Hydrogenation of Hydrocarbons through Partial Oxidation in Supercritical Water

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We propose a new process for the hydrotreatment of heavy oils in supercritical water (SCW). The discussion in this paper is composed of three parts: (1) hydrogenation through water-gas shift reaction in supercritical water, (2) selective formation of carbon monoxide by partial oxidation in supercritical water and through combinations of these two, and (3) hydrogenation of hydrocarbons through their partial oxidation in supercritical water. In the experiments involving hydrogenation of dibenzothiophene, carbazole, and naphthalene, faster hydrogenation rates could be obtained in a CO–SCW atmosphere than in a H_2–SCW atmosphere. Even in the case of a H_2–CO_2–SCW atmosphere, similarly faster reaction rates were obtained, which suggests that an intermediate species of the water-gas shift reaction is the actual reason for the high hydrogenation rates. Partial oxidation experiments were conducted for hexylbenzene and *n*-hexadecane. The selectivity of CO increased with increasing density of water, while CO_2 was the main product of the gas-phase reaction. Partial oxidation of dibenzothiophene (with a sulfur-treated $NiMO/Al_2O_3$ catalyst) and *n*-hexadecane (without catalysts) were also examined. Hydrodesulfurization of dibenzothiophene proceeds effectively in water. For *n*-hexadecane oxidation, the alkane/alkene ratio increased with increasing water density. The observed product distribution is probably due to the production of carbon monoxide, which is followed by the formation of active hydrogenating species via the water-gas shift reaction. This work demonstrates that hydrogenation reactions can be greatly accelerated in supercritical water through the use of either direct introduction of carbon monoxide or in situ formation of carbon monoxide through the partial oxidation of hydrocarbons.
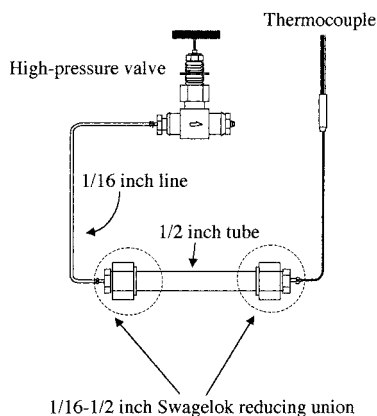
Introduction

Currently, the petroleum oil supply is becoming heavier, and its sulfur and nitrogen content is increasing, while demand for lighter liquid oils is increasing. Because of the dwindling amount of petroleum, heavier bitumens, tar sand, and oil shale will soon have to be used. Steam stimulation is often used to recover the highly viscous oil from reservoirs. As a result, heavy oil emulsions are formed at wellheads. Ng and Tsakiri[1] proposed a new single-stage process for upgrading heavy oil emulsions. The process used emulsion breaking, in situ hydrogen generation through the water-gas shift reaction ($CO + H_2O = CO_2 + H_2$), and sulfur removal. They studied desulfurization of benzothiophene and dibenzothiophene using CO and H_2O to produce hydrogen in a trickle bed catalyst reactor at 320–350 °C and atmospheric pressure. Although the proposed process has some advantages including lower energy consumption and lower cost, the following points should be considered. For the above process, there are four phases in the reaction atmosphere, namely, hydrogen gas, liquid water, liquid oil, and solid catalyst phases, and this causes high mass-transfer interphase resistance.

For the case of the catalytic hydrocracking processes, coke deposition, which deactivates the catalysts, is a serious problem. One idea to address these problems is to use supercritical conditions for the reaction media, as both hydrogen and oils are miscible with SCW.[2,3]

Some reseachers[1,4,5] reported effective hydrogenation via the water-gas shift reaction under supercritical conditions. Kumar et al.[4] and Hook and Akgerman[5] conducted experiments on the desulfurization of dibenzothiophene by feeding CO and steam to a catalyst bed ($CoO–MoO_3/Al_2O_3$) at 58–69 atm and 595–648 K. They reported that, by the in situ generation of hydrogen through the water-gas shift reaction, desulfurization that was 1 order of magnitude faster took place.[5] A similar hydrogenating effect through the water-gas shift reaction was reported for the extraction of coal with a CO–SCW mixture at 400 °C and 14–24.5 MPa,[6] 400 °C and 14 MPa,[7] and 405 °C and 21.9 MPa.[8] However, most of these studies were for the reaction in low-density (vapor) steam and not in a dense SCW phase. Under dense SCW conditions, a homogeneous reaction atmosphere for H_2–oils–SCW can be expected. Paspek and Klein[9] studied the upgrading of shale oil in supercritical water and reported that the yield of coke drastically decreased with increasing water density. Thus, coke deposition that leads to catalyst deactivation should be inhibited.

This was a starting point for our research. We have studied catalytic hydrogenating desulfurization by the in situ generation of hydrogen in dense supercritical water and confirmed that, even under these conditions, a higher reaction rate is obtained in CO–SCW than in H_2–SCW. Similar results were obtained for the denitrogenation of carbazole and the hydrogenation of naphthalene, although sufficient data were not supplied with previous papers. The next point of our research was fora CO source to be supplied. In general, the H_2

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Figure 1. Schematic diagram of a batch-type reactor.

production cost governs a considerable portion of hydrocarbon refining, including coal liquefaction, hydrocracking, and hydrogenating desulfurization. Unfortunately, the CO production cost is more or less the same as the H_2 cost. Recently, we found that CO can be selectively produced by the partial oxidation of hexylbenzne in supercritical water. This result suggested that we might be able to achieve hydrotreatment or hydrodesulfurization by using O_2 instead of costly H_2 or CO in supercritical water. Thus, in this study, the hydrogenation of hydrocarbons through partial oxidation in supercritical water has been studied in detail.

In this paper, we summarize our recent works concerning (1) hydrogenation through water-gas shift reaction in dense supercritical water, (2) selective formation of carbon monoxide by partial oxidation of hydrocarbons in supercritical water, (3) pyrolysis of *n*-alkane in SCW to compare product distribution of partial oxidation of *n*-alkanes in SCW, and (4) hydrogenation of hydrocarbons through their partial oxidation in supercritical water while supplying original results for (1) the hydrogenation of carbazole and naphthalene via the water-gas shift reaction and (2) the partial oxidation of *n*-hexadecane. By integrating these results, we discuss the possibility of the proposed process of hydrogenation of heavy oils through partial oxidation in supercritical water.

Experimental Section

1. Hydrogenation of Dibenzothiophene, Carbazole, and Naphthalene. Experiments were conducted with stainless steel (SUS 316) tube bomb reactors (6 cm³). A schematic of the reactor is shown in Figure 1. For the hydrogenation of dibenzothiophene (DBT), 0.3 g of a DBT−toluene solution (DBT content = 10 wt %) was loaded into a reactor. For the hydrogenation of carbazole or naphthalene, 0.05 g of carbazole or 0.03 g of naphthalene was introduced into a reactor. For all of the substances, the loaded amounts of water ranged from 0 to 3.0 g (water densities = 0−0.5 g/cm³); the loaded amounts of CO, H_2, or CO_2 ranged from 2.5 to 4.0 MPa; and the loaded amount of a sulfur-pretreated $NiMo/Al_2O_3$ catalyst was 0.15 or 0.3 g. The molar amount of gas loaded was 15−20 times larger than the amount of DBT, carbazole, or naphthalene.

The loaded reactor was submerged in a fluidized sand bath (Takabayashi Riko Co., model TK-3) whose temperature was controlled to be 400 ± 1 °C. The heating time required was around 3 min. After a reaction time

of 5−60 min, the reactor was taken out of the bath and rapidly cooled in a cold water bath.

The produced gas was collected in a syringe that was connected to the outlet of the gas sampler to measure its volume. The identification and quantification of this gas was conducted by GC-TCD. After the produced gas was sampled, the liquid products with water and the $NiMo/Al_2O_3$ catalyst were recovered by rinsing the reactor with acetone. The acetone-soluble compounds (including reactant and liquid products) and acetone-insoluble compounds (including the $NiMo/Al_2O_3$ catalyst and the material deposited on the catalyst) were divided by filtration with a membrane filter. An external standard was added to acetone solution for analytical purposes. Identification and quantification of the liquid products in the acetone solution was conducted by GC-MS and GC-FID. The amount of carbon in the acetone-insoluble fraction was evaluated using a TOC (total organic carbon) detector after the sample was dried at 60 °C for 1 day.

Conversion of reactant was evaluated from the amount of reactant recovered and the amount of reactant loaded. The product yield was evaluated from the carbon base.

2. Partial Oxidation of Hexylbenzene and *n*-Hexadecane and Pyrolysis of *n*-Hexadecane. The experimental and analytical methods used for the partial oxidation and pyrolysis experiments were basically the same as above. The loaded amount of hexylbenzene or *n*-hexadecane was 0.3 g. The amount of water ranged from 0 to 3.0 g (water densities = 0−0.5 g/cm³). Oxygen was loaded so that the O/C ratio was 0.3. In the case of the pyrolysis experiments, argon gas (Ar) was loaded after the air in the reactor was replaced. The reaction temperature was 400 °C, and the reaction time was 5 min for partial oxidation experiments and 1 h for pyrolysis. For the *n*-hexadecane experiments, tetrahydrofuran (THF) was used for recovery of the liquid products.

The gas composition and the ratio of *n*-alkane to 1-alkene were determined on the basis of mole percentage.

3. Catalytic Hydrodesulfurization of Dibenzothiophene through Partial Oxidation. Also for this series of experiments, the same experimental and analytical methods were employed. A DBT−hexylbenzene solution (DBT content = 10 wt %) was used as a sample. The DBT−hexylbenzene solution (0.3 g) and sulfurized $NiMo/Al_2O_3$ catalyst (0.3 g) were loaded with 2.5 g of water (water density = 0.42 g/cm³). Then, oxygen gas was introduced into the reactor (2.7 MPa). The reaction temperature was 400 °C, and the reaction times were from 10 to 60 min.

Results and Discussion

1. Hydrogenation of Dibenzothiophene, Carbazole, and Naphthalene. Figure 2 shows the results for DBT hydrogenation through the water-gas shift reaction obtained at a water density of 0.42 g/cm³. In both H_2−SCW and CO−SCW, the main products were biphenyl (BP) and cyclohexylbenzene (CHB), which are hydrogenated products of DBT. As shown in this figure, the rate of hydrogenation of DBT in CO−SCW was higher than that in H_2−SCW. We also conducted the experiments involving the hydrogenation of DBT in CO_2−H_2−SCW at a water density of 0.42 g/cm³. As shown in Figure 2, through the addition of CO_2 to H_2−
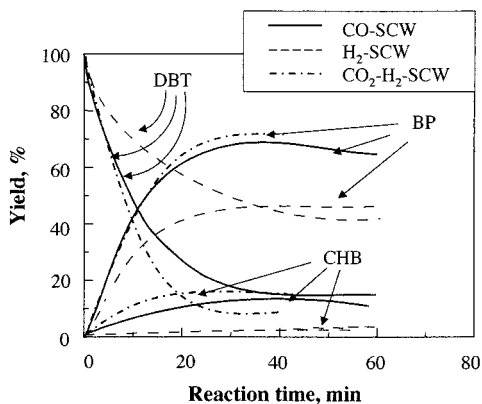
Figure 2. Hydrodesulfurization of DBT in H_2-SCW, CO-SCW, and CO_2-H_2-SCW (T = 400 °C, water density = 0.42 g/cm^3).[11]

(A) Naphthalene

(B) Tetralin
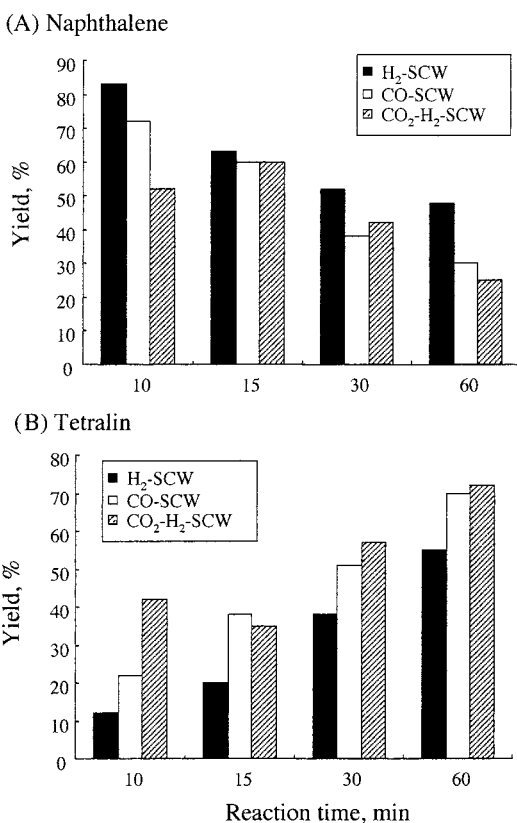
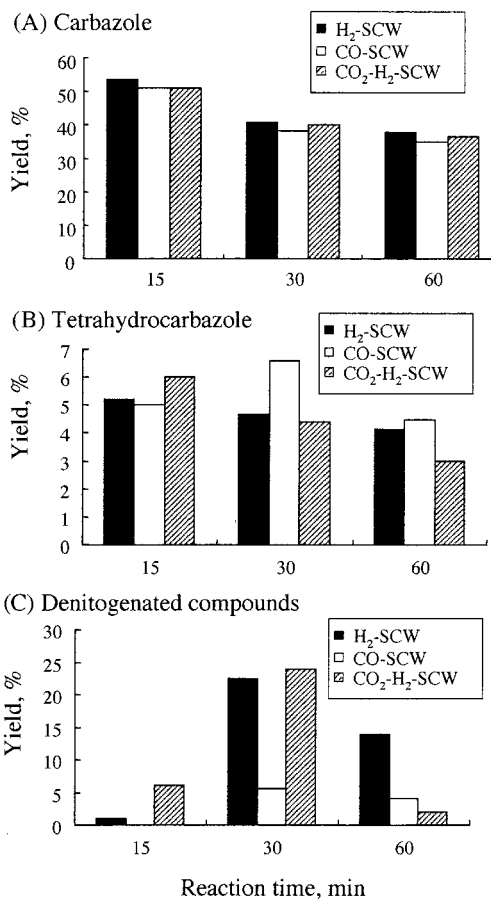**Figure 3.** Hydrogenation of naphthalene in H_2-SCW, CO-SCW, and CO_2-H_2-SCW (T = 400 °C, water density = 0.3 g/cm^3).[12,13]

SCW, the rate of hydrogenation of DBT was enhanced.[10,11]

Figure 3 shows the results for the hydrogenation of naphthalene (NP) at 400 °C and a water density of 0.3 g/cm^3. Tetralin (NP) and Decalin (DL) were the main products. As in the DBT experiments, the rate of naphthalene hydrogenation in CO-SCW and in CO_2-H_2-SCW was higher than that in H_2-SCW.[12,13] Similar results were obtained for the denitrogenation of carbazole, namely, a faster reaction in CO-SCW and CO_2-H_2-SCW than in H_2-SCW at a lower water density, as shown in Figure 4. However, for this system, the suppression of the hydrogenation rate with increasing water density was observed, which suggests the need for a new catalyst suitable for the dense SCW hydrogenation.

Under the above conditions, CO, H_2, and CO_2 are miscible with SCW, and thus, the differences observed

(A) Carbazole

(B) Tetrahydrocarbazole

(C) Denitogenated compounds

Figure 4. Hydrodenitrogenation of carbazole in H_2-SCW, CO-SCW, and CO_2-H_2-SCW (T = 400 °C, water density = 0.05 g/cm^3).

in CO-SCW, H_2-SCW, and CO_2-H_2-SCW are not due to the phase separation.

From the results for the hydrogenation of DBT, carbazole, and naphthalene, we suppose that an intermediate species of the water-gas shift reaction in supercritical water is an active hydrogenating species. Because of the existence of large amounts of water in the system, the equilibrium of the water-gas shift reaction is on the H_2 + CO_2 side. The high reaction rate observed in CO_2-H_2-SCW suggests that the active hydrogenating species might be a species that is energetically similar to CO_2 + H_2. One possible species is HCOOH, as suggested by Melius et al.[14] Further study is required for clarification of the active hydrogenating species and reaction mechanism.

2. Partial Oxidation of Hexylbenzene and *n*-Hexadecane. CO and CO_2 gas formation during the partial oxidation of hexylbenzene ($C_{12}H_{18}$) and *n*-hexadecane ($C_{16}H_{34}$) in SCW was examined. The O/C ratio was set at 0.3, which means that the amount of O_2 supplied was 0.109 and 0.107, respectively, of the amount required for complete combustion. The results are shown in Figures 5 and 6. For a water density of 0 g/cm^3, the experiment was conducted in an oxygen atmosphere. Even under partial oxidation conditions, the main product was CO_2. For both hexylbenzene and *n*-hexadecane (*n*-C_{16}) oxidation, the CO selectivity increased with increasing water density. In a higher-density region, the H_2 selectivity became higher. This suggests occurrence of the water-gas shift reaction (CO + H_2O = CO_2 + H_2). Assuming that the formation of hydrogen and CO_2 at high water densities was a result
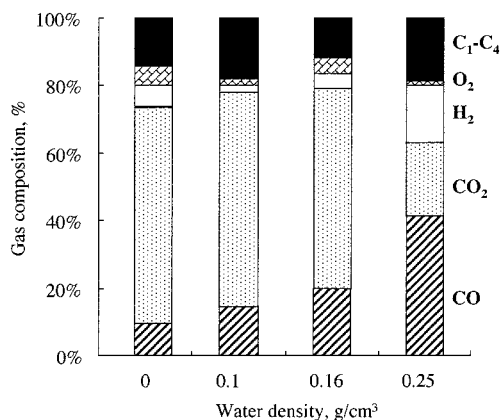
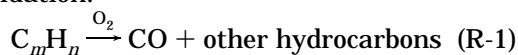**Figure 5.** Gas composition for the partial oxidation of hexylbenzene (T = 400 °C, reaction time = 5 min).[11,15]
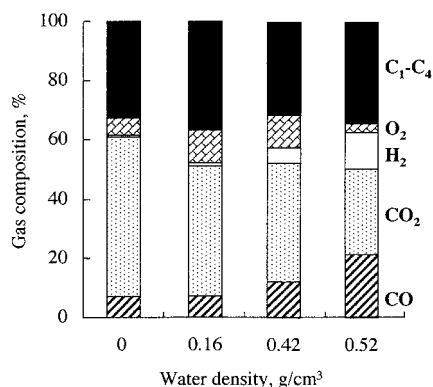
Figure 6. Gas composition for the partial oxidation of n-hexadecane (T = 400 °C, reaction time = 5 min).[12]
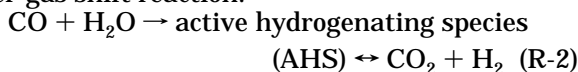
of the water-gas shift reaction, the selectivity of CO would be extremely high.[11,12,15] If CO_2 production were only from the water-gas shift reaction, CO_2 selectivity should be the same as H_2. However, the H_2 selectivity is lower than that of CO_2. One possible reason for this is the contribution of the direct formation of CO_2, and another is the consumption of H_2 by hydrogenation of the hydrocarbons. This issue will be discussed later in this paper.

3. Hydrogenation of n-Hexadecane and Dibenzothiophene through Partial Oxidation. The above results suggest the possibility of hydrogenation of hydrocarbons through partial oxidation followed by the water-gas shift reaction.
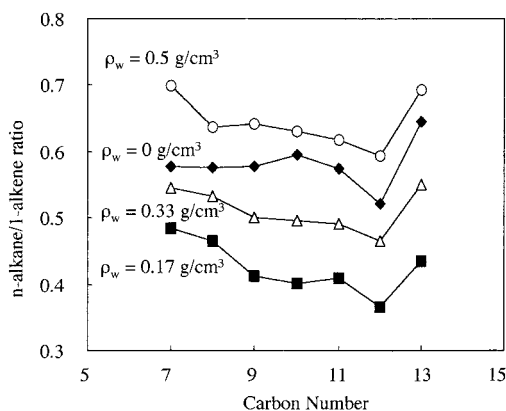
Partial oxidation:

$$C_mH_n \xrightarrow{O_2} CO + \text{other hydrocarbons} \quad \text{(R-1)}$$

Water-gas shift reaction:
$$CO + H_2O \rightarrow \text{active hydrogenating species}$$
$$\text{(AHS)} \leftrightarrow CO_2 + H_2 \quad \text{(R-2)}$$

Pyrolysis: $C_mH_n \rightarrow n\text{-alkane} + 1\text{-alkene}$ (R-3)

Hydrogenation: $1\text{-alkene} + H_2$ or $\text{AHS} \rightarrow n\text{-alkane}$
(R-4)

Prior to a discussion of hydrogenation through partial oxidation, note that a pyrolysis experiment for n-C_{16} was performed to determine the product distribution. At 400 °C and 1 h, the products of n-C_{16} pyrolysis were n-alkanes (carbon number = 1−15) and 1-alkenes (carbon number = 2−15), even in dense SCW.[16,17]

Figure 7. n-Alkane/1-alkene ratio for n-C_{16} pyrolysis in SCW (T = 400 °C, reaction time = 60 min).[17]
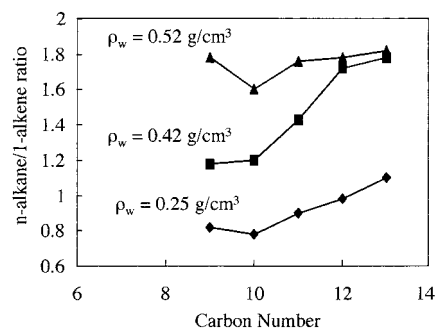
**Figure 8.** n-Alkane/1-alkene ratio for the partial oxidation of n-C_{16} (T = 400 °C, Reaction time = 5 min).

In SCW, the n-alkane/1-alkene ratio varied with water density, as shown in Figure 7.[17] Figure 7 shows the results for 400 °C and 0.22 M (0.3 g of n-C_{16} loaded in the reactor). The n-alkane/1-alkene ratio decreased at a water density of 0.17 g/cm^3 and then increased up to a water density of 0.5 g/cm^3. The detailed mechanism has not yet been elucidated.

We analyzed the product distribution from the partial oxidation of n-C_{16}, focusing on the hydrogenation of 1-alkene. Figure 8 shows the n-alkane/1-alkene ratio obtained from the partial oxidation of n-C_{16}. The n-alkane/1-alkene ratio increased with increasing water density. The n-alkane/1-alkene ratio obtained was higher than that found for pyrolysis in SCW, which is shown in Figure 7. This result suggests that the hydrogenation of 1-alkene to n-alkane took place under the conditions used.

We examined the hydrodesulfurization of DBT with a $NiMo/Al_2O_3$ catalyst through partial oxidation in dense SCW. The product distribution from the partial oxidation in DBT−hexylbenzene solution is shown in Figure 9. As shown in this figure, the yield of dibenzothiophene decreased and the yield of biphenyl and cyclohexylbenzene increased with increasing reaction time, although the reaction rate was a little lower than those observed in the H_2, CO, or $CO_2 + H_2$ experiments, as shown in Figures 2 and 9. The reason for the lower reaction rate is probably the insufficient production of CO or H_2 under the conditions used. Another possible reason is damage to the catalyst, as suggested by Aki et al.[18] Hydrogen sulfide was detected, while sulfur oxide was not. This result clearly shows that the hydrogenation of DBT occurred even through the partial oxidation of hexylbenzene in SCW.[11]

The above results for hydrogenation through partial oxidation show that the partial oxidation of hydrocar-
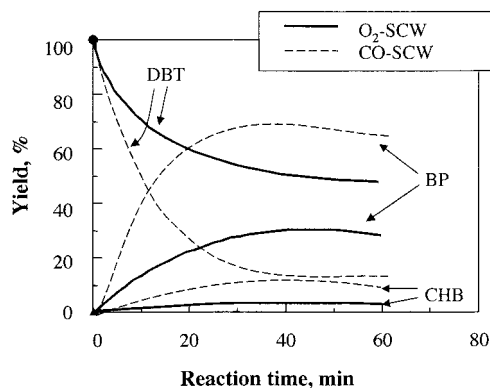
Figure 9. Hydrogenation of DBT through partial oxidation in O_2-SCW and $CO-$SCW ($T = 400$ °C, water density $= 0.42$ g/cm^3).[11]

bons is probably due to the formation of CO followed by the water-gas shift reaction to form an active hydrogenating species. The generation of an active hydrogenating species through this method can have a wide range of applications, especially in the hydrotreatment of heavy oils.

Conclusion

In this paper, we reported on a new hydrogenating process for the hydrotreatment of heavy oils in supercritical water. Hydrogenation occurs faster in $CO-$SCW and H_2-CO_2-SCW than in H_2-SCW. In the experiments involving partial oxidation, the CO selectivity increased with water density. Through this group of studies, this work demonstrates that hydrogenation reactions can be greatly accelerated in supercritical water through the use of either direct introduction of carbon monoxide or in situ formation of carbon monoxide through partial oxidation. A wide range of hydrogenation applications is possible with the findings presented in this work.

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