Hydrothermal gasification of phenol water on novel carbon-supported Ni catalysts prepared by the sol–gel method using tartaric acid and aluminum tri-*sec*-butoxide

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A B S T R A C T

The purpose of this study is to prepare novel carbon-supported Ni (Ni/C/Al$_2$O$_3$) catalysts by the sol–gel method and to perform the hydrothermal gasification of phenol water as a model of wastewater. Catalysts were prepared by the combination of aluminum tri-*sec*-butoxide (ASB) and tartaric acid as an organic template and the addition of active metal, nickel nitrate hexahydrate at the preparation of catalysts. After calcination under the nitrogen atmosphere, the larger amounts of active metal species were built at the carbon skeletal in the catalysts. Introduction of tartaric acid dispersed metal Ni with high loading on carbon derived from ammonium tartrate. Hydrothermal gasification was performed under the following conditions: 350 °C, pressure of 20 MPa, phenol water of 2–20 g/L, and LHSV of 48 h^{-1}. 16N63C21A catalyst, which represents 16 wt.% Ni, 63% carbon in tartalic acid, and 21% Al$_2$O$_3$ at the preparation of the catalyst, showed the highest activity and the highest carbon balance between feed and products within 8 h among all the Ni catalysts. The activity of each catalyst increased with the elapse of time and the phenol conversion reached 100 % under the condition and phenol concentration of 2 g/L. No deactivtion was observed.

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1. Introduction

The production of fuel gases such as hydrogen by steam reforming of aromatic compounds is one of attractive methods to utilize heavy carbon resources such as coal, heavy oil or biomass [1,2]. However, the deactivation of the catalysts by coke formation is easy to occur in steam reforming of aromatic compounds at the higher temperature. In recent years, much attention has been focused on the production of fuel gases by hydrothermal gasification of wastewater including aromatic compounds at low temperature and high pressure. The wastewater containing a small amount of organic compounds has a bad influence on the environments due to the difficulty of the natural detoxifying. The biodegradation by the activated sludge method has been widely used for detoxifying such wastewater. In the case of the activated sludge method, however there are some problems that sludge retention time (SRT) is as long as 3–6 days, because of the slow reaction rate, and that a vast place is required for the location of institutions. In addition, waste sludge after processing must be burned, where huge energy is needed for combustion processing as another method. Therefore, the efficient processing of wastewater has been desired. For this purpose, the decomposition of organic compounds in wastewater using hydrothermal gasification and the manufacturing of fuel gases

such as H$_2$ and CH$_4$ have been investigated, so far [3–25]. Whereas fuel gases can be produced through the decomposition of organic compounds by hydrothermal gasification, it cannot be done by the activated sludge method.

Many researchers have investigated gasification processes of model biomass, real biomass, low rank coal and organic wastes in supercritical water [3–25]. Phenol is frequently used as a model organic compound for supercritical water oxidation (SCWO) research [8,10,16,26], because it is ubiquitous in industrial wastewaters and it is also a good "worst case" model pollutant, where phenol oxidation is slower than the oxidation of other organic compounds that are often present in industrial wastewaters. Moreover, the oxidation of substituted phenols and other aromatic compounds often proceeds through a phenol intermediate product. Although phenol can be gasified in supercritical water, its gasification often needs a high temperature (above 600 °C) and proper catalyst [10,16]. Therefore, it is necessary to further investigate phenol gasification in supercritical water in order to improve biomass gasification efficiency and reveal its reaction mechanism.

In the previous reports, Ni wire [10], Ni/Al$_2$O$_3$ [4,5,9,12,15,20–28,22], Ni/C [8,19,20], Raney Ni [24], Ru/Al$_2$O$_3$ [11,21–28] and Ru/C [17,21–28] catalysts were used for hydrothermal gasification of aqueous solution containing a small amount of organic compounds as a model wastewater. The operation at high space velocity (SV) was difficult for Ni/Al$_2$O$_3$ catalysts [4,5]. The Ni/C catalysts could not support a large amount of Ni, and ion-exchange resin as a source of C may be expensive as well

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as Ru in Ru/Al$_2$O$_3$ or Ru/C catalysts [4,5,8]. Ni/Al$_2$O$_3$ catalyst is not only highly active for gasification of carbohydrates, but also had better hydrogen selectivity compared with Ru/C and Ru/Al$_2$O$_3$ [21]. Silica coating on Ni catalyst prevents the sintering of Ni metal particles during the propane steam reforming [12]. Silica-coated Ni catalysts result in high catalytic activity and improved catalyst stability. Supercritical water gasification (SCWG) with bimetallic Ni–M/Al$_2$O$_3$ (M = Cu, Co and Sn) was investigated [18]. Cu could improve the catalytic activity of Ni catalyst in reforming the reaction of methane to produce hydrogen in SCWG. Ru/CeO$_2$–Al$_2$O$_3$ shows high hydrogen yield and hydrogen selectivity for water gas shift at ultrahigh temperature (700 °C) [11]. In addition, it is known that alkali metal salt has a catalytic activity under severe supercritical condition [6], and that Na$_2$CO$_3$ can serve as a catalyst or an additive for phenol supercritical water partial oxidative gasification (SWPO) [16].

We have studied on the simple evaluation system for the reforming, so far. So, we focused on Ni/C/Al$_2$O$_3$ catalysts with high Ni loadings and high activity, because Ni/C(active carbon) catalysts cannot support a large amount of Ni and carbon support derived from ion-exchange resin may be expensive as shown above. Very recently, novel carbon-supported Ni catalysts for wastewater treatment by the hydrothermal gasification were prepared by the sol–gel method using polyethylene glycol (PEG) and aluminum tri-*sec*-butoxide (ASB) [27]. Phenol and glycerol aqueous solutions were used as a model wastewater and the reaction conditions were mainly investigated. The catalysts prepared using more PEG tended to show higher phenol conversion and higher yields of gases (methane and carbon dioxide) for hydrothermal gasification under the same condition. The sol–gel derived catalysts, especially sg-16N63C21A (LHSV = 48 h^{-1}, phenol water 2–10 g/L), exhibited higher catalytic activity than (1) catalyst prepared without PEG (sg-16N84A), (2) catalyst prepared by the impregnation method (i-16N/sg-11C73A) and (3) commercial reference Ni catalyst (ref. Ni).

In the present study, novel carbon-supported Ni (Ni/C/Al$_2$O$_3$) catalysts for wastewater treatment by the hydrothermal gasification were prepared by the sol–gel method using tartaric acid as an organic template and ASB. Several hydrothermal gasification reactions on the Ni/C/Al$_2$O$_3$ were carried out using phenol as a model wastewater and the effects of the addition of tartaric acid and the amount of Ni added on the catalytic performance were investigated. Further, the results from Ni catalysts were compared with those from Ru/C/Al$_2$O$_3$ and Ru/C catalysts.

2. Experimental

2.1. Preparation of Ni/C/Al$_2$O$_3$ and Ru/C/Al$_2$O$_3$ catalysts

The reagents for the preparation of Ni/C/Al$_2$O$_3$ and Ru/C/Al$_2$O$_3$ catalysts were ASB (Al[OCH(CH$_3$)C$_2$H$_5$]$_3$, Tokyo Chemical Industry Co., Ltd.) as a source of Al$_2$O$_3$, ion-exchange water (prepared with Auto Still AW 200, Yamato Co., Ltd.), ethyl alcohol (GR, Nacalai Tesque, Inc.), 2-butanol (GR, Nacalai Tesque, Inc.), L-tartaric acid (TA, GR, Nacalai Tesque, Inc.) as a carbon template, NH$_3$aq (28 wt.%, GR, Nacalai Tesque, Inc.), nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O, GR, Nacalai Tesque, Inc.) as a source of Ni and ruthenium (III) chloride *n*-hydrate (RuCl$_3$·*n*H$_2$O, GR, Wako Pure Chemical Industries, Ltd.) as a source of Ru.

Fig. 1 shows a flowchart for the preparation of Ni/C/Al$_2$O$_3$ catalysts. Table 1 shows the amounts of reagents used for the preparation of Ni and Ru catalysts. A typical preparation method for 16N63C21A, where figures represent the weight ratios of Ni, carbon in initially added tartaric acid and Al$_2$O$_3$ derived from ASB used, respectively, was as follows: 0.021 mol (5.17 g) of ASB and 10.85 g of ethanol were added into 200 mL beaker and the mixture was stirred at 0 °C. 0.014 mol (4.07 g) of Ni(NO$_3$)$_2$·6H$_2$O was dissolved into 7.57 g of EtOH and the resulted solution was added dropwise into ASB/ethanol solution at 0 °C to give a white green slurry. 0.066 mol (9.77 g) of tartaric acid
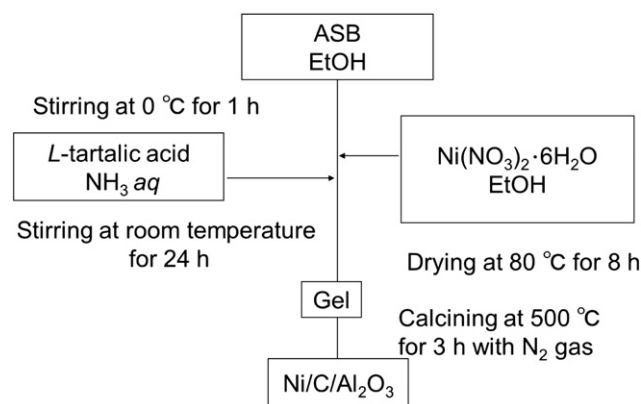
was dissolved into 8.01 g of 28% NH$_3$ aqueous solution and this solution was dried to remove water at elevated temperature. The resultant ammonium tartrate solid was added directly into the above prepared white green slurry. The mixture was stirred at 0 °C for 1 h and then at room temperature for 24 h. After that, the mixture was dried at 80 °C for 8 h to obtain a paste. The paste was extruded by a cylinder for ceramics having 2 mm hole. The extruded paste was heated at the heating rate of 5 °C/min under nitrogen stream and was calcined at 500 °C for 3 h. The resulted black solid was ground in the range of 355–600 μm and was used for characterization and hydrothermal reaction. 39N32C29A was prepared similarly. 5N95A, 16N84A and 39N61A were prepared similarly without tartaric acid. 5Ru/95A catalyst was prepared using RuCl$_3$·*n*H$_2$O, ASB and 2-butanol as a solvent with similar sol–gel method. Although carbon sources other than ASB were not added in the preparation of 5Ru/95A, carbon remained from ASB after calcination under nitrogen stream because the amount of water added for hydrolysis was small. 5Ru/95A was regarded as one of Ru/C/Al$_2$O$_3$. Further, the Ru/C/Al$_2$O$_3$ catalysts prepared using PEG and ASB showed lower activities than 5Ru/95A catalyst in an unpublished result. Therefore, only 5Ru/95A was selected as a representative catalyst of Ru/C/Al$_2$O$_3$. N, C and A of sample names in this paper represent the weight ratio of Ni, carbon in initially added tartaric acid and Al$_2$O$_3$ derived from ASB used, respectively.

2.2. Characterization of Ni/C/Al$_2$O$_3$ and Ru/C/Al$_2$O$_3$ catalysts

X-ray diffraction patterns of the samples were obtained by using a Ultima IV (Rigaku Corp.) diffractometer equipped with nickel-filtered CuKα_1 X-ray source (λ = 0.15405 nm) operated at 40 kV and 20 mA under the following conditions: scan mode CONTINUOUS, slit (SS) 1° (DS) 1° (RS) 0.3 mm, present time 1 s, scan speed of 4°/min, and measurement range of 2θ = 10–70°. The XRF analysis was carried out using EDX-720 (Shimadzu Corp.) in order to analyze the composition of catalysts except for carbon content. In this case, it was assumed that

Fig. 1. Flowchart for preparation of Ni/C/Al$_2$O$_3$ catalysts by the sol–gel method.

Table 1
Amounts of reagents used for the preparation of Ni and Ru catalysts.

Sample name[a]	Number of moles (mol)			
	ASB	H$_2$O	Tartaric Acid	Ni(NO$_3$)$_2$ · 6H$_2$O or RuCl$_3$ · *n*H$_2$O
5N95A	0.093	0.161	0	4.26×10^{-3}
16N84A	0.082	0.083	0	0.014
16N63C21A	0.021	0	0.066	0.014
39N61A	0.060	0	0	0.033
39N32C29A	0.028	0	0.033	0.033
5Ru95A	0.093	0.186	0	2.47×10^{-3}

[a] N: Ni; C: Carbon in tartaric acid added at the preparation; A: Al$_2$O$_3$ from ASB; figures: weight ratio.