Steam reforming of toluene over perovskite-supported Ni catalysts

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ABSTRACT

Hydrogen production by steam reforming of toluene as a model aromatic hydrocarbon has been investigated with various Ni/perovskite catalysts. Among them, $Ni/LaAlO_3$ catalyst showed high catalytic activity. Partial substitution of the La site of $LaAlO_3$ support with other elements (Sr, Ba or Ca) was conducted for the $Ni/LaAlO_3$ catalyst, and substitution with 30% Sr promoted catalytic activity and selectivity to hydrogen. Optimization for the Ni loading amount over $Ni/La_{0.7}Sr_{0.3}AlO_{3-\delta}$ catalyst revealed that 5 wt% $Ni/La_{0.7}Sr_{0.3}AlO_{3-\delta}$ had the highest toluene conversion and the smallest amount of carbon deposition. To elucidate the role of doped Sr, the catalytic natures of Sr-substituted catalyst $Ni/La_{0.7}Sr_{0.3}AlO_{3-\delta}$ and Sr-supported catalyst $Ni/Sr/LaAlO_3$ were compared. Results show that Sr-ions should be incorporated in the $LaAlO_3$ perovskite structure to show high catalytic performance. Based on results of transient response test with $H_2{}^{18}O$ on $Ni/La_{0.7}Sr_{0.3}AlO_{3-\delta}$, $Ni/Sr/LaAlO_3$, and $Ni/LaAlO_3$ at reaction temperature of 873 K, the formation of ^{18}O-products was observed only on $Ni/La_{0.7}Sr_{0.3}AlO_{3-\delta}$ catalyst derived from redox between the lattice oxygen in the perovskite and water. Lattice oxygen in the $La_{0.7}Sr_{0.3}AlO_{3-\delta}$ support worked as active oxygen species to enhance its catalytic nature.

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1. Introduction

Biomass has attracted increasing attention as an alternative energy resource to fossil fuels because it can be regarded as a CO_2 neutral feedstock [1]. Biomass comprises cellulose, hemicellulose, and lignin. The latter includes many aromatic compounds in its structure, which are difficult to decompose. Moreover, aromatic-tar production in gasification process causes severe problems such as plugging of the reactor. In addition, tar remaining in the gasification reactor degrades the heating value of products. Therefore, tar removal has been strongly desired. Catalytic steam reforming of aromatic compounds is a promising method of tar removal. Hydrogen, which is produced in steam reforming of aromatic compounds, is not only an important chemical feedstock; it is useful for ammonia synthesis, petroleum refinery; and for running fuel cells.

Catalytic steam reforming of aromatic hydrocarbons has been investigated over many catalytic systems. Supported Rh catalyst shows excellent catalytic performance for this reaction with low coke formation. Polychronopoulou et al. [2–5] conducted steam reforming of phenol over MgO-based supported Rh catalysts. Supported Rh catalyst showed better catalytic performance than that of commercial Ni-based catalyst in their comparison. Generally,

noble metals like as Rh have high cost, therefore, low metal loading amount or high metal dispersion is strongly required in catalytic systems. Polychronopoulou et al. also investigated the effect of Rh loading amount to catalytic performance. Even 0.1 wt% Rh catalyst showed higher catalytic performance than in the case of 0.3 wt% and 0.5 wt%, and they concluded small or high dispersed Rh particle was more effective to this reaction. Supported Rh catalyst was also investigated for the gasification of cellulose with air to synthesis gas by Asadullah et al. [6,7]. They reported supported Rh catalyst showed excellent catalytic performance compared to other noble metals (Ru, Pt and Pd) supported catalysts.
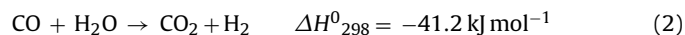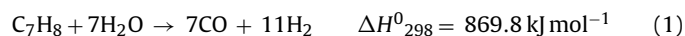
Supported Ni [8–16], Co [17,18] and Fe [19] catalysts have been also reported because of their low cost compared to noble metals. Among these, supported Ni catalysts have been investigated extensively. Supported Ni catalysts show high catalytic activity for steam reforming reaction, however, they have been known to be deactivated easily by coke formation [20,21]. Therefore, many researches concerning highly active and stable Ni catalysts for steam reforming of aromatic hydrocarbon have been conducted. Park et al. [9] investigated steam reforming of benzene and confirmed that 15 wt% $Ni/CeO_2(75\%)–ZrO_2(25\%)$ catalyst showed higher catalytic activity and resistance to coke formation than a commercial Ni catalyst did. They concluded that these results were attributable to the high redox property of the support resulting from its high oxygen transport and storage capacity. Zhang et al. [10] investigated 3.0 wt% Ni/olivine catalyst and 3.0 wt% Ni/olivine catalyst doped

with 1.0 wt% CeO_2 in steam reforming of benzene or toluene. By adding CeO_2 to Ni/olivine catalyst, both catalytic activity and resistance to coke formation were improved in both reactions. They concluded that the improvement of redox property of the catalyst by adding CeO_2 affected the catalytic activity and stability. Li et al. [13,14] used Ni/mayenite ($Ca_{12}Al_{14}O_{33}$) catalyst in steam reforming of toluene and confirmed higher catalytic activity and stability than those of commercial-like Ni/xCaO/(1−x)MgO catalyst. Mayenite includes free oxygen species (O_2^- and O_2^{2-}) in its structure and shows a high redox property. As described above, the high redox property of the support is extremely important for high activity and resistance to coke formation on Ni catalysts in steam reforming of aromatic compounds.

Perovskite (ABO_3) also has been known to have a redox property and has been used in various reactions using their lattice oxygen [22–28]). Stathopoulos et al., [23] performed the deNOx reaction by CH_4 and H_2 over $La_{0.8}Sr_{0.2}FeO_{3-x}$ catalyst. From XRD and XPS analyses, $SrFe^{3+, 5+}O_{3-x}$ (mixed valence for Fe) phase was observed. They mentioned that this phase showed excellent ability for oxygen reversible adsorption and was attributable to high catalytic property. Urasaki et al., [24] performed steam reforming of methane over various perovskite-supported Ni catalysts. The Ni/$LaAlO_3$ catalyst showed higher catalytic activity and stability than those of conventional Ni/α-Al_2O_3 catalyst. They concluded that the lattice oxygen in the $LaAlO_3$ played important roles in promoting the oxidation of CH_x species adsorbed onto metallic Ni and for suppressing coke formation. The substitution of A or B site with other elements can improve the intrinsic properties of perovskite [29–33]. Nguyen et al. [29] confirmed that the lattice oxygen mobility of $LaAlO_3$ perovskite can be improved by substituting the A site with Sr and that $La_{0.9}Sr_{0.1}AlO_{3-\delta}$ shows the highest lattice oxygen mobility.

In this work, we examined steam reforming of toluene using perovskite-supported Ni catalysts. Steam reforming reaction proceeds as Eq. (1), following WGS (water gas shift) reaction proceeds as Eq. (2).

$$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2 \qquad \Delta H^0_{298} = 869.8 \, kJ \, mol^{-1} \qquad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^0_{298} = -41.2 \, kJ \, mol^{-1} \qquad (2)$$

We hoped high catalytic activity and suppression of coke formation by the lattice oxygen of perovskite support. Additionally, catalytic performances over perovskite-supported Ni catalysts were compared to over supported Rh catalysts. The contribution of lattice oxygen to the reaction was confirmed by the reaction using $H_2^{18}O$.

2. Experimental

Perovskite type oxides and La_2O_3 were prepared using a citric acid complex method. Metal nitrate precursors (Kanto Chemical Co. Inc.) were dissolved in water. Then, excess citric acid and ethylene glycol (Kanto Chemical Co. Inc.) were added to the solution. The molar ratio of metal/citric acid/ethylene glycol was 1/3/3. This solution was evaporated in a water bath at 353 K for 16 h and dried on a hot plate with stirring. Then, dried powder was pre-calcined at 673 K for 2 h, and calcined at 1123 K for 10 h. Catalyst support of α-Al_2O_3 was obtained by calcination of γ-Al_2O_3 (JRC-ALO-8) at 1573 K for 3 h. Perovskites, La_2O_3 and Al_2O_3 were impregnated with solution of Ni or Rh nitrate precursors (Kanto Chemical Co. Inc.), then dried and calcined at 1073 K for 1 h. Ni/Sr/$LaAlO_3$ (i.e. Sr was not incorporated in the perovskite but impregnated on the perovskite) was prepared by sequential impregnation of Sr and Ni. Structures of catalysts were observed using XRD (RINT-2000; Rigaku Corp.). BET specific surface area of the perovskite oxide was measured by N_2 adsorption at 77 K (Autosorb-1; Quantachrome Instruments).

Catalytic activity tests for steam reforming of toluene were conducted in a fixed bed quartz reactor at atmospheric pressure. Catalysts were sieved in 250–500 μm and diluted with SiC. The standard reaction temperature was 873 K. Standard feed gas composition was C_7H_8/H_2O/Ar = 3/42/55 mL min^{-1} (SATP), GHSV was about 12,000 h^{-1}, W/F = 3.4 g h mol^{-1}. Limiting for mass transport was negligible in this condition. Pre-reduction was conducted in H_2/Ar = 5/45 mL min^{-1} (SATP) at 1073 K for 0.5 h. Formation rates of products were analyzed using GC-TCD and GC-FID. Toluene conversion and selectivity to product and hydrogen yield were defined as shown below.

$$C_7H_8 \, conversion \, (\%) = \frac{r_{CO} + r_{CH_4} + r_{CO_2} + 6 \times r_{C_6H_6}}{7 \times C_7H_8 feed}$$
$$\times 100, \quad r : \text{formation rate of each product} \qquad (3)$$

$$Selectivity \, to \, product \, (\%) = \frac{\text{Formation rate of each product}}{r_{CO} + r_{CH_4} + r_{CO_2} + 6 \times r_{C_6H_6}} \times 100 \qquad (4)$$

$$Hydrogen \, yield \, (\%) = \frac{r_{H_2}}{18 \times C_7H_8 feed} \times 100 \qquad (5)$$

Transient response tests using $H_2^{18}O$ with a quadruple mass spectroscopy (Q-mass, HPR20; Hiden Analytical Ltd.) were conducted at 873 K to observe the reactivity of lattice oxygen. Pre-reduced catalyst of 25 mg was used. Procedures were the following:

(1) First reaction in C_7H_8/10% $H_2^{18}O$ and 90% $H_2^{16}O$ or 30% $H_2^{18}O$ and 70% $H_2^{16}O$/Ar/He = 3/42/10/145 mL min^{-1} (SATP) for 30 min. (Operation – 1)
(2) Purging with He for 2 h
(3) Second reaction in C_7H_8/H_2O/Ar/He = 3/42/10/145 mL min^{-1} (SATP). (Operation – 2)

Ar was added as an internal standard gas for detection with the Q-mass device. The analysis for all possible ^{18}O-containing species by Q-mass spectrometer was based on m/z = 20($H_2^{18}O$), 30($C^{18}O$), 46($CO^{18}O$), and 48($C^{18}O_2$). The amount of carbon deposition on each catalyst after 3 h reaction was determined by analyzing CO and CO_2 formed in the temperature programmed oxidation (TPO). The feed gas composition was O_2/N_2 = 10/90 mL min^{-1} (SATP) and the rate of temperature increase was 10 K min^{-1}.

3. Results and discussion

3.1. Catalytic activities for steam reforming of toluene over perovskite-supported catalysts

First, we conducted steam reforming of toluene as a model aromatic compound on various perovskite-supported catalysts (Ni/$LaAlO_3$, Ni/$LaFeO_3$, Ni/$BaTiO_3$, Ni/$SrTiO_3$, and Ni/$SrCeO_3$) under the following conditions: W/F = 13.5 g h mol^{-1}, S/C = 3.0, reaction temperature = 873 K, and Ni loading = 10 wt%. Catalytic activities on these catalysts are presented in Table 1. Among these catalysts, Ni/$LaAlO_3$ catalyst showed the highest toluene conversion (81%) and hydrogen yield (60%). Therefore, the $LaAlO_3$ support was the most appropriate among various perovskite supports for steam reforming of toluene.

Further investigations for elucidating the role of each element and the perovskite structure were conducted using Ni/$LaAlO_3$, Ni/La_2O_3, and Ni/α-Al_2O_3 catalysts in severe conditions: W/F = 3.4 g h mol^{-1}, S/C = 2.0, reaction temperature = 873 K and Ni loading = 5 wt%. Further investigations were conducted under the