# Fuel Gas Production from Waste Paper over Supported Metal Catalysts in High-Temperature Liquid Water

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## Introduction

The utilization of biomass and organic waste is very important to realize a sustainable society. Also, environmentally benign processes are desirable. In this paper, we report a fuel gas production technique from waste paper, which cannot be recycled as paper, over supported metal catalysts in high-temperature water.

### Materials and Methods

Fuel gas production from paper (Nippon Paper Industries Co., Ltd.) in hightemperature water was carried out with a batch system.[1,2] Cellulose powder (Advantec Co., Ltd., Advantec D, 40-100 mesh) and microcrystalline cellulose (Alfa Aesar) were also used as a reference reactant. Gaseous products were analyzed by a GC-TCD. Liquid and solid products in the tube were recovered with water and filtered to separate water-insoluble fraction from water-soluble fraction. Amounts of organic carbon in the water-soluble fraction were evaluated using a total organic carbon analyzer.

### **Results and Discussion**

We conducted a screening of catalysts for the gasification of the cellulose powder in water at 573 K for 30 min among Ru/C, Ru/Al<sub>2</sub>O<sub>3</sub>, Rh/C, Rh/Al<sub>2</sub>O<sub>3</sub>, Rh/C, Rh/Al<sub>2</sub>O<sub>3</sub>, Rh/C, Rh/Al<sub>2</sub>O<sub>3</sub>, Pt/C, Pt/Al<sub>2</sub>O<sub>3</sub>, Pd/C, Pd/Al<sub>2</sub>O<sub>3</sub>, Ir/C, Ir/Al<sub>2</sub>O<sub>3</sub>, Ni/C, Ni/Al<sub>2</sub>O<sub>3</sub>, Co/C, Co/Al<sub>2</sub>O<sub>3</sub>, Fe/C, and Fe/Al<sub>2</sub>O<sub>3</sub>. From the result of the screening of catalysts supported ruthenium catalysts (Ru/C and Ru/Al<sub>2</sub>O<sub>3</sub>) were very effective for the gasification of cellulose in high-temperature water.

Table 1 shows the product yields and gas composition of paper and cellulose gasification at 673 and 573 K for 10 min in water over the Ru/C catalyst. The partial pressure of water at 673 K and 0.5 g cm<sup>-3</sup> of water density was 37.1 MPa in a supercritical phase. In the case of 573 K, liquid water with saturated vapor (8.5 MPa) exists in the reactor. The waste paper as well as the cellulose powder was gasified almost completely for 10 min at more than 573 K (Table 1) over the Ru/C catalyst in water.

The waste paper and cellulose powder were also gasified at 523 K in water over the Ru/C catalyst (Figure 1). The waste paper and cellulose powder were gasified completely at 523 K for 3 and 5 h, respectively, indicating that the gasification rate of paper was larger than that of cellulose. We measured XRD patterns of cellulose powder, waste paper and microcrystalline cellulose. Their XRD patterns exhibited a strong peak at  $2\theta = 22.6$  degree due to the cellulose crystalline plane (002). The intensity of the XRD peak for the cellulose powder was larger than those for the paper and microcrystalline cellulose. We estimated the cellulose crystalline sizes using the Scherrer equation. The order of the cellulose crystalline size waste paper > microcrystalline cellulose. On the other hand, the order of gasification yield at 523 K for 30 min wad microcrystalline cellulose > waste paper > waste paper > microcrystalline cellulose.

cellulose powder, indicating that samples having smaller cellulose crystallinity sizes can be gasified easily in high-temperature liquid water.

Table 1. Product yield and gas composition of paper and cellulose gasification at 673 and 573  $\mathrm{K}^{\mathrm{a}}$ 

reactant	reaction	gas yield	gas composition / %				water	water
	temperature	/ C%	$H_2$	$CH_4$	$CO_2$	$C_2 \sim C_4$	soluble	insoluble
	/ <b>K</b>					gases	/ C%	/ C%
cellulose	673	98.4	4.4	51.5	43.9	0.2	0.1	0.0
paper		99.8	5.6	46.9	47.4	0.1	0.0	0.0
cellulose	573	94.2	6.3	40.7	50.9	2.1	1.2	0.0
paper		99.5	4.4	48.1	46.6	0.8	0.0	0.5

<sup>a</sup>Reaction conditions; cellulose or paper 0.10 g, Ru/C catalyst 0.15 g, water 3 g, reaction time 10 min.



**Figure 1.** Yields based on carbon atom for gasification of waste paper (a) and cellulose powder (b) in water at 523 K. The initial amount of paper or cellulose was 0.10 g, and 0.15 g of the Ru/C catalyst was used for the gasification. Yield of gas ( $\bigcirc$ ), water-soluble product ( $\blacktriangle$ ), and water-insoluble product ( $\blacksquare$ ).

#### Significance

We succeeded to demonstrate that waste paper could be used for fuel gas production over supported metal catalysts in high-temperature liquid water.

#### References

- 1. Yamaguchi, A., Hiyoshi, N., Sato, O., Osada, M., and Shirai, M., *Catal. Lett.*, 122, 188 (2008).
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