Original Paper

Hydrothermal Gasification of Phenol Water on Novel Carbon-Supported Ni Catalysts Prepared by the Sol-Gel Method Using PEG

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Novel carbon-supported Ni catalysts (Ni/C/Al₂O₃) for wastewater treatment by the hydrothermal gasification were prepared by the sol-gel method using polyethylene glycol (PEG) and aluminium tri-s-butoxide (ASB). Phenol and glycerin aqueous solutions were used as a model wastewater and as a model byproduct of biodiesel, respectively. It was found from XRD patterns that metal Ni in fresh catalysts increased with increasing PEG, and that amorphous Al₂O₃-support was transformed to boehmite during hydrothermal gasification. N₂ adsorption measurement revealed that effect of amounts of PEG on surface area and pore volume was negligibly small for sol-gel derived catalysts, whereas surface area, pore volume and pore diameter of catalyst prepared by impregnation method decreased during impregnation of Ni. 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 (Figures show 16wt% of Ni, 63wt% of carbon in PEG, 21wt% of Al₂O₃, respectively. Similarly described below. LHSV=48h⁻¹, phenol water 2-20 g/L), exhibited high catalytic activity compared with (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 case, it is considered that Al₂O₃-support does not play an important role in hydrothermal gasification, because the catalytic activity was stable during the reaction, even if the surface area and pore volume decreased, and the boehmite was formed during hydrothermal gasification. However, introduction of PEG dispersed metal Ni with high loading on carbon derived from PEG. Thus, the sol-gel method using PEG was effective in preparation of catalysts for hydrothermal gasification.

水熱ガス化による廃水処理のための新規な炭素担持Ni触媒 (Ni/C/Al₂O₃) を、ポリエチレングリコール (平均分子量 400) および Al トリ -sec- ブトキシドを用いたゾルゲル法により調製した。反応溶液には工業廃水のモデルとしてフェノール水、バイオディーゼルの副生成物であるグリセリン水を使用した。XRD測定の結果より、調製時に加えた PEG の量を増やすと Ni ピークは鋭くなる傾向が見られた。水熱ガス化反応試験後の触媒においてはベーマイトの存在が確認された。N₂吸着測定の結果より、ゾル-ゲル法で作製した触媒は調製時に加えた PEG の量を変化させても比表面積および細孔容積に大きな変化はなかった。しかし含浸法で作製した触媒では Ni を含浸させると表面積、細孔容積および細孔直径は含浸前より減少した。水熱ガス化試験より、同じ条件では調製時に加えた PEG の量が多いほうがフェノール転化率および気体回収率 (=メタンの収率+二酸化炭素の収率) は高い傾向があり、*sg*-16N/63C21A (LHSV = 48 h⁻¹, フェノール水 2 g/L) では 100% という高い活性を示した。特に *sg*-16N/63C21A は市販触媒である ref. Ni よりも高活性であり、条件 (LHSV = 48 h⁻¹, フェノール水 2 g/L) においても高いフェノール転化率を示した。この触媒では先に示したように反応後において比表面積および細孔容積が低下しベーマイトの生成が確認されたが、活性低下は観察されないことからアルミナは反応には大きな役割を果たしていない可能性がある。一方、PEG を加えることにより PEG から生成する炭素上に Ni を高担持量で分散させることができた。含浸法で Ni を担持させた *i*-16N/*sg*-11C73A はほとんど活性を示さず、ゾル-ゲル法はこの反応の触媒作製に有効な方法であることが分かった。

Key Words

Hydrothermal gasification; Phenol water; Carbon-supported Ni; Sol-Gel Method; PEG

1. Introduction

The wastewater containing a small amount of organic compounds has a bad influence on environment 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, 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 ^{1)~15)}. 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, and organic wastes in supercritical water ^{1)~4)}. Phenol is frequently used as a model organic compound for supercritical water oxidation (SCWO) research, because it is ubiquitous in industrial wastewaters and it is also a good "worst case" model pollutant, because 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 ^{1) 2)}. Therefore, it is necessary to further investigate phenol gasification in supercritical water to improve biomass gasification efficiency and reveal its reaction mechanism. Glycerin also has been used as a representative model compound of various types of biomass in the literatures ^{1) 2) 5)~7)}.

In the previous reports, Ni wire ²⁾, Ni/Al_2O_3 ^{5) 8)~10)}, Ni/C ⁴⁾, $Ru/\gamma-Al_2O_3$ ^{5) 9) 10)}, Ru/C ^{5) 11)}, and $RuNi/\gamma-Al_2O_3$ and $RuNi/C$ ⁶⁾ 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_2O_3 catalysts ⁵⁾. The Ni/C catalysts could not support a large amount of Ni ⁴⁾, and ion-exchange resin as a source of C is expensive as well as Ru in Ru/Al_2O_3 or Ru/C catalysts ^{6) 7) 9)~11)}. Ni/Al_2O_3 catalyst is not only highly active for gasification of carbohydrates, but also had better hydrogen selectivity compared with Ru/C and Ru/Al_2O_3 ⁷⁾. Supercritical water

gasification (SCWG) with bimetallic $Ni-M/Al_2O_3$ ($M = Cu, Co$ and Sn) was investigated ¹²⁾. Cu could improve the catalytic activity of Ni catalyst in reforming reaction of methane to produce hydrogen in SCWG. $CoNi/ZrO_2$ catalysts were stable for hydrothermal gasification of PEG aqueous solution ¹³⁾. In addition, it is known that alkali metal salt has a catalytic activity under severe supercritical condition ¹⁴⁾, and that Na_2CO_3 can serve as a catalyst or an additive for phenol supercritical water partial oxidative gasification (SWPO) ¹⁾.

We have studied on the simple evaluation system for the reforming, so far. So, we focused on $Ni/C/Al_2O_3$ catalysts with high Ni loadings and high activity, because Ni/C catalysts cannot support a large amount of Ni and ion-exchange resin as a source of C is expensive. In the present study, novel carbon-supported $Ni/C/Al_2O_3$ catalysts for wastewater treatment by the hydrothermal gasification were prepared by the sol-gel method using polyethylene glycol (PEG) as an inexpensive organic template and aluminium tri-*s*-butoxide (ASB). Several hydrothermal gasification on the $Ni/C/Al_2O_3$ catalysts were carried out using (1) phenol as a model wastewater and (2) glycerin as model byproduct of biodiesel.

2. Experimental Procedure

2.1 Preparation of $Ni/C/Al_2O_3$ Catalysts

The reagents for the preparation of $Ni/C/Al_2O_3$ catalysts were aluminum tri-*s*-butoxide ($Al[OCH(CH_3)C_2H_5]_3$, abbreviated to ASB, Tokyo Chemical Industry Co., Ltd.) as a source of Al_2O_3 , ion-exchange water (prepared with Auto Still AW 200, Yamato Co., Ltd.), ethyl alcohol (GR, Nacalai Tesque, Inc.), polyethylene glycol (PEG, Mw=400, GR, Nacalai Tesque, Inc.) as a carbon template and nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, GR, Nacalai Tesque, Inc.) as a source of Ni. Figs. 1 and 2 show flowcharts for preparation of $Ni/C/Al_2O_3$ catalysts by the sol-gel method and

Fig. 1 Flowchart for preparation of $Ni/C/Al_2O_3$ catalysts by the sol-gel method

Fig. 2 Flowchart for preparation of Ni/C/Al₂O₃ catalysts by the impregnation method

Sample name	Ni (wt.%)	C (wt.%)	Al ₂ O ₃ (wt.%)
<i>sg</i> -16N/84A	16	9	75
<i>sg</i> -16N/11C73A	20	6	74
<i>sg</i> -16N/21C63A	15	23	62
<i>sg</i> -16N/32C53A	20	12	68
<i>sg</i> -16N/53C31A	27	18	55
<i>sg</i> -16N/63C21A	41	7	52

2.2 Characterization of Ni/C/Al₂O₃ Catalysts

area (SA), pore volume (PV), and pore diameter (PD) were calculated by the BET method. To estimate values for mesopores, the BJH method was used. The sample was degassed under 10^{-2} kPa at 300 °C for 3 h before N₂ adsorption measurement.

2.3 Catalytic Hydrothermal Gasification Reaction on Ni/C/Al₂O₃ Catalysts

The gas products were analyzed by the gas chromatography-thermal conductivity detector (GC-TCD) (Shimadzu Corp., GC-8A). Measurement conditions for H_2 using one GC-8A were as follows: Injection temp. 110 °C, Detector temp. 110 °C, Column Porapak T, Column length 2 m, Column temp. 50 °C, carrier gas N_2 . Measurement conditions for CH_4 and CO_2 using another GC-8A were as follows: Injection temp. 110 °C, Detector temp. 110 °C, Column unibeads C, Column length 3 m, Column temp. 100 °C, carrier gas He.

The liquid products were analyzed by the gas chromatography-flame ionization detector detector GC-FID (Shimadzu Corp., GC-17A). Measurement conditions for phenol aqueous solutions were as follows: Injection temp. 240 °C, Detector temp. 240 °C, ATTN 4, Split ratio 100, Column DB-1, Column length 60 m, Column diameter 0.25 mm

Column temp. 150 °C. Measurement conditions for glycerin aqueous solutions were as follows: Injection temp. 240 °C, Detector temp. 240 °C, ATTN 1, split ratio 100, Column BP-1, Column length 60 m, Column diameter 0.25 mm Column temp. 180 °C.

If $\text{CH}_4 : \text{CO}_2 = a : b$, the coefficients, the m and n in the following reaction of phenol aqueous solutions are $m = 6a/(a + b)$ and $n = 6b/(a + b)$, respectively

Similarly, the m and n in the following reaction of glycerin aqueous solutions are $m = 3a/(a + b)$ and $n = 3b/(a + b)$, respectively

In these equations, it is assumed that only CH_4 and CO_2 are formed as products with carbon from phenol or glycerin.

3. Results and Discussion

3.1 Characterization of Ni/C/Al₂O₃ Catalysts

Table 1 summarizes compositions (wt%) of fresh Ni/C/Al₂O₃ catalysts determined by XRF analysis. For each catalyst, carbon content decreased compared with the nominal composition. This means that a part of PEG was decomposed to release gaseous materials during heat-treatment under N₂. As a result, catalyst with relatively high Ni loadings was obtained, because carbon was substituted for Al₂O₃ in the nominal composition of catalysts maintaining Ni content (16 wt%).

Fig. 4 shows XRD patterns of fresh Ni catalysts. Ni phase was observed for all the catalysts and tend to increase with increasing PEG, indicating that Ni species were reduced during heat-treatment under N₂ in the presence of PEG. The crystalline size of Ni, which was determined from diffraction line around 44°, for each catalyst is given in this figure. The crystalline size of catalysts prepared using PEG is much smaller than that of *sg*-16N/84A prepared without PEG. **Fig. 5** indicates XRD patterns of *sg*-16N/63C21A catalysts before and after hydrothermal gasification, where P and G mean the phenol and glycerin, respectively. The boehmite (AlO(OH)) phase was observed for all the catalysts after reaction. The crystalline size of Ni increased after the reaction. This means that the remarkable sintering of Ni occurred during the reaction. The sintering of Ni to this degree maintained catalytic activity even if a part of amorphous Al₂O₃-support was transformed to AlO(OH) crystal during hydrothermal gasification. This result is consistent with the fact that RuNi/

Fig. 4 XRD patterns of fresh Ni catalysts

Fig. 5 XRD patterns of *sg*-16N/63C21A catalysts before and after hydrothermal gasification. (P: phenol, G: glycerin)

Fig. 6 XRD patterns of ref. Ni catalysts before and after hydrothermal gasification

Al₂O₃ was not resistant under the SCWG condition, but RuNi/C exhibited higher stability⁶⁾. It is likely that the presence of carbon support would enable to maintain active Ni species on the catalyst. **Fig. 6** shows XRD patterns of ref. Ni catalysts (Engelhard5256, NiO > 55 wt% (XRF), bulk density 0.84g/cc) before and after hydrothermal gasification. NiO phase with broad peak was observed before the reaction, suggesting that NiO is highly dispersed. However, Ni phase with sharp peak was observed after the reaction.

Table 2 lists physical properties of fresh Ni catalysts,

Table 2 Physical properties of fresh Ni catalysts

Sample name	BET	BET	BET	BJH	BJH	BJH
	SA (m ² /g)	PV (cm ³ /g)	PD (nm)	SA (m ² /g)	PV (cm ³ /g)	PD (nm)
<i>sg</i> -16N/84A	267	0.63	9.5	210	0.59	3.3
<i>sg</i> -16N/11C73A	261	0.59	9.1	136	0.55	3.7
<i>sg</i> -16N/21C63A	265	0.62	9.3	135	0.56	3.7
<i>sg</i> -16N/32C52A	279	0.46	6.6	92	0.38	3.7
<i>sg</i> -16N/63C31A	226	0.43	7.7	103	0.38	3.7
<i>sg</i> -16N/63C21A	272	0.55	9.3	197	0.53	4.2
<i>i</i> -16N/ <i>sg</i> -11C37A	315	0.32	4.0	89	0.17	3.7
ref. Ni	241	0.26	4.3	85	0.17	3.7

Table 3 Physical properties of *sg*-16N/63C21A before and after hydrothermal gasification

Reaction condition	BET	BET	BET	BJH	BJH	BJH
	SA (m ² /g)	PV (cm ³ /g)	PD (nm)	SA (m ² /g)	PV (cm ³ /g)	PD (nm)
fresh	272	0.55	9.3	197	0.53	4.2
12 h ⁻¹ , P 2 g/L	57	0.24	17.0	53	0.24	3.7
48 h ⁻¹ , P 6 g/L	87	0.25	11.5	64	0.24	3.7
48 h ⁻¹ , P 10 g/L	76	0.37	19.1	60	0.36	18.6
48 h ⁻¹ , P 20 g/L	53	0.30	23.1	43	0.31	44.9
48 h ⁻¹ , G 50 g/L	67	0.25	15.1	60	0.25	13.9
48 h ⁻¹ , G 100 g/L	84	0.31	14.7	93	0.31	13.9

Table 4 Physical properties of ref. Ni before and after hydrothermal gasification

Reaction condition	BET	BET	BET	BJH	BJH	BJH
	SA (m ² /g)	PV (cm ³ /g)	PD (nm)	SA (m ² /g)	PV (cm ³ /g)	PD (nm)
fresh	241	0.26	4.3	85	0.17	3.7
48 h ⁻¹ , P 2 g/L	81	0.15	7.5	50	0.13	3.7
48 h ⁻¹ , G 50 g/L	44	0.16	14.5	33	0.16	3.7

P : phenol, G : glycerine

where the SA, PA and PD mean the specific area, the pore volume and the pore diameter determined by N₂ adsorption measurement, respectively. The BET SA and BET PV of sol-gel derived catalysts were 226-279 m²/g and 0.43-0.62 cm³/g, respectively. The effect of amounts of PEG on surface area and pore volume was negligibly small for sol-gel derived catalyst. The catalyst prepared by impregnation method (*i*-16N/*sg*-11C73A) showed small SA, PV and PD compared with catalyst before the impregnation (*sg*-11C73A) (not shown). **Table 3** summarizes physical properties of *sg*-16N/63C21A before and after hydrothermal gasification. The SA and PV decreased after the reaction. This may have arisen from the decrease of micropores related to the transformation of Al₂O₃-support to AlO(OH) and to the sintering of Ni. **Table 4** lists physical properties of ref. Ni before and after hydrothermal gasification. The SA

and PV decreased, and BET PD increased after the reaction, resulting from the decrease in micropores related to the sintering of Ni. It is seen from Tables 3 and 4 that SA for BET and BJH after hydrothermal gasification becomes close to each other. This means that micropores were destroyed mainly during hydrothermal gasification.

3.2 Hydrothermal Gasification on Ni/C/Al₂O₃ Catalysts

First, the effect of reaction condition on phenol and glycerin conversion will be discussed. **Fig. 7** shows the change in the phenol conversion with reaction time of hydrothermal gasification. Ni catalyst prepared by the impregnation method (*i*-16N/*sg*-11C73A) and ref. Ni catalyst (ref. Ni) showed maximum phenol conversion of 33% and 79 %, respectively. The low phenol conversion for *i*-16N/*sg*-11C73A may be due to the fact that Ni does not present

Fig. 7 Change in the phenol conversion with reaction time of hydrothermal gasification (a: 12 h⁻¹, b: 48 h⁻¹)

Fig. 9 Change in the glycerin conversion with reaction time of hydrothermal gasification on sg-16N/63C21A and ref. Ni catalysts (a: 50 g/L, b: 100 g/L, 48 h⁻¹)

as a metal Ni as shown in Fig. 4. On the other hand, Ni catalysts prepared using PEG show much higher phenol conversion than those of ref. Ni catalyst, catalyst prepared by impregnation method (*i*-16N/*sg*-11C73A) and catalyst prepared without PEG (*sg*-16N/84A). Fig. 8 illustrates the change in the phenol and glycerin conversion with reaction time of hydrothermal gasification on *sg*-16N/63C21A. In the case of phenol aqueous solution, high phenol conversion was obtained until the reaction condition becomes severe (LHSV 48 h⁻¹ and 10 g/L). Over this condition, phenol conversion dropped to about 60 %. For the case of glycerin, high glycerin conversion was obtained until the reaction condition becomes severe (LHSV 48 h⁻¹ and 50 g/L). Then, the glycerin conversion decreased to about 40% for LHSV 48 h⁻¹ and 100 g/L.

Fig. 9 shows the change in the glycerin conversion with reaction time of hydrothermal gasification on *sg*-16N/63C21A and ref. Ni catalysts (LHSV 48 h⁻¹ and 50 g/L, 100 g/L). *sg*-16N/63C21A gave high glycerin conversion compared with ref. Ni catalyst for the condition (LHSV 48 h⁻¹ and 50 g/L).

Next, the effect of reaction condition on yields of gases will be discussed. Fig. 10 indicates yields of gases and reactant phenol-C, coke and other per introduced phenol-C

Fig. 10 Yields of gases and reactant phenol-C, coke and other per introduced phenol-C for hydrothermal gasification on various Ni catalysts (a: 6 h⁻¹, b: 12 h⁻¹, c: 48 h⁻¹)

for hydrothermal gasification on various Ni catalysts. In this figure, yield of coke and other was calculated using the following equation.

$$\text{Yield of coke and other} = 1 - (\text{Yield of CH}_4) - (\text{Yield of CO}_2) - (\text{Reactant phenol-C}) \quad \text{Eq. (3)}$$

In this Eq. (3) and Fig. 10, Fig. 11, and Fig. 12, the yields of CH₄ and CO₂ are defined as the molar ratio of a formed amount of each product to an amount of carbon in fed phenol water. Most of hydrogen included in reacted phenol and water was recovered as CH₄ and only a small amount of molecular hydrogen was formed. However, the amount of molecular hydrogen formed was not necessarily consistent with that calculated in Eqs. (1) and (2) probably because the latter value is largely affected by the ratio of CH₄ and CO₂ formed and a part of gaseous products was dissolved in the reactant solution under the high pressure. Therefore, the yields of H₂ are added in Figs. 10-12 as the molar ratio of a formed amount of hydrogen to an amount of carbon in fed phenol water. If phenol-derived carbon can be gasified perfectly, the sum of yield for CH₄ and CO₂ is unity. CH₄, CO₂ and H₂ were major products for sol-gel derived catalysts. The yields of CH₄ and CO₂ tend to increase with increasing PEG. When *sg*-16N/53C31A was

Fig. 8 Change in the phenol and glycerin conversion with reaction time of hydrothermal gasification on sg-16N/63C21A

Fig. 11 Yields of gases and reactant phenol-C, coke and other per introduced phenol for hydrothermal gasification on *sg*-16N/63C21A catalysts

Fig. 12 Yields of gases and reactant glycerin-C, coke and other per introduced glycerin-C for hydrothermal gasification on *sg*-16N/63C21A and ref. Ni catalysts (a: 50 g/L, b: 100g/L, 48 h⁻¹)

used, the yield of carbon exceeded 1. A part of carbon initially included in the catalyst might react with water although the detail of this phenomenon is not clear. As shown in Table 1, *sg*-16N/53C31A has comparatively higher carbon content than other catalysts. The maximum phenol conversion was 33 % for *i*-16N/*sg*-11C73A (LHSV = 12 h⁻¹, 2 g/L) and gases were scarcely produced. Fig. 11 illustrates yields of gases and reactant phenol-C, coke and other per introduced phenol for hydrothermal gasification on *sg*-16N/63C21A catalysts. In the case of phenol aqueous solution, higher yields of gases than 0.8 were obtained until the reaction condition becomes severe (LHSV 48 h⁻¹ and 6 g/L). For the case of glycerin, higher yields of gases than 0.8 were obtained until the reaction condition becomes severe (LHSV 48 h⁻¹ and 50 g/L). Fig. 12 shows yields of gases and reactant glycerin-C, coke and other per introduced glycerin-C for hydrothermal gasification on *sg*-16N/63C21A and ref. Ni catalysts. *sg*-16N/63C21A shows high yields of gases compared with ref. Ni catalyst for 50 g/L. Sharma reported that phenol was gasified by use of Ni/C catalyst at as low as 360 °C under 20 MPa at LHSV of 50

h⁻¹ relatively close to our condition (350 °C under 20 MPa at LHSV of 48 h⁻¹)⁴⁾. It is practically useful that the present *sg*-16N/63C21A catalyst (Ni 15 wt%) is comparable to the Ni/C catalyst⁴⁾, which needs more Ni amount (47wt %).

From Figs. 7 and 10, the catalytic activity for hydrothermal gasification of phenol on *sg*-16N/84A is the lowest among sol-gel derived catalysts. This is because the catalyst has less Ni with larger crystalline size than sol-gel catalyst prepared using PEG based on XRF and XRD analyses. Ni species may have dispersed as inactive nickel aluminate into alumina when PEG is not added in *sg*-16N/84A. It is likely that the presence of carbon on the catalyst would prevent active Ni species from dispersing as inactive nickel aluminate into alumina. On the other hand, the phenol conversion and yields of gases of sol-gel catalyst prepared using PEG tends to increase with increasing PEG. This may resulted more Ni loading of catalyst based on XRF analysis. The effect of LHSV on the phenol conversion for hydrothermal gasification of phenol was negligibly small in the range of 12-48 h⁻¹. The threshold of phenol concentration to maintain high catalytic activity was less 20 g/L. For both phenol conversion (LHSV = 48 h⁻¹, 2 g/L) and glycerin conversion (LHSV = 48 h⁻¹, 50 g/L), the conversion of *sg*-16N/63C21A is higher than that of ref. Ni. It is considered that *sg*-16N/63C21A contains the highly dispersed metal Ni in contrast to ref. Ni.

As mentioned above, carbon-supported Ni catalysts prepared using PEG could load high Ni metal and inhibit the interaction between active Ni species and alumina by placing carbon on an alumina support. As a result, they showed 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). Thus, the sol-gel method using PEG was effective in preparation of catalysts for hydrothermal gasification.

Conclusions

In the present study, novel carbon-supported Ni catalysts for wastewater treatment by the hydrothermal gasification were prepared by the sol-gel method using polyethylene glycol (PEG) and aluminium tri-*s*-butoxide (ASB). The following results were obtained:

1. It was found from XRD patterns that metal Ni in fresh catalysts increased with increasing PEG, and that amorphous Al₂O₃-support was transformed to boehmite during hydrothermal gasification.
2. N₂ adsorption measurement revealed that effect of amounts of PEG on surface area and pore volume was negligibly small for sol-gel derived catalysts, whereas sur-

face area, pore volume and pore diameter of catalyst prepared by impregnation method decreased during impregnation of Ni.

3. 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=48h⁻¹, phenol water 2-10 g/L), exhibited high catalytic activity compared with (1) catalyst prepared without PEG, (2) catalyst prepared by the impregnation method and (3) commercial reference Ni catalyst. In the present case, it is considered that Al₂O₃-support does not play an important role in hydrothermal gasification, because the catalytic activity was stable during the reaction, even if the surface area and pore volume decreased, and the boehmite was formed during hydrothermal gasification. However, introduction of PEG dispersed metal Ni with high loading on carbon derived from PEG. Thus, the sol-gel method using PEG was effective in preparation of catalysts for hydrothermal gasification.

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