Subcritical water regeneration of catalysts poisoned by sulfur

Mitsumasa Osada,[a] Osamu Sato,[a] Kunio Arai,[b] and Masayuki Shirai[a*]
[a)] Research Center for Compact Chemical Process, National Institute of Advanced Industrial Science and Technology, 4-2-1, Nigatake, Miyagino, Sendai, 983-8551, Japan
[b)] Graduate School of Environmental Studies, Tohoku University, 6-6-07 Aza-Aoba, Aramaki, Aoba, Sendai, 980-8579, Japan
E-mail: m.shirai@aist.go.jp
Fax: +81-22-237-5224

We studied the regeneration of supported ruthenium catalysts by water at conditions from 250 to 400 °C of temperature and 25 MPa of pressure, namely sub- and supercritical water. We found that deactivated catalysts poisoned by sulfur species could be regenerated by treatment with subcritical water.

INTRODUCTION

Biomass can be used as renewable energy source. Gasification processes of biomass are usually operated at high temperatures from 800 to 1000 °C. If gasification could be proceeded at lower temperatures (around 400 °C), the waste heat from other chemical processes operating at higher temperatures could be used for biomass conversion. Supercritical water gasification with metal catalyst is a candidate for utilization of wet biomass gasification at low temperatures. [1-3] For the gasification process using supercritical water, the development of highly active and tolerant catalysts is very important. Waste biomass contains as much as 0.5 wt% sulfur species, and then deactivation catalysts by sulfur in the waste biomass would be occurred. [4] A simple technique which regenerates catalysts poisoned by sulfur species is required. In this paper, we report the regeneration of supported ruthenium catalysts by water at conditions from 250 to 400 °C of temperature and 25 MPa of pressure, namely sub- and supercritical water.

I- EXPERIMENTAL

Preparation procedure of catalysts is shown in Figure 1. A titania supported ruthenium catalyst (Ru/TiO_2; 2wt% ruthenium on titania) was supplied from Osaka Gas Company, Ltd. The Ru/TiO_2 catalyst was soaked in an aqueous sulfuric acid solution, following drying through evaporation. This catalyst is designated as S-Ru/TiO_2. The molar ratio of sulfur to ruthenium was 1.

Treatment of catalysts was done by an apparatus, which was composed of water loading unit, water preheating unit, packed bed for catalysts, heat exchanger, pressure control unit and solution recovery unit (Figure 2). After1.0 g of catalyst was placed in a packed bed, stainless steel filters were placed in the both tube ends. Distilled water was introduced to the packed bed at a flow rate of 3 ml/min by two high performance liquid chromatography pumps, pressurized in the system up to 25 MPa by a back-pressure regulator and heated by an electric furnace. The packed bed was put into a air bath at 200 °C, temperatures of both the air bath and the extraction solvent were then increased up to 250 ~ 400 °C. At the outlet of the packed bed, an aqueous solution was rapidly quenched by a cooling jacket and subsequently collected continuously into sampling bottles. Amounts of sulfur contained in the aqueous solution were analyzed by ICP. After cooling, catalysts were recovered by opening packed bed, and dried up through evaporation. These catalysts were used for lignin gasification. The catalysts before and after treatment by subcritical and supercritical water were analyzed by XPS and EDX.

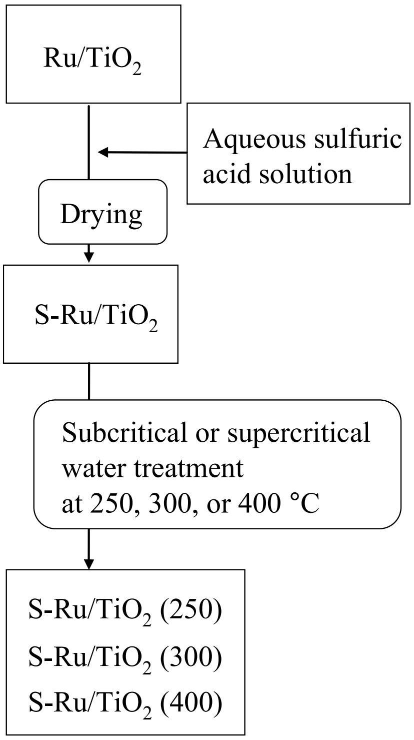

Figure 1. Preparation of catalysts

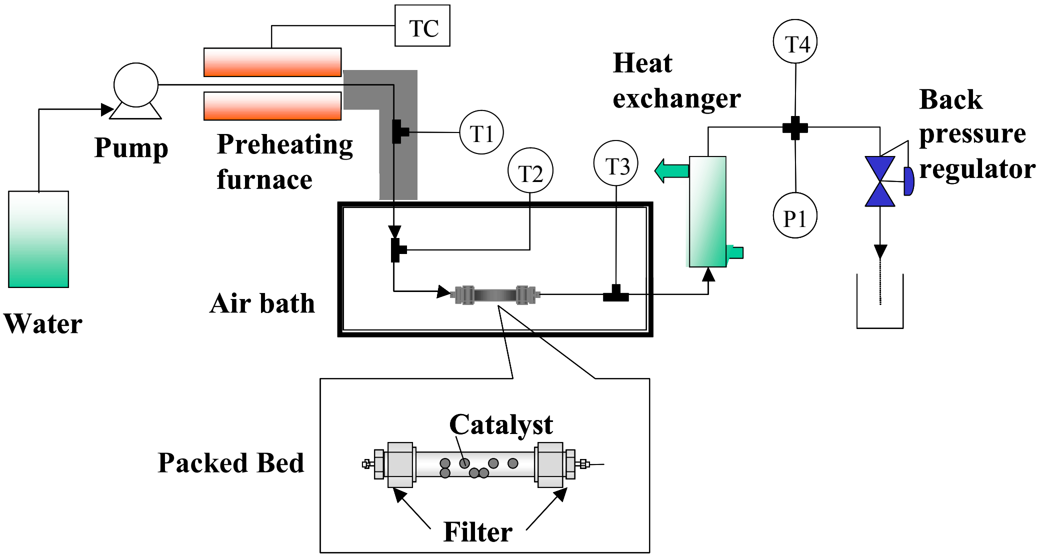

Figure 2. Apparatus for catalyst treatment with subcritical and supercritical water

Organosolv-lignin (lignin) was used and its molecular formula was $C_{42.39}H_{45.46}O_{12.15}$ as determined by elemental analysis. Gasification was conducted with a 6 cm^3 of stainless steel 316 tube bomb reactor with a thermocouple that was inserted internally into the reactor and one port connected to a high pressure valve for purging and gas analysis. 0.375 of catalyst, 0.1 g of lignin, and 3.0 g of water were introduced into the reactor. This amount of water corresponds to 0.5 $g \cdot cm^{-3}$ of water density and gives a partial pressure of water at 400 ^{o}C up to 37 MPa. Air inside the reactor was purged with argon gas. The reactor was submerged into a sand bath. For a typical experiment, the reaction temperature of reactor reached 390 ^{o}C within 2 minutes, and another 2 minutes being required for the reactor to reach 400 ^{o}C. After a given reaction time, the reactor was taken out of the sand bath and rapidly quenched in a water bath to cool to room temperature. Gas products were analyzed with a GC-TCD method. Products recovered were separated into water-soluble and water-insoluble fractions. The water-insoluble fraction was extracted with THF and separated into THF-soluble and THF-insoluble fractions. The THF-insoluble fraction was defined as solid product. The water-soluble and THF-soluble products were analyzed with GC-FID and GC-MS methods. Amounts of organic and inorganic carbon in the aqueous solution were evaluated by a total amount of carbon. Ultimate analysis of the solid product was performed by use of a Carbon-Hydrogen-Nitrogen-Sulfur analyzer. Product yield of carbon basis and the gas composition were defined as below, respectively.

$$\text{Product yield of carbon [Cmol\%]} = \frac{\text{mol of carbon atoms in product}}{\text{mol of carbon atom in lignin loaded}} \times 100 \qquad (1).$$

$$\text{Gas composition [\%]} = \frac{\text{mol of gas product}}{\text{sum of mol gas product}} \times 100 \qquad (2).$$

□- RESULTS AND DISCUSSION

Table 1 shows treatment conditions of S-Ru/TiO_2 catalysts in subcritical and supercritical water and amounts of sulfur remained on catalyst surface detected by EDX and XPS analysis. Amounts of sulfur on the catalyst surface treated at 250 and 300 °C (subcritical water) were lower than that treated at 400 °C (supercritical water). Figure 3 shows the amount of sulfur removed by water treatments. The amount removed by subcritical water at 300 °C was higher than that by supercritical water at 400 °C.

The gasification activities of the catalysts prepared were investigated. Table 2 shows the product yields and the gas composition obtained by the gasification of lignin at 400 °C, 0.5 g/cm^3 of water density after 180 min. Lignin was completely gasified to methane (CH_4), carbon dioxide (CO_2) and hydrogen (H_2) in the presence of Ru/TiO_2. [4]

Table 1. Amounts of sulfur on catalyst surface before and after subcritical and supercritical water treatment.

Catalyst	Treatment condition			XPS [atom%]	
	Temperature [°C]	Water density [g/cm^3]	Time [hour]	-SO_4	-SO_3
S-Ru/TiO_2	-	-	-	4.4	3.0
S-Ru/TiO_2 (400)	400	0.83	3	3.4	0.7
S-Ru/TiO_2 (300)	300	0.75	3	1.5	0.2
S-Ru/TiO_2 (250)	250	0.17	3	2.3	0.2

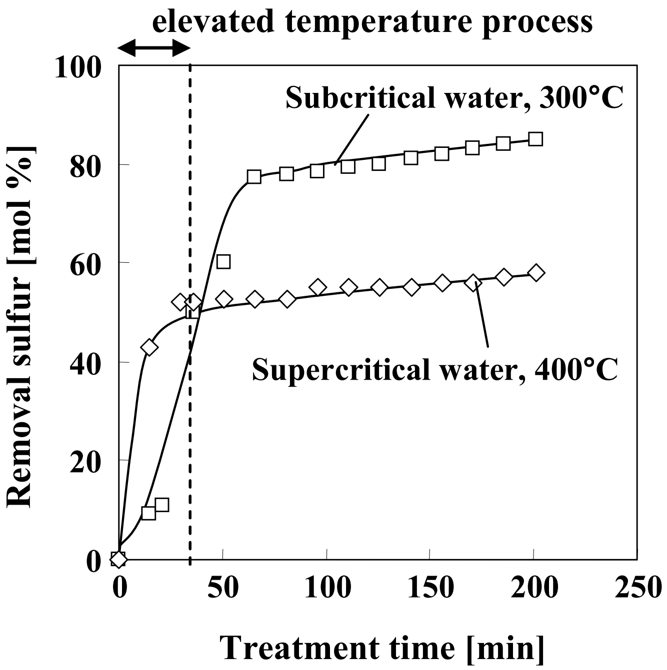

Figure 3. Removal sulfur by treatment with subcritical and supercritical water

For S-Ru/TiO_2, the gas yield lowered and the composition of CH_4 decreased, and those of CO_2 and H_2 increased in comparison with Ru/TiO_2. Also, the amount of THF-insoluble products became larger. Lowering of the gas yield and the formation of THF-insoluble would be regarded as decreasing of the number of surface ruthenium by the sulfur adsorption. The decrease of CH_4 yield in the gasification over S-Ru/TiO_2 would be caused by decrease of ruthenium ensembles by desorption of sulfur atoms on ruthenium metal surface. Ruthenium ensembles are indispensable to cleavage of the carbon-carbon bond of lignin and to proceed methanation reactions.

Table 2. Product yield and gas composition of lignin gasification in supercritical water at 400 °C, a water density of 0.5 g/cm^3, and a reaction time of 180 min.

catalyst	Product yield [Cmol%]				Gas composition [mol%]			
	Gas	Water-soluble	THF-soluble	THF-insoluble	H_2	CH_4	CO_2	C2~C4
Ru/TiO_2	97.7	0.7	1.6	0.0	4.5	49.0	46.5	0.0
S-Ru/TiO_2	21.0	18.3	57.6	3.1	14.5	24.5	57.7	3.3
S-Ru/TiO_2 (400)	26.1	8.1	68.2	2.1	17.2	21.6	52.4	8.8
S-Ru/TiO_2 (300)	47.2	1.7	51.1	0.0	6.6	45.4	44.4	3.6
S-Ru/TiO_2 (250)	47.3	2.6	50.1	0.0	7.4	46.7	42.5	3.4

By pretreatment of S-Ru/TiO_2 catalysts with subcritical water, the gas yield was improved, and THF-insoluble product was not formed. CH_4 selectivity of the catalysts pretreated by subcritical water also increased. On the other hand, S-Ru/TiO_2 (400), which was obtained by supercritical water treatment for S-Ru/TiO_2, the gas yield was slightly improved, and the THF-insoluble product was formed. As shown in Table 1, the amount of sulfur removed by subcritical water treatment was higher than by supercritical water treatment, indicating that a number of sulfur species on the ruthenium surface was removed by the subcritical water treatment and the gasification activities were recovered.

CONCLUSION

Sulfur species on ruthenium metal particles could be removed by the treatment of subcritical water. The catalyst treated in subcritical water showed higher activities for lignin gasification than those in supercritical water.

REFERENCES:

[1] MATSUMURA, Y., MINOWA, T., POTIC, B., KERSTE, S. R. A., PRINS, W., VAN SWAAIJ, W. P. M., VAN DE BELD, B., ELLIOTT, D. C., NEUENSCHWANED, G. G., KRUSE, A., ANTAL, M. J., Biomass and Bioenergy, Vol.29, **2005**, p. 225.

[2] OSADA, M., SATO, T., WATANABE, M., SHIRAI, M., ARAI, K., Combustion Science and Technology, **2005,** in press.

[3] OSADA, M., SATO, T., WATANABE, M., ADSCHIRI, T., ARAI, K., Energy & Fuels, Vol.18, **2004**, p. 327.
[4] OSADA, M., SUZUKI, A., WATANABE, M., SATO, T., SHIRAI, M., ARAI, K., Proceeding of Asian Pacific Confederation of Chemical Engineering, **2004**, 3P-03-020.
[5] DAVDA, R. R., SHABAKER, J. W., HUBER, G. W., CORTRIGHT, R. D., DUMESIC, J. A., Applied catalysis B: Environmental, Vol.56, **2005**, p. 171.