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Oxidation resistance of Ni/La_{0.7}Sr_{0.3}AlO_{3-δ} catalyst for steam reforming of model aromatic hydrocarbon

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ABSTRACT

Oxidative resistance of Ni catalysts supported on various oxides La_{0.7}Sr_{0.3}AlO_{3-δ}, LaAlO₃, and α-Al₂O₃ were investigated for hydrogen production by steam reforming of model aromatic hydrocarbons. Ni/α-Al₂O₃ lost its steam reforming activity by oxidation treatment. In contrast, Ni/La_{0.7}Sr_{0.3}AlO_{3-δ} and Ni/LaAlO₃ catalysts showed steam reforming activity even after the oxidation treatment. The XANES (X-ray absorption near-edge structure) spectra at Ni K-edge for Ni/La_{0.7}Sr_{0.3}AlO_{3-δ} and Ni/α-Al₂O₃ after oxidation treatment revealed that the supported Ni on La_{0.7}Sr_{0.3}AlO_{3-δ} and α-Al₂O₃ were oxidized completely. Although the mean particle size of Ni on Ni/α-Al₂O₃ increased by oxidation treatment or reduction treatment, Ni particles on Ni/La_{0.7}Sr_{0.3}AlO_{3-δ} retained the fine structure after oxidation treatment or reduction treatment. Moreover, TPR (temperature programmed reduction) and XPS (X-ray photoelectron spectroscopy) measurements for elucidating the reducibility of Ni/La_{0.7}Sr_{0.3}AlO_{3-δ} showed that the supported Ni on La_{0.7}Sr_{0.3}AlO_{3-δ} was easily reduced even after the oxidation treatment.

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1. Introduction

Hydrogen, which is used for petroleum refining, ammonia synthesis and other important uses, is now regarded as an important alternative secondary energy source for the future. On-site hydrogen production systems and storage/distribution of hydrogen are critical issues to realize a hydrogen society. For feeding hydrogen to fuel cells, many studies have been conducted for producing hydrogen by reforming hydrocarbons, which can be supplied through a well-established infrastructure. Hydrocarbons intended for use as hydrogen resources include natural gas, liquefied petroleum gas, gasoline, kerosene, diesel oil and others. Of those, the availability

of liquid fuels such as kerosene is favorable in terms of convenience and cost.

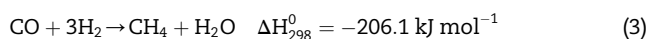
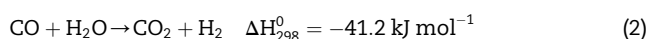
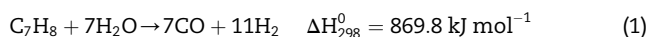
Generally, active metals for steam reforming are, Rh [1–6], Ru, Pt, and Ni [7–23], in which Ni is applied considering its high activity and low price. Ni is more sensitive to coke formation than noble metals, especially in the case of using liquid fuel [7–9]. Many studies for suppressing coke formation on Ni catalyst are conducted by adding second metals to Ni catalyst [10–13] and selecting support having good coke tolerance [14–23]. Urasaki et al. [23] investigated catalytic activity and resistance to coking in the steam reforming of methane over Ni perovskites. They concluded that the lattice oxygen in perovskite plays important roles in

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promoting the oxidation of coke precursor adsorbed onto metallic nickel.

In this study, we examined the steam reforming of toluene as a model compound of liquid fuel including aromatic hydrocarbon over Ni/perovskite catalyst. Recently, some researches have been conducted for efficient reforming of toluene as a model compound of aromatics which are included in liquid fuel or biomass-derived products [24,25]. Steam reforming of toluene is an endothermic reaction (1). Following (1), water–gas shift reaction (2) and methanation reaction (3) proceed.



In our previous reports [26,27], Ni/LaAlO₃ catalyst showed higher toluene conversion than either Ni/ α -Al₂O₃ or Ni/La₂O₃. However, the amount of coke formation on Ni/LaAlO₃ was greater than that on Ni/ α -Al₂O₃. Therefore, we attempted to improve the catalytic performance by partial substitution of La with Sr. Results show that, from Ni/LaAlO₃ to Ni/La_{0.7}Sr_{0.3}AlO_{3- δ} , toluene conversion sharply increased and the coke formation sharply decreased. The lattice oxygen of La_{0.7}Sr_{0.3}AlO_{3- δ} worked as an active oxygen for the oxidation of carbon species on Ni at 873 K, this phenomenon was evidenced by transient response test with H₂¹⁸O.

In a stationary fuel cell system used for a home, the system is started up and shut down daily for the system using polymer electrolyte fuel cells (PEFC), or monthly for the system using solid oxide fuel cells (SOFC). After shut down of the fuel reformer, the reformer is purged with air through the exhaust line. Thereby, the steam reforming catalyst in the fuel reformer is exposed to air. Considering this matter, oxidative resistance is necessary for the steam reforming catalyst. Generally, Ni catalysts are easily oxidized and thereby lose their steam reforming activity [28]. Previously, many studies examining the imparting of oxidative resistance to Ni catalyst were conducted by adding second metals to Ni catalyst [29–34] and by modifying support [35,36]. Tomishige et al. [29–33] investigated the effect of noble metals (Rh, Pt, Pd) added to Ni catalyst on catalytic activity and carbon deposition in oxidative steam reforming of methane. They concluded that the alloyed noble metal–Ni particles had high resistance to deactivation by oxidation and carbon formation. Takehira et al. [35] investigated auto-thermal reforming of methane over supported Ni catalyst prepared from Ni-incorporated Mg–Al hydrotalcite-like compound as a precursor. They concluded that Ni species on Ni/hydrotalcite catalyst are stable even under the presence of oxygen by the high dispersion of Ni.

In this report, as a part of a robustness assessment of Ni/La_{0.7}Sr_{0.3}AlO_{3- δ} , the oxidative resistance test in steam reforming reaction of toluene over Ni/La_{0.7}Sr_{0.3}AlO_{3- δ} was conducted in comparison to Ni/LaAlO₃ and Ni/ α -Al₂O₃. We investigated the causes of oxidative resistance of Ni/La_{0.7}Sr_{0.3}AlO_{3- δ} by examining the state of Ni after calcination, oxidation treatment using XAFS (X-ray absorption fine

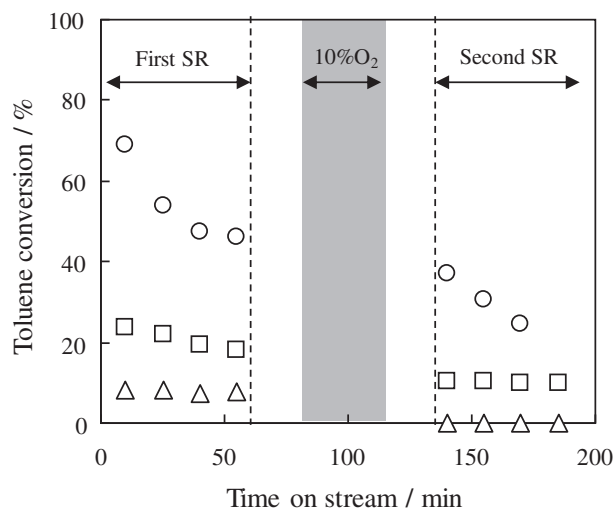


Fig. 1 – Effect of oxidative treatment for catalytic activities on Ni/La_{0.7}Sr_{0.3}AlO_{3- δ} (○), Ni/LaAlO₃ (□), and Ni/ α -Al₂O₃ (△). Reaction conditions, W/F: 3.4 g h mol⁻¹, S/C: 2.0, reaction temperature: 873 K, oxidative treatment, O₂/Ar: 5/45 mL min⁻¹, temperature, 873 K.

structure), TEM (transmission electron microscope), TPR (temperature programmed reduction), and XPS (X-ray photoelectron spectroscopy).

2. Experimental

2.1. Catalyst preparation

Perovskite-type oxides (LaAlO₃ and La_{0.7}Sr_{0.3}AlO_{3- δ}) were prepared using a citric acid complex method. The metal nitrates (Kanto Chemical Co. Inc.) were dissolved into water. Then citric acid and ethylene glycol (Kanto Chemical Co. Inc.) were added to the solution. The molar ratio of total metal ion: citric acid: ethylene glycol was 1:3:3. The solution was evaporated to a gel. Then the gel was dried and pre-calcined at 673 K for 2 h and calcined at 1123 K for 10 h. The α -Al₂O₃ support was formed by calcined γ -Al₂O₃ (JRC-ALO-8) at 1573 K

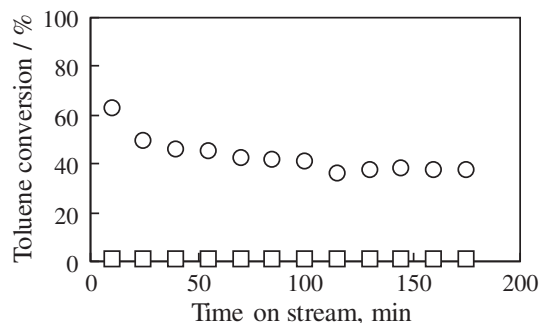


Fig. 2 – Effect of pre-reduction for catalytic activities on Ni/La_{0.7}Sr_{0.3}AlO_{3- δ} with pre-reduction (○), without pre-reduction (□), reaction conditions; W/F: 3.4 g h mol⁻¹, S/C: 2.0, reaction temperature: 873 K.

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