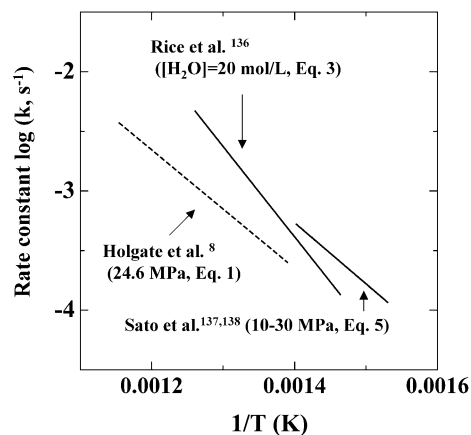
Figure 3. Arrhenius plot of reported water-gas shift reaction rates in near-critical and supercritical water.

batch reactor to deduce the forward reaction rate of the water-gas shift reaction. To reduce error associated with batch heat-up and mixing effects, the researchers used rate data from the latter stage of the reaction. This technique allowed determination of the forward water-gas shift reaction although it is subject to somewhat larger errors.

Sato et al. evaluated the rate constant and paid close attention to the possible effect of water density on the reaction.[137,138] At 400 °C, the rate constant was almost constant from 10 to 30 MPa. At 380 °C, the rate constant exhibited a drastic change at pressures around 25 MPa. This water density dependence of the water-gas shift reaction is very similar to that for HCOOH decomposition, as described in section 5. The rate first gradually decreased to a minimum and then increased around the critical point. The dependence of water density on the reaction rate around the critical point of water was very different from that in the higher temperature region.

We can conclude that the water-gas shift reaction is significantly catalyzed by alkali at lower temperatures. As described below (section 3.2), oxygen enhances the water-gas shift reaction at higher temperatures. These results support the concept of Figure 1, that is, the low temperature water-gas shift reaction being ionic in nature and the high temperature water-gas shift reaction occurring through free radicals. The trend of the water-gas shift reaction at densities around the critical point of water is similar to that observerd for the reaction of HCOOH, providing evidence that the water-gas shift reaction also proceeds via molecular reactions (see section 5 for more detail), as pointed out by Melius and Bergan.[135]

3.2. Oxidation

Holgate and Tester[11,12] conducted experiments with CO in SCW at equivalent molar CO/2O₂ ratios of 0.53 to 1.89 (CO/O₂ ratios of 1.06 to 3.78) at temperatures from 550 to 570 °C and at pressures from 11.8 to 26.3 MPa. CO₂ and H₂ were produced corresponding to the consumption of O₂, which indicates that the direct oxidation of the reducing agent, CO to CO₂, and the formation of H₂ occurred in parallel. This would confirm that CO is a reducing agent of O₂ and that it becomes oxidized in the reaction. Simultaneously,
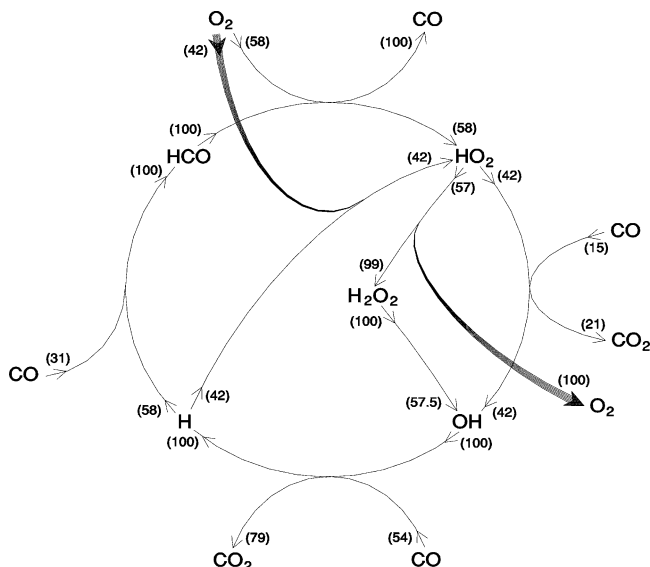
Figure 4. Snapshot of the most important reaction pathways in the oxidation of CO in supercritical water at 600 °C, 25 MPa, and 0.4 s reaction time with an excess of oxygen calculated using the model of Brock et al.[18] Numbers in parentheses give the percentage of the compound reacting via or formed by the specific reaction path. Reproduced with permission from ref 19. Copyright 1997 Forschungszentrum Karlsruhe.

H_2 formation implied that CO is an oxidizing agent of H_2O. In another set of experiments at 437−571 °C and 24.6 MPa,[8] the reaction rate of direct oxidation was evaluated, and the following global rate expression was determined:

$$-d[CO]/dt = 10^{8.5} \times$$
$$\exp\{[-134 \times 10^3 \text{ (J/mol)}]/RT\}[CO]^{0.96}[O_2]^{0.34} \quad (6)$$

The effect of water density was examined by changing the reaction pressure.[11,12] Both the CO conversion and the ratio of CO to CO_2 increased with increasing pressure, which indicates that water promoted H_2 formation.

Oxidation of CO can be viewed as an essential reaction in the mechanisms for CH_4 and CH_3OH oxidation (see sections 6.3 and 7.3). Holgate et al. studied the reaction mechanism of CO oxidation by using a radical elementary reaction network.[9] Ederer and Mas[19] calculated CO oxidation in supercritical water using the model of Brock et al.[18] The main reaction chain is shown in Figure 4. These calculations nicely illustrate that the reaction proceeds via the free radicals HCO, HO_2, OH, and H and that H_2O_2 is an intermediate product.[9,19] The main reaction route is CO oxidation by OH (CO + OH → CO_2 + H), H oxidation by O_2 (H + O_2 → HO_2), H_2O_2 formation by the bimolecular reaction of HO_2 ($2HO_2$ → H_2O_2 + O_2), and decomposition of H_2O_2 to OH (H_2O_2 → 2OH). The effect of water on the CO oxidation can be explained by this reaction pathway. Water promotes OH formation through the reaction between H_2O and HO_2 radical. Throughout the reaction, H_2O_2 is produced, resulting in increasing OH radical formation, which promotes the oxidation of CO. Further, water promotes H_2 formation through the reaction between H radical and H_2O, which

generates OH radicals and H_2. Consequently, the reaction rate and the ratio of H_2 to CO_2 increase with increasing water density.

4. Formaldehyde (HCHO)

Many studies exist on HCHO reaction under SCW conditions.[59,60,62,63,121,139,140] Tsujino et al.[60] conducted batch experiments for the decomposition of s-trioxane (($CH_2O)_3$) by in-situ NMR spectroscopy at 250 °C and 4 MPa. The concentration of HCHO produced from s-trioxane was 3.6 mol/L. The decomposition of s-trioxane to HCHO was rapid, and the Cannizzaro reaction (eq 7) proceeded as

$$2HCHO \rightarrow CH_3OH + HCOOH \quad (7)$$
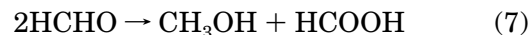
Tsujino et al.[60] proposed that formic acid reacts with HCHO to produce CH_3OH and CO_2 (eq 8, via a hydride transfer reaction) at high concentrations of HCHO (3.6 mol/L) in hot compressed water (250 °C and 4 MPa):

$$HCOOH + HCHO \rightarrow CH_3OH + CO_2 \quad (8)$$
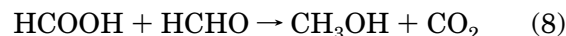
In writing eq 8, H_2 was not detected and the yield of CH_3OH exceeded 50%.

Yamasaki et al.[59] used dichloromethane (CH_2Cl_2) as a source of HCHO and conducted batch experiments with in-situ NMR spectroscopy at 250 °C, 4 MPa, and 0.3 mol/L of CH_2Cl_2 concentration. The Cannizzaro reaction also proceeded for this case, which led those authors to propose that CH_2Cl_2 hydrolyzes to HCHO at the given conditions. CO, CO_2, and H_2 were also produced, and the maximum yield of CH_3OH was slightly lower than 50%, which means that monomolecular HCHO decomposition probably occurred as

$$HCHO \rightarrow CO + H_2 \quad (9)$$
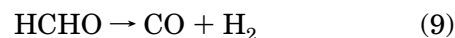
This reasoning follows since the contribution of the HCOOH reaction with HCHO (eq 8) is small at low concentrations (0.3 mol/L). For the case of the reaction of CH_2Cl_2, the effect of HCl must be considered because the hydrolysis of CH_2Cl_2 forms 1 mol of HCHO and 2 mol of HCl.[60] Under acidic conditions, monomolecular HCHO decomposition (eq 9) is likely to be enhanced.[62]

Marrone et al.[139] also conducted decomposition experiments of CH_2Cl_2 in SCW using a flow apparatus at 450−600 °C and at 25 MPa. The range of the concentrations of CH_2Cl_2 was 0.2−0.6 mmol/L in the reactor. They found that CH_2Cl_2 hydrolyzed in SCW and then HCHO decomposed. Since the yield of CO was the highest among the other products (CO_2 and CH_3OH) at all reaction temperatures, monomolecular decomposition (eq 9) was dominant at the given reaction conditions. However, at high temperatures (450−600 °C) and low concentrations (0.2−0.6 mmol/L), a very small amount of CH_3OH was obtained and so the Cannizzaro reaction should proceed in SCW.

Bröll et al.[121] reported selectivities as high as 50 mol % for CH_3OH formed from HCHO in water at lower temperatures of around 300 °C (30 MPa, 2 min
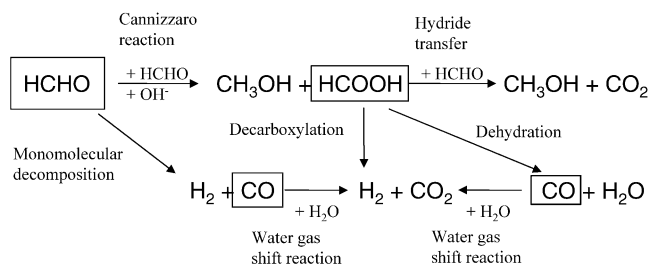
Figure 5. Reaction pathways of HCHO reaction in super-critical water at 400 °C.

Figure 6. Effect of water density of the rates of the water-gas shift reaction and HCOOH decomposition in super-critical water at 380 °C.

reaction time). With increasing temperature, selective formation of CH_3OH became zero, and at temperatures higher than 350 °C, CO and CO_2 were the main products.

Watanabe et al.[62] and Osada et al.[63] found that the Cannizzaro reaction (eq 7) is affected by OH^- and HCHO concentrations in SCW at 400 °C. Watanabe et al. suggested a reaction network for HCHO reaction in SCW at 400 °C, as shown in Figure 5. According to the studies, CH_3OH formation is preferred at high OH^- and HCHO concentrations. Takahashi et al.[140] conducted computer simulations of the association between HCHO and OH ion in SCW and demonstrated that the reaction involving HCHO and OH ion requires water. On the other hand, under acidic conditions and at lower HCHO concentrations, the monomolecular reaction of HCHO (eq 9) is favored. The reaction paths regarding formic acid (HCOOH) in Figure 5 are discussed in the next section.

Following the concept of Figure 1, HCHO reactions are possibly ionic below about 400 °C and around the critical pressure (density). On the other hand, reactions seem to occur via free radicals above about 400 °C and the around critical density. However, ionic reactions possibly proceed even at high temperatures (>400 °C) and at low water densities less than the critical density, as noted by Marrone et al., although the contribution of ionic reactions is likely to be very small due to the higher temperatures and steamlike densities. However, the contribution of ionic HCHO reactions to organic reactions in NCW and SCW still needs to be taken into account.

5. Formic Acid (HCOOH)

HCOOH, being the simplest carboxylic acid, is an intermediate in SCWO chemistry and water-gas shift reactions,[135] and thus many studies have been conducted on HCOOH decomposition.[141–147] For HCOOH decomposition, there are two pathways (Figure 3), which are dehydration,

$$HCOOH \rightarrow CO + H_2O \qquad (10)$$
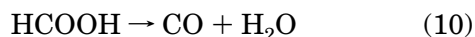
and decarboxylation,

$$HCOOH \rightarrow CO_2 + H_2 \qquad (11)$$
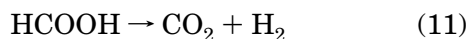
Tsujino et al.[142] conducted experiments of HCOOH decomposition with silica capillary batch type reactors at hydrothermal conditions (250–280 °C, 360–870 kg/m³ water density). They found that the formation rates of CO and CO_2 have reaction orders
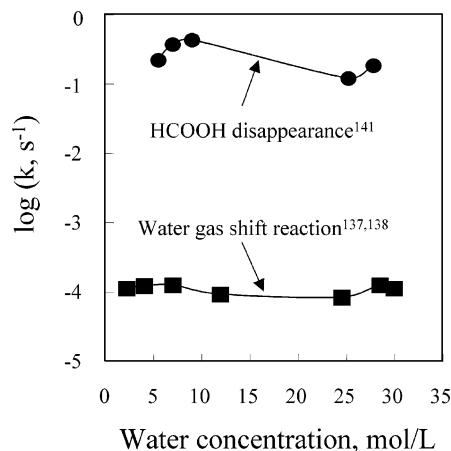
of 1.5 and 1.0, respectively, in HCOOH concentration under the given conditions. Thus, the dehydration must become predominant with increasing HCOOH concentration at low temperatures in the absence of metal surfaces. At higher temperatures, where it is difficult to apply a silica surface, the rates of these two pathways are affected by water densities[141] but can also be catalyzed by the reactor wall[141–147] (see section 9).

Yu and Savage[141] conducted experiments on HCOOH decomposition using a flow apparatus (Hastelloy C-276) at temperatures from 320 to 500 °C, at pressures from 18.3 to 30.4 MPa (91–700 kg/m³ water densities), and at 1.4–80 s reaction times. Initial concentrations of HCOOH ranged from 1.5 to 10 mmol/L. Yu and Savage[141] examined the water density (pressure) dependence on the rate constant of HCOOH disappearance in SCW at 380 °C. Figure 6 shows the dependence of the pseudo-first-order rate constant on water concentration in the system. As shown in Figure 6, the rate constant increased with increasing water concentration up to about 10 mol/L, corresponding to a pressure of 22.2 MPa at 380 °C, and then the rate constant decreased. Furthermore, the rate constant might further increase at concentrations greater than 25 mol/L, as shown in Figure 6. The effect of water concentration on the rate constant of the water-gas shift reaction[137,138] is also shown in Figure 6. Although the order of the rate constant of the water-gas shift reaction is smaller than that of HCOOH decomposition, the trend of the rate constant of the water-gas shift reaction with water concentration is very similar to that of HCOOH decomposition. Thus, as suggested by Melius and Bergan,[135] the structure of the activated complex of the water-gas shift reaction seems to be remarkably similar to that of HCOOH. Concerning HCOOH reactions, formate anion is a possible intermediate at low temperatures and high water densities. Radical reactions predominate at high temperatures and low water densities as well as reactions involving HCHO, as shown in Figure 1. In addition, according to simulation studies, formation of water bridges around the HCOOH molecule creates a complex-like species that aids elimination of $H_2 + CO_2$ via molecular reaction, which means that there are no precise

intermediates such as ions and radicals. It has been suggested that HCOOH decomposition proceeds via molecular reaction around the critical point of water.[55]

6. Methanol (CH₃OH)

6.1. Reforming

Reforming of CH_3OH to form H_2 is a very important step for developing transportation powered by fuel cells. The reforming of CH_3OH has also been investigated in SCW:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \quad \Delta H° = +50 \text{ kJ/mol} \tag{12}$$
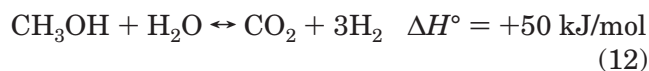
Methane byproduct can be formed through further reaction of CO/CO_2 and H_2, but this is undesirable. Boukis et al.[148,149] reported experiments at 600 °C, 25.0 MPa, and an ~12 s reaction time in a horizontal tube reactor made of the nickel base alloy Inconel 625 and stainless steel 316. They studied the effect of the water to CH_3OH feed ratio on gas composition. They varied the water to CH_3OH feed ratio (mol/mol) from 1 to 33.8, corresponding to a CH_3OH composition of 5−64 wt %. The experiments were conducted without catalyst. The main product of the reaction was H_2, which was formed at concentrations of up to 77 vol %. The CH_4 content in the product gas was up to 30 vol %, and CO_2 was less than 20 vol %. The CO content varied between 1 and 25 vol %. The CH_3OH conversion was as high as 99.9%. For feeds containing up to 26.2 wt % CH_3OH, corresponding to a ratio of water to CH_3OH of 5, reforming occurred mainly according to eq 12 and the yield of hydrogen was close to 3 mol per mole of CH_3OH. The CO yield was very low. At higher CH_3OH compositions, the hydrogen yield decreased and the amount of CO increased. Here, the decomposition of CH_3OH (eq 13) became increasingly important.

$$CH_3OH \leftrightarrow CO + 2H_2 \quad \Delta H° = -92 \text{ kJ/mol} \tag{13}$$

Taylor et al.[150] also conducted experiments on reforming of CH_3OH without catalyst using a flow apparatus that was constructed from Inconel 625. The experiments were run over a wide range of conditions (550−700 °C, 27.6 MPa) at 15−45 wt % CH_3OH concentrations (H_2O/C = 10:2) and for various CH_3OH−water mixture flow rates (0.6−1.2 mL/min). At 700 °C, CH_3OH was completely converted into H_2, CO, CO_2, and small amounts of CH_4 for all CH_3OH concentrations. The amount of H_2 was almost the same (about 70 vol %) for every CH_3OH concentration. The CO_2 formed at 15 wt % CH_3OH was about 20 vol %. With increasing CH_3OH concentration, the amount of CO_2 decreased gradually below 5 vol % at a 0.6 mL/min flow rate. At the highest CH_3-OH concentration, CO formation was dominant, in accord with the results of Boukis et al.,[148,149] which can probably be attributed to the pathway given by eq 13. Taylor et al.[150] also studied the effect of temperature on the reforming. CO formation was dominant in the lower temperature ranges, while CO_2 formation was dominant in the higher temperature

ranges. These results are consistent with expected trends that can be estimated from the heats of reaction (eqs 12 and 13). In these studies, the researchers did not examine the effect of pressure on the reforming step, and therefore, it is difficult to provide comment. However, it can be said that the trend (relative value) is related to the heat of formation rather than its absolute value. Since water is one of the reactants (eq 12), the pressure should have a strong impact for this reaction. In the future, the pressure effect for the reaction should be clarified to allow proper choice of reforming conditions.

These reactions were reported at higher temperatures (>550 °C) and low water densities (<0.09 g/cm³). Thus, the reactions mainly proceed via radical reactions, based on the concept shown in Figure 1.

6.2. Partial Oxidation

Partial oxidation of CH_3OH to HCHO was investigated by Bröll et al.[151] in a differential loop reactor made of Inconel 625, using a jet loop principle. The reaction was studied first without catalyst at 390−450 °C, 22−35 MPa, and a 0.5−60 s reaction time. The CH_3OH concentration was 2 mol %, and the oxygen concentration was 1 mol %. High HCHO selectivity (70%) was found at short residence times (<5 s) and high temperatures (>420 °C), although CH_3OH conversions were low (<5%). At higher conversions, the selectivity toward HCHO decreased. These results were compared with those for three different catalysts (metallic silver, copper, and gold/silver alloy with 97.2 wt % gold) under the same reaction conditions. While Au/Ag alloys showed no effect on the reaction, Ag and Cu metals catalyzed the reaction pathways to CO and CO_2, resulting in a lower selectivity toward HCHO. Analysis of the catalysts showed erosive corrosion for the case of Ag catalyst under supercritical conditions and the formation of a solid layer consisting of Cu(I) and Cu(II) oxide on the Cu catalyst surface.

These reactions were conducted at lower temperatures (<450 °C). The contribution of ionic reaction must be taken into account, although oxidation is normally via radical reaction (Figure 1).

6.3. Total Oxidation

Brock and Savage[13] conducted supercritical water oxidation of CH_3OH at 450−650 °C and 24−25 MPa. They developed a detailed chemical reaction model consisting of 148 elementary reactions and 22 species using CHEMKIN II along with considering the oxidation of C_1 and H_2. Alkam et al.[14] conducted SCWO of CH_3OH at 453−600 °C and 24.6 MPa. They developed a detailed chemical reaction model consisting of 184 elementary reactions and 22 species using CHEMKIN. Brock et al.[18] conducted SCWO of CH_3-OH at 500−589 °C at 25 MPa. They used the CHEMKIN II model proposed by Brock and Savage.[13] Dagaut et al.[15] used the data of Tester et al.[9] (453−544 °C, 24.6 MPa) and CHEMKIN II to develop a model with 127 elementary reactions and 21 species. Brock et al.[21] developed a simple model based on the data of Brock et al.[18] (500−589 °C, 25 MPa) using

Figure 7. Snapshot of the most important reaction pathways of the oxidation of CH$_3$OH in supercritical water at 380 °C and 25 MPa with an excess of oxygen: (a) 30 s and (b) 100 s reaction time calculated using the model of Brock et al.[18] Numbers in parentheses give the percentage of the compound reacting via or formed by the specific reaction path. Reproduced with permission from ref 152. Copyright 2000 Kluwer Academic Publishers.

CHEMKIN II that had 17 elementary reactions and 14 species. In all these calculations, the models were based on well-established gas-phase reaction models of elementary reactions that were corrected for conditions at high pressure. This means that even if water took part in an elementary reaction as a reaction partner, that water would be seen only as a collision partner. Consequently, these models should also be suitable for the calculation of CH$_3$OH oxidation in supercritical CO$_2$, which was reported by Kruse et al.[152] The most striking omission of the above models from gas-phase models is the neglect of the HCOOH formation and degradation. The formation of HCOOH is not observed in gas-phase oxidation but is observed in SCWO.[152]

Figure 7 shows the main reaction pathways calculated by Ederer and Mas[19] and Kruse et al.[152] using the model of Brock et al.[18] at two different reaction times, that is, 30 s (Figure 7a) and 100 s (Figure 7b), at 380 °C and 25 MPa. The CO oxidation shown in Figure 4 is part of this reaction chain. Additional free radicals originating from CH$_3$OH, such as CH$_2$OH and CH$_3$O, take part in the reaction. Remarkably for the SCWO reactions, the OH and the HO$_2$ free radicals play a central role in the oxidation. Sensitivity calculations[19] using the model of Brock el al.[18] show that OH radicals become dominant at high temperatures. Also at lower temperatures, OH radicals play a dominant role at the longer reaction times. In gas-phase oxidations, one can distinguish between a high temperature oxidation with OH radical and a low temperature oxidation with HO$_2$ radical, as one of the main free radicals of the chain reaction. In SCWO, OH is the main free radical at relatively low temperatures and especially at longer reaction times (see Figure 7b). As in the oxidation of CO, the oxidation of CH$_3$OH forms H$_2$O$_2$ as an intermediate, which has been measured experimentally during CH$_3$OH oxidation in SCW.[153]

All of the above studies on CH$_3$OH total oxidation were conducted at relatively high temperatures (>450 °C) and moderate pressures (~25 MPa). Under these conditions, the water density is ~0.1 g/cm^3 and steam-like. Common things observed in the above studies were, (1) at higher temperatures, namely, low water densities, the detailed reaction models studied with the tool CHEMKIN could describe the experimental results well and (2) the discrepancy between the model and the experimental results gradually increased close to the critical point of water. The reason for the model discrepancies can be attributed to thermodynamic factors such as the fugacity of radical species near the critical point of water, as pointed out by Mizan et al.,[154] or other chemical factors such as the participation of water in the reaction pathways. In summary, one can conclude that models of elementary reactions that are developed from gas-phase models are probably most reliable at high temperatures and low pressures. To create a model for temperatures (~400 °C) and densities (~0.3 g/cm^3), the solvent effects of water should probably be considered for each elementary reaction. Despite there being only around 20 elementary reactions that are sensitive concerning the global reaction rate, development of such a model will be a very difficult task, because it is not easy to measure elementary reactions in SCW. A first step in this direction is the studies of the H$_2$O$_2$ dissociation in SCW.[107,108] There has been some progress in elucidating the role of water in free radical reactions.[98]

Boock and Klein[155] proposed lumping strategies for the modeling for SCWO of small alcohols, such as ethanol and propanol, based on the model for SCWO of CH$_3$OH. The lumping strategy is a technique proposed by those authors for developing of SCWO kinetic models. In this method, the elementary reactions are classified, such as initiation, scission, H abstraction, branching, and termination. The kinetic parameters, that is, the pre-exponential factor and activation energy, of each reaction step are estimated from the entropy and enthalpy of the reaction by use of linear free energy relationships. The model that the authors proposed was successful in estimating the kinetics of SCWO of ethanol and propanol based on the kinetic model for SCWO of CH$_3$OH.

In addition to the above CH$_3$OH oxidation described by models consisting of elementary reactions, simplified network models for CH$_3$OH oxidation in
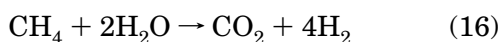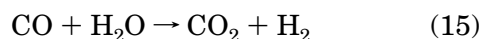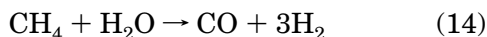
Figure 8. Gas composition after the reaction of methane with water (molar ratio of H_2O/CH_4 = 143:1) at 600 °C: run 1, Raney-Ni and KOH; run 2, Raney-Ni; run 3, NaOH; run 4, K_2CO_3; run 5, KOH; run 6, without catalyst.

SCW have also been reported. Tester et al.[9] conducted supercritical water oxidation of CH_3OH at 453–544 °C and 24.6 MPa and suggested an overall rate for the disappearance of CH_3OH. Anitescu et al.[22] conducted SCWO of CH_3OH at 400–500 °C and 25.3 MPa and developed a network model for disappearance of CH_3OH and formation of CO and CO_2. Watanabe et al.[24] reported a network model for CH_3OH oxidation in SCW based on the model of Anitescu et al.[22] The model of Watanabe et al.[24] showed the possibility that the rate of CH_3OH to form CO and CO_2 could be affected by proton or hydroxyl ion in SCW near the critical point of water. Thus, as found by Mizan et al.[154] and Watanabe et al.,[24] the nonideality or ionic effects of water should be considered in models for radical oxidation near the critical point of water.

7. Methane (CH_4)

7.1. Reforming

The reaction of CH_4 with water has been investigated in hopes of developing a process to produce hydrogen from CH_4 in one reaction step. Experiments[156] were conducted in autoclaves of ~4 cm³ internal volume made of Hastelloy C-276 with a large excess of water primarily at 660 °C and at pressures from 38 to 68 MPa. The overall reactions occurring are

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (14)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (15)$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad (16)$$

Pressure had no significant influence on the reaction, while the temperature and addition of catalysts had a large effect. Figure 8 shows the composition of the product gas, which consisted mainly of H_2 and CH_4. Apparently only a small amount of CO_2 was formed, or any CO_2 formed was mainly present in the liquid phase. Without the addition of catalysts, the hydro-

gen yield was poor (run 6). The addition of bases such as KOH, NaOH, and K_2CO_3 led to an increased H_2 yield (runs 3, 4, and 5). These salts are known to increase the reaction rate of the water-gas shift reaction (see section 3.1). Raney Ni as additive lead to a different gas composition (run 2). Here, the conversion of CH_4 to CO and H_2 increased (eq 13), whereas the conversion for the water-gas shift reaction did not change appreciably (eq 14). The combination of Raney Ni and KOH led to nearly the same hydrogen yield as that for KOH addition, but with a small yield of CO. Here, both dehydrogenation of CH_4 (eq 13) and the water-gas shift reaction (eq 14) occurred. It is likely for experiments with KOH, NaOH, and K_2CO_3 (runs 3, 4, and 5) that the autoclave wall acts as a Ni catalyst by increasing the dehydrogenation of CH_4 (eq 13). Reactor wall effects for catalyzing reactions are discussed in detail in section 9.

These experiments were conducted at 660 °C. On the basis of Figure 1, the reforming of CH_4 is probably via radical reaction. Ni catalyst promotes bond scission of CH_4 and the other radicals. However, alkali catalyst also promotes H_2 formation from CH_4. Further, some portions of KOH dissociate even at higher temperatures and lower water densities. For example, the amount of K^+ ion in KOH aqueous solution at 0.01 mol/kg of KOH concentration at 600 °C and 0.3 g/cm³ is 8.8×10^{-4} mol/kg,[157] which indicates that there is some contribution of ionic mechanisms, and this should be considered as for the HCHO reaction (see section 4) even at higher temperatures.

7.2. Partial Oxidation

Research on CH_3OH for energy production has gained more attention in recent years, because CH_3OH is thought to have an important future as an energy and chemical resource. At present, most CH_3OH is made from CO and H_2 (syngas), which are produced via the steam reforming reaction between CH_4 and H_2O. This two-stage process has high energy consumption and, consequently, high cost. A direct synthesis technique of CH_3OH from CH_4 has been desired for years. Partial oxidation of CH_4 in SCW is one possible method for direct synthesis of CH_3OH from CH_4, as described in the Introduction. It is known that there are two main pathways for CH_4 partial oxidation in SCW.[66] One pathway is direct oxidation into CO without the formation of CH_3OH (eq 17).

$$CH_4 \xrightarrow{k_1} CO \qquad (17)$$
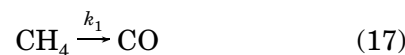
Another pathway for CH_4 partial oxidation is the stepwise oxidation via formation of CH_3OH (eq 18).

$$CH_4 \xrightarrow{k_2} CH_3OH \xrightarrow{k_3} CO \xrightarrow{k_4} CO_2 \qquad (18)$$
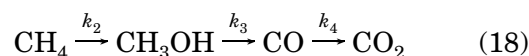
For increasing the yield of CH_3OH, control of k_1/k_2 or $(k_1 + k_2)/k_3$ is required. In the gas phase, CH_3OH is oxidized faster than methane, and therefore, the selectivity of CH_3OH is very poor, probably since k_3

is very fast in the gas phase. Many research groups have investigated the partial oxidation of CH_4 to CH_3-OH in SCW, with the hope that CH_3OH can be stabilized by H_2O, since k_3 seems to be retarded in SCW.[24]

Hirth and Franck[10] conducted CH_4 partial oxidation experiments at temperatures from 380 to 500 °C and pressures from 30 to 100 MPa in SCW. They set the ratio of O_2/CH_4 at 0.025 and confirmed that a high CH_3OH selectivity ($S = [CH_3OH]/([CH_4]_{initial} - [CH_4]_{final}) \times 100$) could be obtained at higher pressures (S reached up to 20 mol %) during the initial stages of the reaction. CH_4 conversion was not shown in the reference.[10]

Savage et al.[68] studied the partial oxidation of CH_4 without a catalyst in a batch reactor (349−481 °C, 1−9 min, water densities from 150 to 350 kg/m³, CH_4/H_2O ratios from 0.05 to 0.27, O_2/CH_4 ratios from 0.04 to 0.1). CH_3OH, CO, and CO_2 were the main products. The CH_4 conversion was up to 6%, and the selectivity of CH_3OH was between 4 and 75%, but high CH_3OH selectivity could only be achieved at very low conversions. The maximum yield of CH_3OH was 0.7% relative to the initial CH_4 content. Comparison with an existing model for CH_4 oxidation (see below[3]) showed higher conversions and selectivities than those predicted. At this moment it is not known in detail; however, the partial oxidation of methane to methanol was conducted at around the critical point of water. Since the contribution of ionic reaction mechanisms probably cannot be neglected, the free radical model used could not describe the experimental results precisely.

Lee and Foster[69] studied the partial oxidation without catalyst. They used a flow reactor at 25 MPa, and reaction times of 6−84 s under conditions of laminar flow. In that work, the maximum selectivity found was 35% at conversions of 1−3% at temperatures between 400 and 410 °C. Since oxygen was the rate-limiting species in their studies, reaction kinetics were determined on the basis of oxygen concentration:

$$-d[O_2]/dt = 10^{28.8 \pm 2.7} \times$$
$$\exp[(-400 \pm 38 \times 10^3)/RT][O_2]^{0.3}[CH_4]^{1.3} \quad (19)$$

Dixon and Abraham[66] made comparisons between gas-phase and SCW partial oxidation of CH_4 to CH_3-OH in batch reactors with Cr_2O_3 as catalyst. Conditions were 450 °C and 11.4−43.9 MPa, and reaction times were between 5 and 40 min. At a given reaction time, the conversion achieved from the gas-phase catalysis was approximately twice that obtained from reaction in SCW. No CH_3OH was observed in the gas-phase oxidation. For the case of oxidation in SCW, the CH_3OH yield was low, but measurable. The highest selectivity was 40% at a conversion of 10% CH_4 (0.0724 mol/L O_2 concentration, 33 MPa, 5 min reaction time).

Aki and Abraham[67] conducted partial oxidation experiments with Cr_2O_3/Al_2O_3 and MnO_2/CeO as catalysts in a flow system at temperatures between 400 and 475 °C, at 24.1 MPa and for reaction times from 13 to 31 s. Nitrogen containing 0.5% CH_4 and

O_2 dissolved in water at atmospheric pressure (4.79×10^{-6} mol of O_2/mol of H_2O) were used as reactants. For comparison, the reactor was packed with Al_2O_3, and for that case, no conversion was observed. Using Cr_2O_3/Al_2O_3 and MnO_2/CeO as catalysts, the main products were CH_3OH, HCOOH, and acetic acid (CH_3COOH). Minor products were acetone and ethanol, and the amounts of CO and CO_2 were below detection limits. MnO_2/CeO lead to higher conversions and lower selectivities concerning the formation of CH_3OH, despite lower reaction times caused by different packings. The conversions achieved were between 2.3% (Cr_2O_3/Al_2O_3, 400 °C) and 17.8% (MnO_2/CeO, 475 °C) of the converted CH_4. The maximum selectivity of CH_3OH was 1.7% at 6% conversion (Cr_2O_3/Al_2O_3, 475 °C, 32.4 s, O_2/CH_4 ratio of 0.024). HCOOH was produced with a maximum selectivity of 70% at a conversion of 6.7% (MnO_2/CeO, 400 °C, 12.8 s, O_2/CH_4 ratio of 0.005). The activation energy was 40.7 kJ/mol for the case of Cr_2O_3/Al_2O_3 catalyst and 48.6 kJ/mol for MnO_2/CeO catalyst, which is nearly half the value of the activation energy of the uncatalyzed reaction. Calculations showed that mass transfer limitations could be neglected for these experiments.

By the research group of Tohoku University, experiments for CH_3OH synthesis from CH_4 partial oxidation in SCW have been conducted. Experiments were conducted with a small batch type reactor[158] and with a flow apparatus.[76] Experimental conditions were 400 °C, 20−40 MPa, 0.01−0.5 O_2/CH_4 ratio, and a 1 s to 15 min reaction time. For all cases, a high CH_3OH selectivity (50%) was obtained at low CH_4 conversions (0.2%).[76,158] When CH_4 conversion was increased, the CH_3OH selectivity drastically decreased, in accord with other reports.[66,68,69]

In the studies by Bröll et al.,[73,75] the effect of different catalysts is reported and compared with experiments without catalyst. The catalysts investigated were chips of Inconel 625 and sheets of Cu, Ag/Cu alloy (72% Ag), Ag, Au/Ag alloy (2.8% Ag), and Ag on Al_2O_3. The reaction conditions were 375−500 °C, 22.0−35.0 MPa, 0.1−4 mol % CH_4, 0.1−2 mol % O_2, and a mass flow rate between 25 and 100 g/min (~1−20 s reaction time). The experiments were conducted in a differential loop reactor as described in section 5.2. The O_2 was produced in a preheater from an aqueous solution of H_2O_2. In the experiments without catalyst, selectivity toward HCHO and CH_3-OH was high (50−80%) but only at very low CH_4 conversions (<1%). The global rate expression in the experimental region they determined was

$$-d[CH_4]/dt = k[CH_4]^{1.3}[O_2]^{0.4} \quad (20)$$

with an activation energy of 240 kJ/mol and an activation volume of −2250 cm³/mol. The experiments with catalyst showed surprising results: The use of catalysts lead to a decrease in CH_4 conversion at the reaction conditions. The Ag sheet and the Inconel chips gave a slight increase in CH_3OH selectivity at mild conditions of low temperatures, low pressures, short reaction times, and an excess of CH_4. The sheets of Ag, Cu, and Ag/Cu alloy, and the Ag
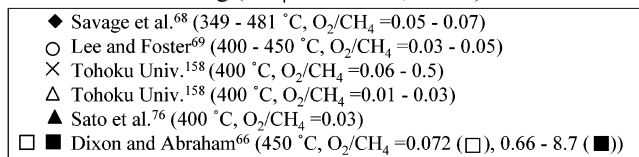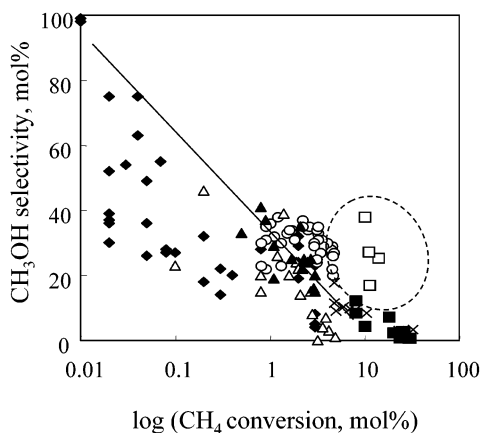
Figure 9. Relationship between CH_4 conversion and CH_3-OH selectivity at CH_4 partial oxidation in supercritical water.

on Al_2O_3 produced a catalytic effect on the reaction in that undesired formation of CO_2 was increased relative to the formation of the partially oxidized products by these materials. The last catalyst, Ag on Al_2O_3, exhibited severe leaching at the reaction conditions. The activation energy ranged from 180 kJ/mol for the silver sheet to 290 kJ/mol for the Ag/Cu sheet. Activation volumes were between -1900 and -3200 cm^3/mol.

As shown in all the above previous reports for CH_4 partial oxidation, the CH_3OH selectivity is a function of CH_4 conversion. Figure 9 shows the relationship between CH_4 conversion and CH_3OH selectivity that have been reported.[66,68,69,76,158] At lower CH_4 conversions (almost zero), a CH_3OH selectivity of 100% can be obtained without catalyst.[66,68,69,76,158] In Figure 9, no significant pressure effect on CH_3OH selectivity can be seen. The trend of CH_3OH selectivity with CH_4 conversion with Cr_2O_3 catalyst[47] is different from that without catalyst. This means that the redox reaction of O_2 with catalyst is effective for direct formation of CH_3OH from CH_4 in SCW. However, the stability of Cr_2O_3 in SCW is not high.[159,160] In summary, for effective partial oxidation processes, highly stable and active catalysts, such as ZrO_2, TiO_2, RuO_2, and so forth,[44,62] need to be developed.

7.3. Total Oxidation

Webley and Tester[6] examined CH_4 oxidation in SCW at $560-650$ °C and 25 MPa with a flow type apparatus. The fuel equivalence ratio ($CH_4/2O_2$) ranged from 0.6 to 3.2 (CH_4/O_2 ranged from 1.2 to 6.4). The CH_4 conversion was $20-63$% for a $6.2-11.6$ s residence time. The main product was CO_2, but CO was also produced. They summarized the reaction rate by using a global rate expression as follows:

$$-\mathrm{d}[CH_4]/\mathrm{d}t = 10^{11.4} \times$$
$$\exp[(-179 \times 10^3)/RT][CH_4]^{0.99}[O_2]^{0.66} \quad (21)$$
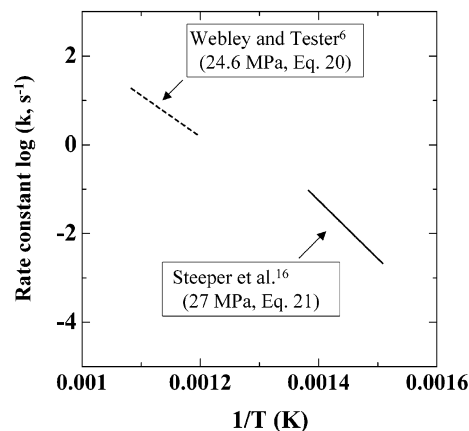
Figure 10. Arrehenius plot of the overall rate of CH_4 total oxidation in supercritical water.

where the units are the same as those for the water-gas shift study (see section 3.1). They pointed out that CH_4 was oxidized to CO and subsequently the CO was oxidized to CO_2.

Savage et al.[20] conducted CH_4 oxidation experiments at 25 MPa and temperatures between 525 and 587 °C with a flow type apparatus for reaction times between 3.2 and 7.6 s. The O_2/CH_4 ratios were from 4.5 to 19, which was $2-5$ times larger than that for the case of Webley and Tester.[6] CH_4 conversion was from 3 to 70%, and the products were CO_2 and CO, with CO being the main product below 10% CH_4 conversion.

Steeper et al.[16] conducted in-situ observation of methane oxidation with Raman spectroscopy. Experiments were run at $390-450$ °C and $3.5-27$ MPa and for $0.5-1.3$ fuel equivalence ratios. At 27 MPa, the global rate expression determined was

$$-\mathrm{d}[CH_4]/\mathrm{d}t = 10^{17.1} \times$$
$$\exp[(-251 \times 10^3)/RT][CH_4]^{1.84}[O_2]^{-0.06} \quad (22)$$

where the units are the same as those for eq 20. The reaction order with respect to CH_4 was larger than that obtained at higher temperatures, and the reaction order with respect to oxygen was almost zero. This means that the concentration of fuel is an important factor for determining the reaction rate. An Arrhenius plot of the rate constants reported is shown in Figure 10.

The mechanism of methane oxidation has been studied with free-radical elementary reaction models. The main reaction pathways of CH_4 oxidation in these studies are as follows: at first, CH_4 is converted to HCHO or CH_3OH and radicals such as CH_3OO are oxidized to HCHO and then to CO and then CO is oxidized to CO_2.

Webley and Tester[6] attempted to express the SCWO of CH_4 by an elementary reaction model consisting of 17 chemical species and 66 reversible reactions. They proposed the reaction pathway for their experimental conditions ($560-650$ °C, 25 MPa). However, they pointed out that a more detailed examination of the elementary reaction model was needed because of its low accuracy for predicting CH_4 conversion. Brock and Savage[13] proposed a detailed
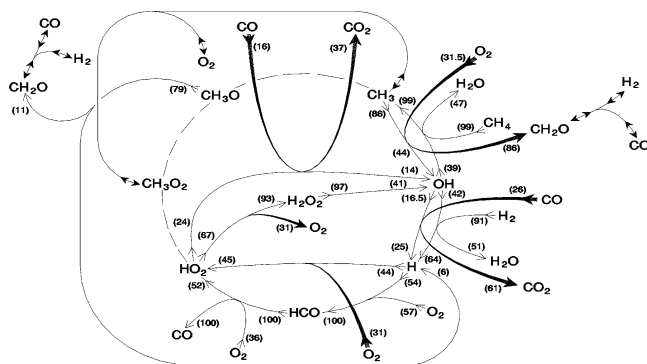
Figure 11. Snapshot of the most important reaction pathways of the oxidation of CH$_4$ in SCW at 600 °C, 25 MPa, and 0.3 s reaction time with an excess of oxygen calculated using the model of Brock et al.[18] Numbers in parentheses give the percentage of the compound reacting via or formed by the specific reaction path. Reproduced with permission from ref 19. Copyright 1997 Forschungszentrum Karlsruhe.

chemical kinetics model for SCW oxidation of C$_1$ compounds and hydrogen. Their model included 148 reversible elementary reactions and 22 chemical species. They found the HO$_2$ radical to be an important chemical species and revised the model by considering the heat of formation of HO$_2$ radical. The model could predict the experimental reaction rate of CH$_4$ conversions obtained in the high temperature region (560−650 °C). Savage et al.[20] applied the same type model (150 elementary reactions and 22 species) at 25 MPa and 525−587 °C and found that the model was applicable at those conditions. They performed sensitivity analysis and found that CH$_4$ concentration was important in reactions such as OH + H$_2$O$_2$ = HO$_2$ + H$_2$O, OH + HO$_2$ = H$_2$O + O$_2$, H$_2$O$_2$ = OH + OH, and HO$_2$ + HO$_2$ = O$_2$ + H$_2$O$_2$, that is, those controlling concentration of OH. This controlling nature of the OH concentration can be clearly illustrated by a picture of the main chain reaction of CH$_4$ oxidation. Figure 11 shows the calculated main chain reaction of the oxidation of CH$_4$ (600 °C, 25 MPa) for an excess of oxygen and for a 0.3 s reaction time using the same kinetic model as that used for Figures 4 and 7. Under these conditions, the reaction of OH radical with CH$_4$ is the only CH$_4$ consuming step. Steeper et al.[16] evaluated the effect of water concentration. The reaction rate for methane conversion first increased to a maximum with increasing water concentration and then sharply decreased at higher water concentrations. The elementary reaction model proposed by Alkam et al.[14] can explain this behavior. The first increase of reaction rate is due to the enhancement of unimolecular decomposition of H$_2$O$_2$ with water as a collision partner, and the decrease is from methane formation being promoted with water as reactant.

Oxidation of CH$_4$/CH$_3$OH mixtures in SCW was also examined by Savage et al.[23] with a flow reactor at 540 °C and 27.3 MPa with a CH$_3$OH/CH$_4$ ratio of 0−15. The presence of CH$_3$OH led to higher CH$_4$ conversion, which could be predicted by the elementary reaction model.

## 8. Chlorinated Methanes (CH$_2$Cl$_2$ and CH$_3$Cl)

As mentioned above (see section 4), CH$_2$Cl$_2$ in SCW undergoes rapid hydrolysis to HCHO and HCl.[59,139] The first reaction step is assumed to be nucleophilic substitution of chlorine by water. The intermediate formed, CH$_2$OHCl, is unstable and quickly forms H$_2$-CO and HCl in the second reaction step. In NCW, the reaction was found to be faster than in SCW, despite the higher temperatures of the supercritical conditions. This can be explained by considering the first reaction step, in which the S$_N$2 reaction is strongly dependent on the properties of the solvent. At system conditions where water has a higher relative dielectric constant, the activated complex of this reaction step is probably stabilized so that the activation energy is lowered. Theoretical studies of the hydrolysis of CH$_2$Cl$_2$ using a modification of the Kirkwood solution model show the influence of the relative dielectric constant on the reaction rate. At supercritical conditions, the conversion is much lower due to a low relative dielectric constant, and this trend is shown by both the model and data.[161] These solvent effects on the S$_N$2 reaction were captured quantitatively in a correction factor applied to the Arrhenius equation incorporated into a global rate expression proposed for CH$_2$Cl$_2$ hydrolysis.[162]

CH$_3$Cl should show rapid hydrolysis to CH$_3$OH, which is one of the reasons why this reaction has been the focus of theoretical studies. The fast hydrolysis of other reaction pathways that occurs is of minor practical interest. Nucleophilic substitution of chloride by chloride in CH$_3$Cl occurs via CH$_3$Cl + Cl$^-$ → Cl$^-$ + CH$_3$Cl. For example, Pomelli and Tomasi[163] calculated reaction profiles for this reaction *in vacuo*, in ambient water, and in supercritical water under different conditions using a polarizable continuum model. In their results, the *ab initio* calculated Gibbs free energy at SCW conditions was always in between the Gibbs free energy of the reaction *in vacuo* and that of the reaction in ambient water.

9. Reactor Wall Effect on Reactions

For SCW studies, researchers have used high temperature and pressure apparatus made of iron, chromium, and nickel alloys such as stainless steel, Hastelloy, Inconel, and so on. Since the metal wall of the inner surface of a reactor can possibly act as a catalyst, especially at high temperatures, the effect of the reactor wall on the reactions should be considered. For HCOOH decomposition, several studies on the wall effect have been reported. However, for the water-gas shift reaction, few studies exist on the wall effects of the reactor,[164] and thus, discussion on wall effects is limited.

Bjerre and Sørensen[143] conducted the decomposition of HCOOH with autoclaves at 260 °C and 1000 mL of water loading. The loaded amount of HCOOH was 6.1 g. They used two kinds of stainless steel reactors: reactor A had an alloy composition of 17.2% Cr, 11.1% Ni, 2.7% Mo, and Fe, and reactor B had an alloy composition of 27% Cr, 31% Ni, 3.5% Mo, 1% Cu, and Fe. The composition of reactor A is similar to that of stainless steel type 316 (69% Fe,
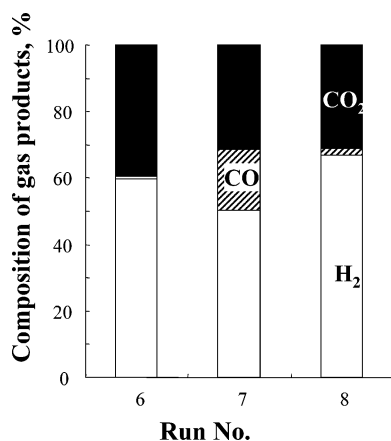
Figure 12. Effect of the inner surface of the reactors on the gas composition of HCOOH decomposition.

17% Cr, 11% Ni, 2% Mo). Reactor A was aged, while reactor B was new. In their studies, only the composition of the gas product was reported, as shown in Figure 12. Run 6 was the experiment with reactor A, and run 7 was the experiment with reactor B. Run 8 was conducted using reactor B with a catalyst that was derived by dissolving parts of the wall surface with HF. The composition of the catalyst was 75% Fe_2O_3, 12% Cr_2O_3, 10% NiO, and a small amount of Cu and Mo. As shown in Figure 12, the composition of CO was negligibly small in runs 6 and 8. On the other hand, about 18% CO was formed in run 7. From our analysis, these results are evidence that either one or both decarboxylation and the water-gas shift reaction were catalyzed by reactor A (run 6) and also by the catalyst derived from the reactor wall (run 8).

In the experiments of Yu and Savage (see section 5),[141] the yield of CO was always negligibly small under all conditions and the ratio of H_2 to CO_2 (H_2/CO_2) was 0.9−1.2, namely, almost unity. It appears that decarboxylation (eq 11) was predominant probably because water could have a catalytic effect.[141] Quantum chemical calculations show that the decarboxylation of HCOOH is possibly catalyzed by the water molecule.[144,145] They[141] examined the effect of the reactor wall on the pseudo-first-order rate constant of HCOOH decomposition at 380 °C and 25.3 MPa, by changing the S/V ratio (surface-to-volume ratio) of the reactor. The first-order rate constant varied from 0.1 to 0.16 s^{-1} according to the S/V ratio of 15−37 cm^2/cm^3 used. Those authors concluded that the effect of the reactor wall on the reaction was small, because the change in the rate constant was not so significant.

Maiella and Brill[144] conducted in-situ observations of the HCOOH reaction in SCW (280−330 °C, 27.5 MPa) with FT-IR. In their study, the authors used several types of tubing to examine the effect of the reactor wall on the reaction: two different types of stainless steel type 316 tubing (SS316a and SS316b), 90/10 Pt/Ir tubing, and Ti tubing. According to their results,[144] except for SS316a, the time profile of CO_2 proportionally increased with time. For SS316a, the formation of CO_2 exhibited an unusual two-step increase. To explain the phenomenon, the authors proposed that HCOOH decomposition is easily catalyzed by the reactor wall and thus the reaction
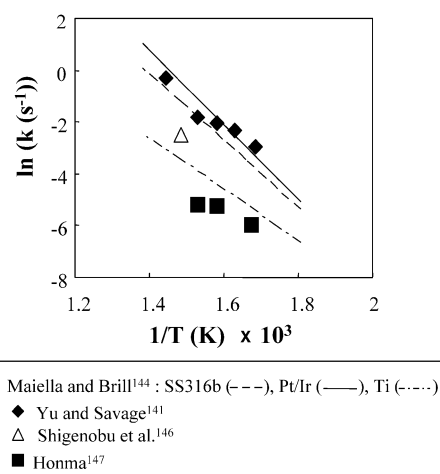
Figure 13. Arrhenius plot of the reported rates of HCOOH disappearance in supercritical water at about 25 MPa.

phenomenon changed drastically according to reactor history, even for the same materials (SS316a and SS316b). Maiella and Brill[144] reported several Arrhenius equations for the pseudo-first-order rate constant of HCOOH decomposition according to the different reactors used.

Figure 13 shows an Arrhenius plot for HCOOH decomposition in SCW under conditions close to 25 MPa. The data of Yu and Savage,[141] Shigenobu et al.,[146] and Honma[147] are plotted with the values of Maiella and Brill[144] obtained by extrapolating their results at 27.5 MPa with temperature. For the results of Maiella and Brill, the order of the rate constants was Pt/Ir > SS316b > Ti, as mentioned in their work. The rate constants of Yu and Savage (Hastelloy C-276, S/V = 30 cm^{-1}) were very similar to those of Maiella and Brill with Pt/Ir or SS316b (S/V = 20−50 cm^2/cm^3). On the other hand, the rate constants of Shigenobu et al. (SS316, S/V = 40 cm^2/cm^3) and Honma (SS316, S/V = 23 cm^2/cm^3) were similar to the rate constants measured for Ti by Maiella and Brill and thus much lower than those with Hastelloy C-276,[141] SS316b, or Pt/Ir.[144] Among the results for SS316 by Maiella and Brill, Shigenobu et al., and Honma, the rate constants reported by Maiella and Brill were the highest and those by Honma were the lowest. The differences between the rate constants of various researchers at 380 °C were about 4 orders of magnitude. These differences can almost certainly be attributed to the reactor history or reactor material.

Tsujino et al.[142] studied the effect of adding SS316, Hastelloy C-276, or Inconel 625 powders on HCOOH decomposition in SCW. They reported that these added alloys promoted the formation rate of CO_2. Thus, they suggested that decarboxylation of HCOOH is affected by a metal or a metal oxide dramatically.

From the studies on HCOOH decomposition in water described above, it is clear that the reaction behavior is difficult to reproduce even under the same conditions. This poor reproducibility can be attributed the catalytic effect of the reactor metal surface in the reaction. Although some researchers have studied the mechanism of HCOOH reaction and the role of water on the reaction by use of computational techniques

(MO[145] and QM/MM[147]), reliable experimental kinetic data are still lacking.

10. Conclusions

C$_1$ chemistry in NCW and SCW will become much more important in the immediate future because industrial applications for SCWO, SCWG, the water-gas shift reaction, and various organic reactions are being put into practical use. Fundamental knowledge of C$_1$ chemistry is, thus, necessary for industrial applications with NCW and SCW. Good progress has been made for elucidating reaction mechanisms for CO, CH$_3$OH, and CH$_4$ total oxidation at high temperatures and at low water densities. Global rate constants have been obtained for the water-gas shift reaction, and detailed reaction models for oxidation have become available. However, studies on HCHO reactions have not been carried out in great detail yet. Even in SCW, the Cannizzaro reaction is found to be predominant in the moderate temperature regions (<450 °C). At higher temperatures (>450 °C), the monomolecular decomposition reaction (HCHO → CO + H$_2$) is the main reaction. The Cannizzaro type reaction is catalyzed by alkali, while the monomolecular reaction is possibly enhanced by acid.

The effect of water density on HCOOH decomposition at 380 °C is similar to that on the water-gas shift reaction at the same temperature. This behavior possibly indicates that the reaction profile of HCOOH reaction is similar to that of the water-gas shift reaction. Further research using spectroscopic and theoretical studies for the equilibrium of CO + H$_2$O with HCOOH should make the relations definite.

Reforming and oxidation of CH$_3$OH in SCW have been studied. For oxidation, many detailed kinetic models using CHEMKIN have been proposed. At this moment, the next steps for modeling seem to be to take into account the nonideality of species or radicals in the SCW reaction media. Emerging reaction phenomena, such as molecular reactions, may have to be considered in new formulations as models are developed that bridge radical and ionic reaction regions.

For CH$_4$, reforming and oxidation studies have been conducted, as well as for CH$_3$OH synthesis. The detailed kinetic model for CH$_4$ is based on CH$_3$OH oxidation, and thus, considerations for the CH$_4$ oxidation model are similar to those for the CH$_3$OH oxidation model. In addition, a lot of studies on CH$_4$ partial oxidation with and without catalyst have been conducted with the hope to develop a direct synthesis process of CH$_3$OH from CH$_4$ using SCW. CH$_3$OH selectivity drastically decreases with increasing CH$_4$ conversion in the absence of catalyst. On the other hand, some catalysts increase CH$_3$OH selectivity, which should also be useful in furthering research on CH$_3$OH oxidation catalysts.

Chlorinated methanes are readily hydrolyzed in SCW. The S$_N$2 reaction mechanism seems to explain the hydrolysis of halogenated CH$_4$ in NCW and SCW.

The catalytic effect of the reactor has been studied in detail for the HCOOH reaction. Such studies are still lacking for many reactions and should be examined in the near future. The development of new reactor materials or new reactor configurations may accelerate progress in this area.

The next step of development of C$_1$ chemistry with NCW and SCW will be to assess the effect of nonideality on various reactions and reaction pathways. Although this step can be performed presently with computationally techniques, it is probable that this topic is closely related to the challenge of decoupling wall effects from the apparent and true reaction mechanisms.

11. Outlook

According to the available research, future work should probably focus on the following subjects: simple compounds and compounds that are more complex but have related pathways. For example, C$_2$ and C$_3$ compounds (alcohol, aldehyde, carboxylic acid, and ketone) related to biomass, which will be energy and chemical resources in the near future, must be studied because supercritical water gasification (SCWG) and supercritical water refinery (SCWR) of biomass are candidates for generating energy and manufacturing chemicals from biomass. In addition, of paramount importance is to resolve possible wall effects on reported studies, since this influences models and their development.

The effect of nonideality of water (such as fugacity, dielectric effect, hydrogen bonding, ionic interaction, and so on) must be taken into consideration for development of a comprehensive understanding of kinetics in SCW. Water itself must be a catalyst for a reaction as well as a reactant. The catalytic participation of water on dehydrogenation of ethanol has been revealed by computational studies.[165−167] In the future, close collaboration between experimental and computational studies will be needed, since the chemistry of simple C$_1$ compounds is expected to be more and more important for future development.

For wall effects, many creative experimental studies will be required. In particular, new reactor wall materials must be studied, such as stabilized components (platinum, titanium, stabilized zirconia, silica nitride, and so on) for developing SCWG and SCWR processes and knowing the wall effect of these materials. Recently, several reactions were conducted in a quartz tube reactor.[164] More experimental studies using new reactor materials and reactor configurations are needed to explore and develop highly promising C$_1$ chemistry in high temperature and high pressure water.

12. Acknowledgments

13. Note Added after ASAP Publication

This review was released ASAP on 11/19/04. In eq 12, the ΔH value was changed from negative to positive. The review was reposted on 12/8/04.

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