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Hydrogen production from woody biomass over supported metal catalysts in supercritical water

Aritomo Yamaguchi [a], Norihito Hiyoshi [a], Osamu Sato [a], Kyoko K. Bando [a], Mitsumasa Osada [b], Masayuki Shirai [a,*]

[a] Research Center for Compact Chemical Process, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyaginoku, Sendai 983-8551, Japan
[b] Department of Chemical Engineering, Ichinoseki National College of Technology, Takanashi, Hagisho, Ichinoseki, Iwate 021-8511, Japan

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ABSTRACT

Hydrogen was produced from woody biomass, lignin, in supercritical water over supported metal catalysts using a batch reactor. The order of metal species for the lignin gasification was following: ruthenium > rhodium > platinum > palladium > nickel. The order of hydrogen production was following: palladium > ruthenium > platinum > rhodium > nickel. Titania and activated carbon were stable supports of noble metal catalysts for lignin gasification in supercritical water. Hydrogen percentage of gaseous products from lignin increased with shorter reaction time and higher reaction temperature.

1. Introduction

Conversion of biomass to fuels has attracted much attention for building of a sustainable society because combustion of fossil fuel causes global warming by the green house effect of carbon dioxide [1]. Lignin is one of the major fractions of woody biomass, which is a polymer of aromatic compounds, such as coniferyl alcohol, sinapyl alcohol, and coumaryl alcohol, and constitutes up to 30% of the weight and 40% of the energy of biomass [2]. Gasification to hydrogen or methane from lignin is expected for its efficient use as a high quality energy source. Steam reforming is a technology for lignin gasification; however, high temperature (1073–1273 K) is required for the steam reforming [3]. Low temperature methods are more desirable because waste heat from industrial processes, such as ironmaking or cement production, can be utilized. Supercritical water gasification ($T_c = 647.3$ K, $P_c = 22.1$ MPa) is a promising technique to reduce the lignin gasification temperature. We have previously reported that supported ruthenium, rhodium, platinum, palladium, and nickel catalysts are active for the lignin gasification in supercritical water at 673 K [4]. We have also reported that lignin was converted to alkylphenol and formaldehyde via hydrolysis in supercritical water and then alkylphenol and formaldehyde decomposed to gases over metal catalysts [4–6]. The metal surface sites of the catalysts are active for the decomposition of alkylphenol and formaldehyde in supercritical water [7]. In this report, we describe the lignin gasification in supercritical water in view of hydrogen production.

Three main reactions of gaseous products formation such as the water gas reaction of carbon (Eq. (1)), the water–gas shift reaction (Eq. (2)), and the methanation reaction (Eq. (3)), proceed during the lignin gasification in supercritical water as follows:

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \qquad \Delta H_{298} = 131\ \mathrm{kJ\,mol^{-1}}, \tag{1}$$

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \qquad \Delta H_{298} = -41\ \mathrm{kJ\,mol^{-1}}, \tag{2}$$

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g) \qquad \Delta H_{298} = -206\ \mathrm{kJ\,mol^{-1}}. \tag{3}$$

Equilibrium gas composition of lignin gasification under subcritical or supercritical water at 30 MPa was calculated by CHEMKIN III (Fig. 1) [8]. In the calculation, molecular formula of lignin was $C_{43}H_{45}O_{12}$ and initial ratio of lignin and water was 1/10 (w/w). The equilibrium composition of gaseous products from lignin gasification depends on reaction temperature. Methane and carbon dioxide are the main products below 800 K. Hydrogen increases drastically above 600 K and methane decreases with increasing temperature. Hydrogen and carbon dioxide are the main products above 850 K. In this paper, we report the catalytic

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* Corresponding author. Tel.: +81 22 237 5219; fax: +81 22 237 5224.
E-mail address: m.shirai@aist.go.jp (M. Shirai).

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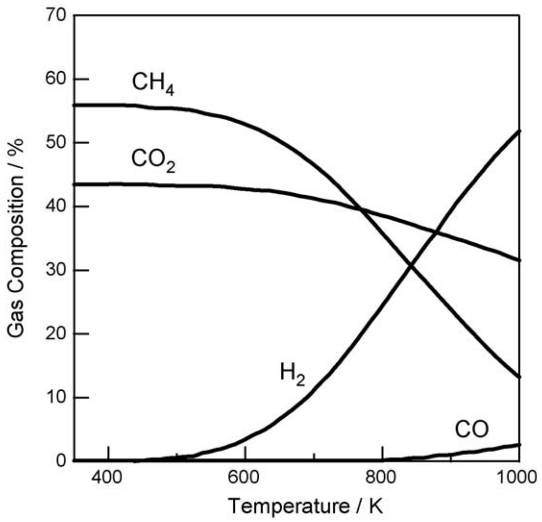

Fig. 1. Equilibrium gas composition of lignin gasification under subcritical or supercritical water at 30 MPa calculated by CHEMKIN III. Molecular formula of lignin is $C_{43}H_{45}O_{12}$ and the weight ratio of initial lignin and water is 1:10.

gasification of lignin in supercritical water at 673 and 723 K. The equilibrium composition of gaseous products depends on the initial ratio of lignin and water. From the calculation results, the selectivity of hydrogen increased with an increase of initial water ratio in reactant and partial pressure of water.

2. Experimental

Lignin (organosolv-lignin powder, Aldrich, molecular weight 1000–1500, Fig. 2) was purchased from Aldrich and used without further purification [4]. Supported ruthenium, rhodium, platinum, and palladium catalysts were purchased from Wako Pure Chemical Industries. Supported nickel catalysts were prepared by an impregnation method using charcoal powder (Wako Pure Chemical Industries) and an aqueous solution of nickel (II) nitrate (Wako Pure Chemical Industries). The nickel catalyst was dried at 373 K and treated under hydrogen flow at 673 K to reduce nickel species. Metal loading of all the catalyst used was 5 wt%. Gasification of lignin was carried out in a SUS 316 tube (inner volume 6.0 cm^3) [9,10]. Catalyst (0.15 g), lignin (0.10 g), and water (3.0 g for the reaction at 673 K or 1.4 g for the reaction at 723 K) were loaded in the reactor. The reactor was purged with argon gas and then submerged into a molten-salt bath (KNO_3–$NaNO_3$) at the reaction temperature for a given reaction time. The partial pressure of water at 673 (or 723) K and 0.50 (or 0.23) g cm^{-3} of water density was 37.1 MPa in the supercritical phase in the both cases [11]. After the reaction, the tube was submerged into a water bath for cooling down to ambient temperature. Gaseous products were analyzed by a gas chromatography (Shimadzu, GC-8A) using a Shincarbon ST column and a thermal conductivity detector. Liquid and solid products in the tube were recovered with water and filtered to separate water-insoluble fraction from the water-soluble fraction. The amount of organic carbon in the water-soluble fraction was evaluated using a total organic carbon analyzer (Shimadzu, TOC-V_{CSN}). The water-insoluble fraction was washed with tetrahydrofuran (THF) and filtered to separate a THF-insoluble solid fraction from a THF-soluble fraction. The amount of THF-insoluble product (char) was estimated by subtracting the weight of the catalyst loaded from the amount of THF-insoluble solid fraction. A product yield and gas composition are defined as given below

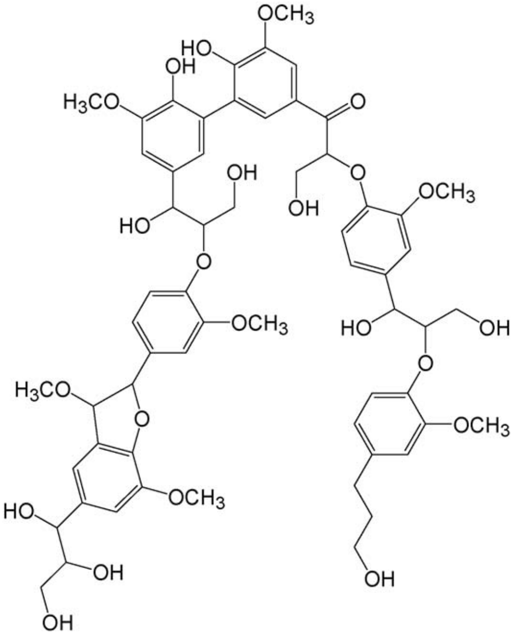

Fig. 2. Model structure of organosolve lignin.

$$\text{Product yield based on carbon (C\%)} = \frac{\text{(mol of carbon atom in product)}}{\text{(mol of carbon atom in lignin loaded)}} \times 100, \tag{4}$$

$$\text{Gas composition (\%)} = \frac{\text{(mol of gas product)}}{\text{(sum of mol of gas product)}} \times 100, \tag{5}$$

$$\text{Product yield based on hydrogen (H\%)} = \frac{\text{(mol of hydrogen atom in product)}}{\text{(mol of hydrogen atom in lignin loaded)}} \times 100. \tag{6}$$

The activity of lignin gasification over a repeatedly used catalyst was conducted as follows. After the lignin gasification at 673 K for 3 h, the catalyst was recovered by filtration and then dried at 333 K for 24 h. The subsequent lignin gasification was carried out at 673 K using the recovered catalyst, lignin (0.10 g), and water (3.0 g).

3. Results and discussion

Small amounts of gases (8.4 C% yield) were obtained from lignin after the treatment with water and a charcoal support without metal species at 673 K for 1 h. Table 1 shows product yields and composition of gas products of catalytic lignin gasification in supercritical water at 673 K. The yields of gaseous products were enhanced by the presence of supported metal catalysts, suggesting that these catalysts are active for the lignin gasification in supercritical water. The order of gas yield based on carbon was the following: Ru/C > Rh/C > Pt/C > Pd/C > Ni/C. The ruthenium catalyst was the most active for lignin gasification; however, the selectivity for hydrogen in gaseous products was the lowest (3.1%). Ruthenium metal surface is expected to be active for the methanation reaction (Eq. (3)). Thus, the gas composition from lignin gasification over Ru/C approached to the thermodynamic equilibrium at 673 K. Table 2 shows gaseous product yields based on hydrogen for catalytic lignin gasification in supercritical water at 673 K. The gas yields based on hydrogen over the metal catalyst was larger than that based on carbon, suggesting that water molecules participated in the lignin gasification (Eqs. (1) and (2)). On the other hand, in the case of Pd/C, the selectivity and yield of hydrogen was high; although, the Pd/C catalyst was not so active for the lignin gasification. These results indicate that lignin was

Table 1
Product yield and gas composition of catalytic lignin gasification in supercritical water[a].

Catalyst	Gas yield (C%)	Gas composition (%)					Water soluble (C%)	THF soluble[b] (C%)	THF insoluble (C%)
		H_2	CO	CH_4	CO_2	C_2–C_4 gases			
Charcoal	8.4	6.9	23.6	15.4	52.8	1.4	10.9	42.3	38.4
Ru/C	87.5	3.1	0.7	47.4	48.2	0.6	0.1	9.4	3.0
Rh/C	37.2	6.6	0.0	38.7	52.7	2.1	3.1	31.9	27.8
Pt/C	22.2	7.6	0.0	25.5	64.4	2.5	3.0	46.8	31.0
Pd/C	20.0	15.4	7.0	16.6	59.3	1.7	13.5	32.1	34.3
Ni/C	19.0	6.0	1.2	23.1	67.7	2.0	13.9	15.6	51.5

[a] Reaction conditions: lignin 0.10 g, catalyst 0.15 g, water density 0.50 g cm^{-3}, reaction temperature 673 K, reaction time 1 h.
[b] THF soluble (C%) was calculated as: 100 – (gas yield (C%)) – (water soluble (C%)) – (THF insoluble (C%)).

Table 2
Product gas yield based on hydrogen of catalytic lignin gasification in supercritical water[a].

Catalyst	Gas yield (H%)			
	H_2	CH_4	C_2–C_4 gases	Total
Charcoal	1.1	5.0	0.7	6.8
Ru/C	5.4	177.9	2.9	186.2
Rh/C	4.6	54.7	4.4	63.7
Pt/C	5.1	34.4	5.1	44.7
Pd/C	10.3	15.2	2.3	27.8
Ni/C	2.7	20.8	2.7	26.2

[a] Reaction conditions: lignin 0.10 g, catalyst 0.15 g, water density 0.50 g cm^{-3}, reaction temperature 673 K, reaction time 1 h. The results in Table 1 are recalculated.

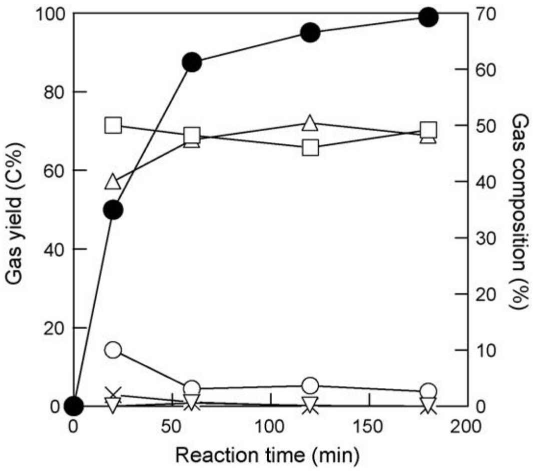

Fig. 3. Carbon yield and gas composition for lignin gasification over Ru/C in supercritical water of 0.5 g cm^{-3} in water density at 673 K. The initial amount of lignin was 0.10 g, and 0.15 g of the catalyst was used for one batch. Gas yield (left axis, ●) and gas composition (right axis, H_2 (○), CH_4 (△), CO (×), CO_2 (□), and C_2–C_4 gases (▽)).

initially converted to hydrogen and carbon monoxide at high selectivity and then methanation reaction between hydrogen and carbon monoxide proceeded. The latter step seemed to be slow over the Pd/C catalyst. Fig. 3 shows the gas yield and composition of lignin gasification over Ru/C in supercritical water as a function of the reaction time. The gas yield increased until 1 h and most of lignin was gasified at 1 h. At the initial stage of the lignin gasification over Ru/C, the selectivity for hydrogen and carbon monoxide was higher, compared to that after 1 h of the reaction. This result also supports that lignin was initially gasified to hydrogen and carbon monoxide at high selectivity, followed by the methanation reaction. Higher selectivity for hydrogen from lignin is obtained by short contact time between initial gas products and metal surfaces.

The percentage of hydrogen in the product increased with reaction temperature as expected by equilibrium composition (Fig. 1). Table 3 shows product yield and composition of gaseous products of catalytic lignin gasification in supercritical water at 723 K. All the lignin used was gasified over the Ru/C catalyst at 723 K and the hydrogen percentage increased to 7.2% from 3.1% at 673 K, corresponding to the equilibrium composition.

We also investigated the stability of supported ruthenium catalyst for lignin gasification. The Ru/γ-Al_2O_3 catalyst showed the high gasification activity (gas yield 76.0 C% at 673 K for 3 h); however, Ru/γ-Al_2O_3 deactivated at the second run of batch process (gas yield 16.2 C% at 673 K for 3 h) (Table 4). Ruthenium metal particles aggregated during first run because the surface area of Al_2O_3 support drastically decreased due to its crystal structure change from γ-Al_2O_3 to α-Al_2O_3 [12]. Silica was not suitable as the support of metal particles for the lignin gasification in supercritical water because silica was dissolved in water at 673 K. In the case of both Ru/C and Ru/TiO_2, the surface area of supports and particle size of ruthenium metal did not change after the lignin gasification, as revealed by TEM images [12]. They kept activities for the lignin gasification after several times of usage (Table 4). We concluded that titania and activated carbon were stable supports for noble metal catalysts during the lignin gasification in supercritical water.

Table 3
Product yield and gas composition of catalytic lignin gasification in supercritical water[a].

Catalyst	Gas yield (C%)	Gas composition (%)					Water soluble (C%)	THF soluble[b] (C%)	THF insoluble (C%)
		H_2	CO	CH_4	CO_2	C_2–C_4 gases			
Ru/C	100.0	7.2	0.0	48.1	44.7	0.0	0.0	0.0	0.0
Rh/C	91.8	7.4	0.0	47.3	45.0	0.3	0.0	0.0	8.2
Pt/C	49.6	9.7	0.2	28.7	57.8	3.6	1.4	32.2	16.8
Pd/C	41.2	11.1	0.0	27.8	57.7	3.3	2.9	29.7	26.2
Ni/C	28.2	9.5	2.2	25.4	59.6	3.2	3.3	21.5	47.0

[a] Reaction conditions: lignin 0.10 g, catalyst 0.15 g, water density 0.23 g cm^{-3}, reaction temperature 723 K, reaction time 1 h.
[b] THF soluble (C%) was calculated as 100 – (gas yield (C%)) – (water soluble (C%)) – (THF insoluble (C%)).

Table 4
Product yield and gas composition of lignin gasification over repeatedly used catalyst in supercritical water[a].

Catalyst	Gas yield (C%)	Gas composition (%)				
		H_2	CO	CH_4	CO_2	C_2–C_4 gases
Ru/TiO_2[b]						
1st use	97.7	4.5	0.0	49.0	46.5	0.0
2nd use	97.6	4.8	0.0	44.2	50.2	0.9
3rd use	96.5	4.2	0.0	43.4	51.1	1.3
Ru/C						
1st use	98.0	3.4	0.0	49.4	46.8	0.4
2nd use	97.3	3.5	0.0	49.0	46.9	0.6
3rd use	95.2	3.8	0.0	48.0	47.3	0.9
Ru/Al_2O_3						
1st use	76.0	2.7	0.0	46.2	50.0	1.1
2nd use	16.2	21.5	0.0	30.6	43.8	4.1

[a] Reaction conditions: lignin 0.10 g, catalyst 0.15 g, water density 0.50 g cm^{-3}, reaction temperature 673 K, reaction time 3 h.

[b] Ruthenium loading was 2 wt% and 0.375 g of the catalyst was used.

4. Conclusion

Hydrogen and methane were produced from lignin in supercritical water over several supported metal catalysts using a batch reactor. The order of catalysts for the lignin gasification was following: Ru/C > Rh/C > Pt/C > Pd/C > Ni/C. The order of hydrogen production was following: Pd/C > Ru/C > Pt/C > Rh/C > Ni/C. Titania and activated carbon were stable supports of noble metal catalysts for lignin gasification in supercritical water.

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