Reactions in Supercritical Water

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Towards Understanding the Catalytic Reforming of Biomass in Supercritical Water**

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Biomass conversion to transportation fuels (such as biodiesel, Fischer–Tropsch diesel, ethanol, dimethyl ether, methanol, biomethane, and hydrogen) has been the subject of many studies.[1,2] Biogenic synthetic natural gas (Bio-SNG) is particularly interesting as it is an attractive alternative that can be produced with a high efficiency from almost any kind of biomass. Furthermore, the combustion of Bio-SNG produces less atmospheric pollutants compared to liquid and solid fuels, and Bio-SNG can be distributed using the existing natural gas grid.[3]

Biomass with a high water content ("wet biomass") usually poses a great challenge to thermochemical processes. The water in the biomass needs to be removed to a residual content of 10–15 wt% before thermal processing. Water removal therefore requires a lot of energy for wet biomass with an initial water content greater than 80 wt%. Processing biomass in hot pressurized water was found to have many advantages over gas-phase thermochemical processes such as pyrolysis and gasification by steam and/or air.[4] Evaporation of the water in the biomass is avoided when working above the critical pressure of pure water (that is, at $p > 22.1$ MPa). Near- and supercritical water is a green solvent that may replace organic solvents for a number of organic syntheses.[5] We have shown that waste biomass can be catalytically converted to Bio-SNG in supercritical water. The process has a high efficiency and low environmental impact.[6,7]

A catalyst with ruthenium supported on granular carbon showed good gasification efficiency and was found to be stable for at least 220 hours on stream with a clean feed.[8] Ruthenium catalysts also showed good performance for the production of hydrogen from ethanol in supercritical water at higher temperatures.[9]

Ethanol can be regarded as a simple model compound for the supercritical water gasification (SCWG) of wet biomass, since it contains both carbon–carbon and carbon–oxygen bonds. The catalytic reforming of ethanol can be formally described as shown in Equations (1)–(3):

$$C_2H_5OH + H_2O \rightarrow CH_4 + CO_2 + 2\,H_2 \quad (1)$$

$$0.5\,CO_2 + 2\,H_2 \leftrightarrow 0.5\,CH_4 + H_2O \quad (2)$$

$$\text{net}: \; C_2H_5OH \rightarrow 1.5\,CH_4 + 0.5\,CO_2 \quad (3)$$

According to Equation (3), the dry product gas can contain a maximum methane concentration of 75%. In practice, the product also contains a small amount of hydrogen, which corresponds to the thermodynamic equilibrium value for the methanation reaction [Eq. (2)], and leads to lower methane yields.

The mechanism of ethanol reforming in supercritical water has not been reported to date. The catalytic steam reforming of ethanol has been summarized by Haryanto et al.[10] Mariño et al.[11] studied the steam reforming of ethanol on supported Cu–Ni catalysts at 300°C and atmospheric pressure. They proposed that acetaldehyde could be an important intermediate from which methane could be directly formed by decarbonylation [Eqs. (4) and (5)].

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \quad (4)$$

$$CH_3CHO \rightarrow CO + CH_4 \quad (5)$$

The water–gas shift reaction also occurs [Eq. (6)]. However,

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (6)$$

the dehydration of ethanol to ethylene is believed to be the main pathway to coke formation, especially in the presence of acidic sites [Eq. (7)].[12]

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad (7)$$

In contrast to the Cu–Ni catlysts, no coke is formed with ruthenium supported on $MgAl_2O_4$.[13]

Park and Tomiyasu[14] investigated the SCWG of organic compounds over ruthenium dioxide. Based on UV/Vis absorbance measurements of solutions containing naphthalene, RuO_2, and phenanthroline (as a ligand for Ru^{II} species), they proposed a redox-type reaction mechanism involving Ru^{II} and Ru^{IV} species. In contrast, ex situ extended X-ray absorption fine structure (EXAFS) spectroscopic analyses of a quenched ruthenium catalyst supported on charcoal used in the SCWG of lignin revealed the presence of metallic ruthenium.[15]

The aim of the present study was to rationalize the reaction mechanism and to identify the active Ru species of the supported ruthenium catalyst (2 wt% Ru on carbon[9,16])

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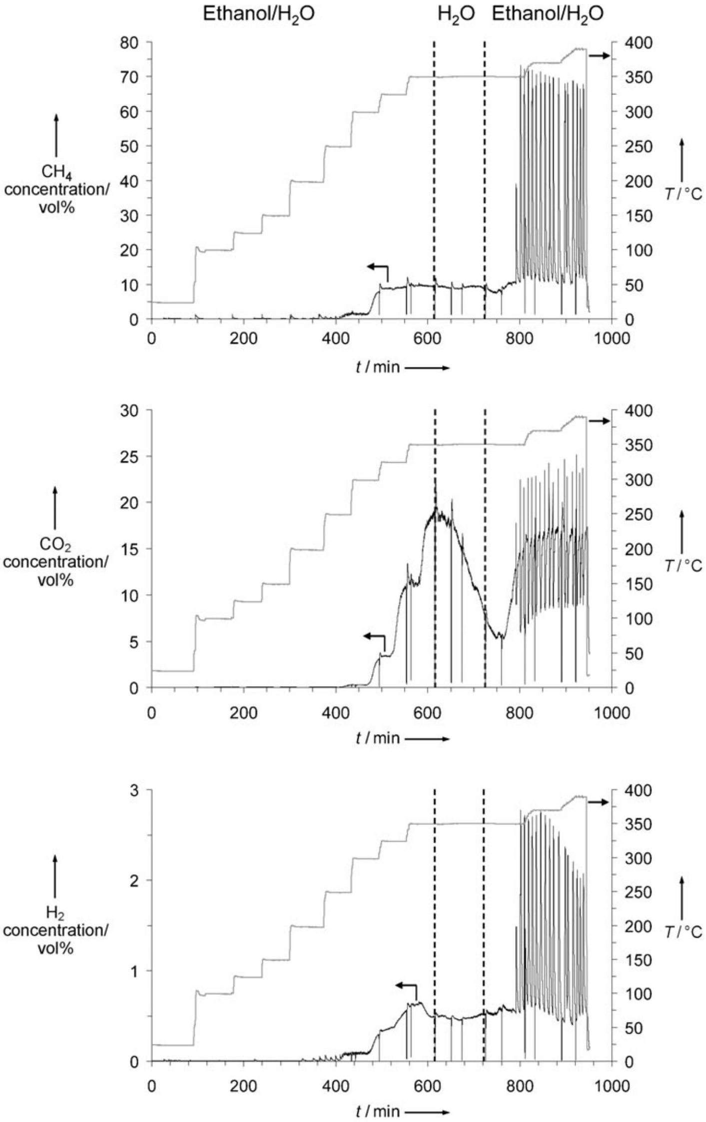

Figure 1. Concentrations of CH_4, CO_2, and H_2 in the dry gas at different times on-stream, corresponding to different reaction conditions. The dotted vertical lines indicate changes in the feed. Negative spikes in the concentration are caused by emptying of the gas–liquid phase separator. Note that the gas stream was diluted with argon.

during the SCWG of ethanol. The gas-phase concentrations of methane, carbon dioxide, and hydrogen, measured online during the SCWG of ethanol at different fluid temperatures, are shown in Figure 1. Dilution by the argon purge flow (compare Figure 3S in the Supporting Information) meant that a maximum methane concentration of 54% was expected at full conversion [Eq. (3)].

Carbon monoxide was only observed in trace amounts (< 1 vol%) under all reaction conditions and is therefore not shown in Figure 1. Gasification started around 250 °C, as can be seen from the onset of methane, CO_2, and hydrogen production. The methane concentration increased from approximately 1 vol% to 9 vol% when the fluid temperature was increased from 250 °C to 300 °C. A further increase of the fluid temperature to 320 °C and 350 °C did not result in a higher methane concentration. In contrast, both the carbon dioxide and hydrogen concentrations increased further when the fluid temperature was increased stepwise from 300 °C to 350 °C. Interestingly, the methane and the hydrogen concentrations did not decrease after switching the feed from an ethanol (5 wt%)/water mixture to distilled water (Figure 1, between $t = 620$ min and 725 min), whereas the carbon dioxide concentration decreased steadily over time.

When the feed was changed back from distilled water to the ethanol/water mixture (Figure 1; after 725 min, $T_{\text{fluid}} = 350$ °C), the concentrations of the gas species increased only slightly. The fluid temperature was then increased to 370 °C ($t = 800$ min). Strong oscillations in all three gas species concentrations were observed under these conditions. The measured mean concentrations of hydrogen (ca. 1.5 vol%) and methane (ca. 45 vol%) were comparably higher, and that of carbon dioxide (ca. 15 vol%) was lower, than those recorded before the catalyst was treated with distilled water at 350 °C ($t = 600$ min), thus indicating a higher catalyst activity. The experiment was abruptly terminated at 390 °C by a rupture of the sapphire capillary after approximately 950 min. We suspect that the mechanical stress induced by the oscillations for more than two hours was the cause of the capillary breakage.

During the oscillations, the methane and hydrogen concentrations increased sharply, while the carbon dioxide concentration simultaneously decreased (Figure 2). The fact that the argon concentration decreased concomitantly (not shown) means that the increase of the volumetric flow of product gases from the reactor into the phase separator (see Experimental Section in the Supporting Information) was in phase with the concentration oscillations. The flow of argon added to the phase separator was held constant by a mass flow controller and can thus be used as an internal

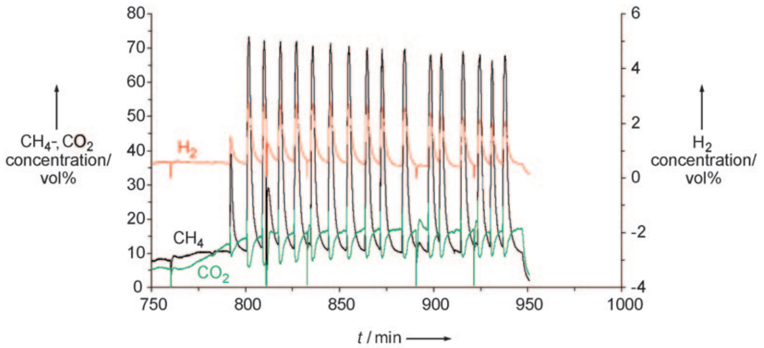

Figure 2. Close-up view of the oscillating gas composition. The feed was 5 wt% of ethanol in water. The temperature was increased stepwise from 350 °C to 390 °C (compare Figure 1).

standard to calculate the total volumetric flow from the reactor. The calculated volumetric flow at the concentration peaks was approximately 10 times higher than that between the peaks. At the peaks, the molar flow of carbon out of the reactor was approximately four times higher than the molar flow of carbon fed to the reactor. This result implies that carbon-containing products must have accumulated in the reactor and/or on the catalyst for about 9 minutes (corresponding to the period between two peaks). These products were then quickly converted to predominantly form methane and hydrogen, which were released suddenly, thus causing the observed increase in total flow and methane and hydrogen concentrations. Then the accumulation of the carbon-containing intermediates restarted and produced the next oscillation. What exactly triggered the sudden release of these products is not known.

These observations led us to propose the following reaction mechanism: ethanol adsorbs on the catalyst and decomposes to acetaldehyde and hydrogen [Eq. (4)] starting at around 250 °C. Acetaldehyde accumulates to a certain extent on the surface, because its formation from ethanol is faster than its decomposition to methane and CO [Eq. (5)]. This accumulation may have led to partial deactivation at the lower temperatures. The accumulation of organic intermediates in the liquid phase at the lower temperatures was confirmed by the total organic carbon analysis (see the Supporting Information). Carbon monoxide remains strongly adsorbed and reacts quickly with water to form CO_2 and H_2 [water–gas shift reaction, Eq. (6)]. Thus, only trace amounts of CO are detected in the gas phase of the effluent. Carbon dioxide is then further hydrogenated to methane [Eq. (2)]. The net overall stoichiometry can be represented by Equation (3), which predicts a CH_4/CO_2 molar ratio of 3. The measured concentrations at 250 °C and 300 °C are consistent with this value, but the concentrations measured at higher temperatures are not. At 350 °C the CH_4/CO_2 ratio is approximately 0.6. The increase in CO_2 without increase in methane and hydrogen implies the decarboxylation of another surface intermediate, presumably derived from acetaldehyde. When the feed is switched to pure water, no more acetaldehyde is produced, and the acetaldehyde accumulated on the surface is slowly used up still producing CH_4 and H_2 [Eqs. (5),(6),(2)]. CO_2 is rapidly hydrogenated to methane [Eq. (2)] and thus its concentration decreases. It is interesting to note that the peak gas composition released during the oscillatory period, that is, approximately 70 % CH_4, 17 % CO_2, 3 % H_2, comes close to the composition expected for reforming of ethanol according to Equation (3), that is, 75 % CH_4 and 25 % CO_2. In this case, the diluting effect from the argon added to the phase separator is strongly reduced because it mixes with a reactor flow that is approximately 10 times higher.

The role of the Ru catalyst in the SCWG of ethanol was studied simultaneously by using in situ X-ray absorption near edge spectroscopy (XANES; the spectra of the as-received catalyst, the reduced catalyst, and the oxidized catalyst are shown in Figure 2S in the Supporting Information). The XANES spectrum of the reduced catalyst shows a double-peak structure characteristic of metallic Ru between 22.1 keV and 22.18 keV. The XANES spectra recorded in the presence of water and ethanol at a pressure of 25 MPa at different reaction temperatures are shown in Figure 3. A reduction of the as-received catalyst occurred between 125 °C and 150 °C.

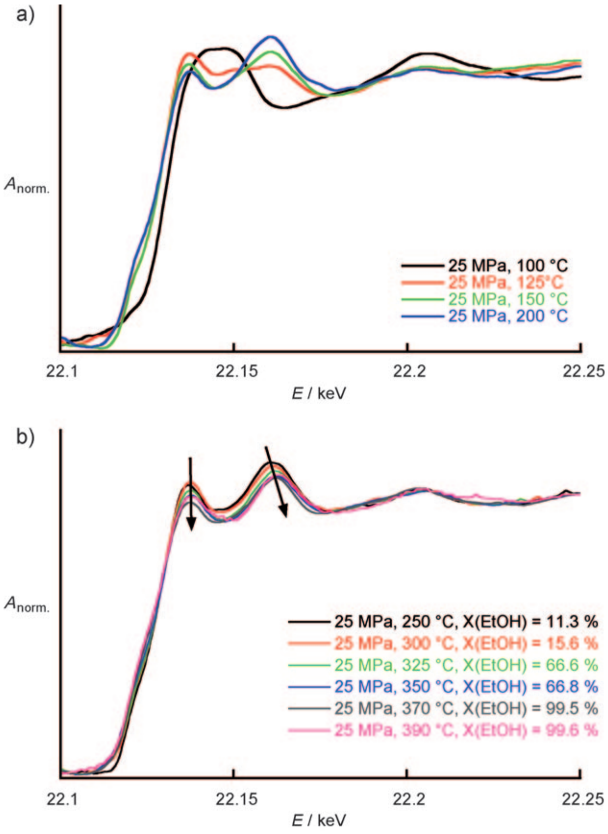

Figure 3. XANES spectra recorded during the hydrothermal gasification of a 5 wt% ethanol solution at 25 MPa. a) 100–200 °C, b) 250–390 °C. X = conversion.

Metallic ruthenium was formed, as indicated by the appearance of the characteristic double peak structure between 22.1 keV and 22.17 keV (Figure 3 a) and a shift of the absorption edge position to lower energies (see, for example, [17]). As the temperature was further increased, the position of the absorption edge did not change, thus suggesting that the ruthenium catalyst remained fully reduced. It was not possible to reoxidize the ruthenium with a flow of pure water at 350 °C. These results put the Ru redox couple mechanism postulated by Park et al.[14] for pure RuO_2 in supercritical water into question.

A systematic decrease of the intensities of the double-peak edge feature (22.13 and 22.17 keV) and a small shift of the second peak (22.17 keV) to higher energies was observed with increasing ethanol conversion (Figure 3 b, indicated by arrows). This shift to higher energies was complete at 350 °C after flushing with water, and coincided with full conversion. The double-peak edge feature was attributed by full multiple-scattering calculations to multiple scattering within the Ru atomic shell (22.13 keV) and to single-scattering events involving the absorber and the coordinating atoms (22.17 keV).[18] Thus, the systematic changes in these three features with increasing conversion suggest a change in the local coordination of the Ru atoms with increasing conversion.

These changes may reflect the presence of adsorbed ethanol, water, hydrogen and other carbon species (e.g., CO, CH_3CO, COH_x). At low conversion (in the low-temperature region), the catalyst surface may be covered mainly with acetaldehyde, as suggested by the mass spectrometry data. With increasing temperature, this acetaldehyde is increasingly removed or replaced by a different pool of carbonaceous species, therefore leading to a shift in the position of this peak to higher energies.

The systematic changes in the XANES spectra with increasing ethanol conversion are consistent with the suggested reaction mechanism. Ethanol may be adsorbed and dehydrogenated to acetaldehyde on the surface of the reduced ruthenium particles, followed by a cleavage of the C–C bond and the formation of carbonaceous surface species.

In conclusion, this study has shown that the decomposition of ethanol to CO_2, CH_4, and H_2 started around 250 °C and that it was complete above approximately 350 °C during the sub- and supercritical water gasification of ethanol over a carbon-supported ruthenium catalyst. XANES studies showed that the catalyst was already fully reduced at 250 °C and remained so even when reaching supercritical conditions. Our findings point to the hypothesis that the reforming of ethanol on a supported Ru catalyst in sub- and supercritical water proceeds along the same mechanistic lines as does the steam reforming of ethanol at low pressures.

Experimental Section

A dedicated setup was designed for operation up to 400 °C and 25 MPa (see Figure 3S in the Supporting Information). The key part of the setup is a sapphire capillary fixed-bed catalytic reactor (length: 200 mm, ID: 3.48 mm, OD: 5 mm).

The pseudocritical temperature for pure water at 25 MPa is 385 °C. For pressures higher than the critical pressure of 22.1 MPa, the pseudocritical temperature is the temperature at which the isobaric heat capacity exhibits a maximum, and it is used to define the transition from the sub- to the supercritical state. Operating conditions below this temperature are considered "subcritical" and the ones above this temperature "supercritical".

XANES spectra were recorded in transmission mode at the ruthenium K-edge (22.118 keV) at the SuperXAS beamline of the Swiss Light Source (SLS). Reference spectra of the oxidized and reduced catalyst samples were collected in a silica capillary under ambient conditions. Detailed experimental procedures are given in the Supporting Information.

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