



Highly active and stable Co/La_{0.7}Sr_{0.3}AlO_{3-δ} catalyst for steam reforming of toluene



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ABSTRACT

We investigated steam reforming of toluene as a model compound of aromatic hydrocarbons included in biomass tar over Co supported La_{0.7}Sr_{0.3}AlO_{3-δ} (LSAO), perovskite oxide. Ni-supported LSAO catalyst has shown high activity and coke resistance from the redox property of lattice oxygen in/on the LSAO support. Co is known as an active metal for this reaction, so Co/LSAO catalyst was investigated in this work. Co/LSAO catalyst, which showed high steady-state activity and stability, was characterized using H₂¹⁸O isotopic transient response tests, STEM, FT-IR, Arrhenius plot and partial pressure dependence to elucidate high and stable catalytic activity. *In situ* FT-IR measurements revealed that reaction intermediates on Co/LSAO desorbed at 873 K or lower temperatures. Although redox property of lattice oxygen did not change at around 848 K based on isotopic transient tests, the Arrhenius plots indicate that the rate-determining step changed at around 848 K because of reaction intermediate decomposition desorption. Fast reaction and desorption of absorbed intermediates on Co/LSAO enable catalytic stability during toluene steam reforming.

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1. Introduction

Biomass has been attractive as an alternative resource to fossil fuels because of its wide distribution, carbon-neutrality, and renewability. Biomass gasification is a promising technology for producing H₂-rich synthesis gas (H₂ + CO) in terms of economic and ergonomic efficiency. However, the products contain a considerable amount of tar, which causes plugging of the reactor. Biomass tar consists mainly of aromatic hydrocarbons and oxygenates. A novel method for removing these heavy aromatics is being eagerly sought. Steam reforming reaction of aromatics is receiving increasing attention because the produced H₂ is applicable not only as a chemical feedstock for ammonia synthesis and petroleum refining, but also as a renewable secondary energy source for operating fuel cells. Furthermore, steam reforming of aromatics can produce H₂ from unconventional resources such as oil shale, oil sands, and peat.

Catalytic steam reforming of aromatic hydrocarbons is performed over many metal-supported catalysts such as Rh [1–4], Ni [5–16], Co [17–23], and Fe [24–26]. Particularly, Ni-supported

catalysts are investigated more extensively [27] because Ni is suitable for industrial use because of its low cost and high activity. Conversely, activity of Ni-supported catalyst is easily deactivated by coke formation during the reaction [28,29]. Generally, Co-supported catalyst generates less coke and methane as byproducts during steam reforming reaction of heavy hydrocarbons [17–23] and oxygenates [30–35]. Wang et al. reported that Co/α-Al₂O₃ showed higher toluene conversion and less carbon deposition compared to Ni/α-Al₂O₃ in steam reforming of tar and toluene [19].

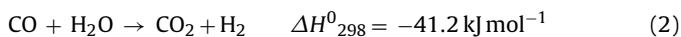
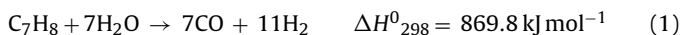
Controlling coke formation in steam reforming is an important research topic. Many studies of the subject have been conducted [36–39]. Rostrup-Nielsen reported partial sulfur poisoning of Ni inhibits carbon formation without suppressing reforming reaction of methane [36]. Sugisawa et al. described that La addition to Ni/Al₂O₃ enhances H₂O activation ability for steam reforming of *n*-dodecane, which suppresses coking on a catalytic surface [37]. For aromatic hydrocarbons, catalytic decomposition of aromatic rings is difficult, and carbon deposition is more problematic [38].

Lattice oxygen of the catalyst support can activate a reaction with the redox property and remove deposited carbon oxidatively [1,5,8,40–47]. Oemar et al. reported that La_{0.8}Sr_{0.2}Ni_{0.8}Fe_{0.2}O₃ shows high activity and carbon resistance on steam reforming of toluene because of the great amount of lattice oxygen in/on perovskite oxide [41]. Previously, we conducted toluene steam

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reforming over Ni/La_{0.7}Sr_{0.3}AlO_{3-δ} (LSAO) [48–52]. The reaction can be described as:



In the reaction, lattice oxygen suppresses coke formation and activates toluene with a redox mechanism [48–52]. According to an earlier IR study, toluene reacts with lattice oxygen and forms oxygenate intermediates on LSAO [51]. The redox property of LSAO supports is substantial for coke removal and activating toluene. As described above, Co metal was expected to be beneficial for steam reforming of formed oxygenate intermediates on LSAO. Therefore, steam reforming of toluene as a model compound of aromatic hydrocarbons was performed over Co/LSAO catalyst in this work. In addition, this catalyst has been characterized based on isotope transient tests, FT-IR, STEM, Arrhenius plot, and partial pressure dependence. Based on these results, stable catalytic activity and metal-support interaction are discussed for Co/LSAO.

2. Experimental

2.1. Catalyst preparation

Perovskite-type oxide, La_{0.7}Sr_{0.3}AlO_{3-δ} (LSAO) for catalyst support was prepared using the citric acid complex method. More details related to the citric acid complex method were explained in previous reports [48,49,51]. The obtained LSAO support was impregnated with a solution of cobalt (II) nitrate (Kanto Chemical Co. Inc.). Subsequently, it was dried and calcined at 1073 K for 1 h. The Co impregnation was conducted likewise a Ni impregnation method explained elsewhere [48,49,51]. The size of the obtained catalyst was adjusted to 250–500 μm with sieving.

2.2. Activity test

Catalyst activity tests were conducted in a tubular reactor, in which 25 mg of catalyst was charged into a fixed bed and diluted with SiO₂. After pre-reduction at 1073 K, toluene steam reforming was conducted at 873 K in the gas consist of 1.5% C₇H₈:21% H₂O:5% Ar:72.5% He vol% (total flow rate: 200 mL min⁻¹) for 180 min. Detailed information related to activity tests was presented in previous reports [48–50,52]. In such experimental conditions, the effect of mass transportation was negligible, as confirmed by our preliminary experiments. The product gas of this reaction was measured using GC-FID (GC-8A; Shimadzu Corp.) and GC-TCD (GC-8A; Shimadzu Corp.). Toluene conversion and H₂ yield were defined with a toluene feed rate (mmol s⁻¹) and the following formation rate of products: r_{CO} (mmol s⁻¹) for CO, r_{CH_4} (mmol s⁻¹) for CH₄, r_{CO_2} (mmol s⁻¹) for CO₂, r_{H_2} (mmol s⁻¹) for H₂.

$$\text{Toluene conversion (\%)} = \frac{r_{\text{CO}} + r_{\text{CH}_4} + r_{\text{CO}_2}}{\text{C}_7\text{H}_8 \text{ feed rate} \times 7} \times 100 \quad (3)$$

$$\text{H}_2 \text{ yield (\%)} = \frac{r_{\text{H}_2}}{\text{C}_7\text{H}_8 \text{ feed rate} \times 18} \times 100 \quad (4)$$

After the reaction for 180 min, the amount of deposited carbon was measured using temperature programmed oxidation (TPO) measurements using a thermogravimetry. The temperature was increased from 298 K to 1173 K at 10 K min⁻¹ in the gas composition of 90% N₂:10% O₂ vol% (total flow rate: 100 mL min⁻¹).

2.3. Isotopic transient response test

To evaluate the lattice oxygen mobility on the Co/LSAO catalyst, isotope transient tests were conducted. Details of the procedures used for isotopic transient tests have been

described [48–50,52]. Isotopic water was introduced with gas consisting of 1.5% C₇H₈:14.7% H₂¹⁶O:6.3% H₂¹⁸O:5% Ar:72.5% He vol% (total flow rate: 200 mL min⁻¹) to replace lattice oxygen in/on the LSAO support by ¹⁸O. After purging in an inert gas, the second reaction was conducted in the gas composition of 1.5% C₇H₈:21% H₂¹⁶O:5% Ar:72.5% He vol% (total flow rate: 200 mL min⁻¹). Products of the second reaction were detected using a quadrupole mass spectrometer (Q-Mass, HPR20; Hiden Analytical Ltd.). The observed signals of m/e were 2(H₂), 4(He), 15(CH₄), 18(H₂O), 20(H₂¹⁸O), 28(CO), 30(C¹⁸O), 40(Ar), 44(CO₂), 46(C¹⁶O¹⁸O), 48(C¹⁸O₂), 78(C₆H₆), and 91(C₇H₈). The effect of Ar²⁺ ($m/z=20$) signal to H₂¹⁸O was negligible [48–50,52]. The lattice oxygen release rate was calculated with signals of 30(C¹⁸O), 46(C¹⁶O¹⁸O), and 48(C¹⁸O₂).

2.4. Catalyst structure analysis

X-ray diffraction measurements (RINT-2000; Rigaku Corp.) were conducted to ascertain the perovskite-type structure of the obtained support using Cu Kα X-ray radiation of 40 kV at 20 mA. Results confirmed that all resulting catalyst supports had a perovskite structure. The supported Co metal particle size was measured using a scanning transmission electron microscopy (STEM; HF-2210; Hitachi Ltd.). More details related to STEM measurement have been explained in our earlier reports [50,52]. Metal particle diameter was obtained using hemisphere approximate measuring major axis and minor axis of ellipsoid-shaped particles. The most frequent value in a distribution chart of particle diameters (more than a hundred) was regarded as a mean particle size. Subsequently, a metallic surface area and a metal-support perimeter of the one hemisphere were calculated with the mean particle size obtained. After that, such values of a hemisphere were integrated to total metallic surface area and metal-support perimeter depending on loaded amount of the active metal.

2.5. Fourier transform infrared (FT-IR) measurement

Adsorbing features of toluene and reaction intermediates on the Co/LSAO catalyst were examined using a Fourier transform infrared spectrometer (FT/IR-6100; Jasco Corp.). A previous report has described details of the procedures of this measurement [51]. The Co/LSAO catalyst was shaped to a 20 mm φ disk. After pre-reduction at 1073 K and background measurement at 323 K, the feed gas was introduced through a bubbler within 2 mL min⁻¹ (gaseous) of toluene feed rate, then it was purged with N₂ gas [51]. Subsequently, the IR cell was heated and kept at 373, 473, 573, 673, 773, and 873 K for 10 min independently in N₂ gas. After each heating operation, the cell was cooled to 323 K. Then the IR spectrum was measured. Figures in a previous report present a comprehensive view of the relevant spectra [51].

2.6. Evaluating the reaction mechanism on Co supported LSAO catalyst

The apparent activation energy of toluene steam reforming on Co/LSAO was estimated using Arrhenius plots. Activity tests were conducted at temperatures of 723–923 K. The loaded amount of catalyst was decreased to 10 mg for obtaining kinetic values. The reaction rate was calculated from the formation rate of CO, CO₂, and CH₄ analyzed with GC-FID (GC-8A; Shimadzu Corp.).

Partial pressure dependences of the reaction rates on H₂O and toluene on the Co/LSAO catalyst were measured at each temperature: 748 K and 898 K. The feed gas composition was C₇H₈:H₂O:Ar:He = 1.5:(15, 21 or 27):5:(78.5, 72.5 or 66.5) vol% (total flow rate: 200 mL min⁻¹) and C₇H₈:H₂O:Ar:He = (1, 1.5 or 2):21:5:(73, 72.5 or 72) vol% (total flow rate: 200 mL min⁻¹)

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