Toluene steam reforming reaction on Co supported perovskite catalyst

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Abstract: Steam reforming of toluene as a model compound of biomass tar on various Co supported perovskite catalysts were conducted to evaluate function of supports. Among Co catalysts supported on various perovskite oxides, $Co/La_{0.7}Sr_{0.3}AlO_{3-\delta}$ showed the highest activity. STEM measurements and XPS measurements revealed the coexistence of La ion and lattice oxygen defect brought an anchoring effect to supported metal. $H_2{}^{18}O$ steady-state isotopic transient kinetic analyses and water dissociation rate analyses using ^{18}O revealed a high lattice oxygen release rate and a water dissociation rate induce high catalytic activities. The anchoring effect and redox property are important for the high catalytic performance of $Co/La_{0.7}Sr_{0.3}AlO_{3-\delta}$ catalyst on toluene steam reforming.

Keywords: Toluene steam reforming, Perovskite-type oxides, Hydrogen production.

1. Introduction

Catalytic steam reforming is a practical way for producing hydrogen and carbon monoxide from biomass. Aromatic hydrocarbons included in the biomass are less reactive and are liable to form coke on a catalyst surface during a reforming reaction1). Therefore, controlling coke deposition is extremely important for steam reforming of aromatic hydrocarbons, such as toluene, phenol, and naphthalene. We have found that metal catalysts supported on $La_{0.7}Sr_{0.3}AlO_{3-\delta}$ showed high catalytic activities for toluene steam reforming with less coke formation because of its characteristics of metal and $La_{0.7}Sr_{0.3}AlO_{3-\delta}$ support1-3). For this study, Co metal was supported on various perovskite-type oxides to elucidate functions of catalyst supports.

2. Experimental

All perovskite-type oxide catalyst supports were prepared using a citric acid complex method. The obtained perovskite-type oxide supports were impregnated with a solution of cobalt nitrates. Subsequently, it was dried and calcined at 1073 K for 1 h. The particle size of the obtained catalyst was adjusted to 250-500 μm with sieving.

Catalyst activity tests were conducted in a tubular reactor, in which 25 mg of catalyst was charged into a fixed bed and diluted with SiO_2. Steam reforming was conducted at 873 K after pre-reduction at 1073 K. The reaction gas composition was C_7H_8:H_2O:Ar:He = 1.5:21:5:72.5 (vol%), with a 200 mL min^{-1} total flow rate and 180 min time on stream. The product gas of this reaction was analyzed using a GC-FID (GC-8A; Shimadzu Corp.) and a GC-TCD (GC-8A; Shimadzu Corp.). To evaluate the catalyst characteristics, $H_2{}^{18}O$ steady-state isotopic transient kinetic analyses, OH dissociation rate analyses using $^{18}O_2$, XRD, STEM, BET and XPS measurements were conducted.

3. Results and discussion

Toluene steam reforming reaction was conducted on several 10wt% Co catalysts supported on various perovskite-type oxides ($La_{0.7}Sr_{0.3}AlO_{3-\delta}$, $La_{0.7}Ca_{0.3}AlO_{3-\delta}$, $La_{0.7}Ba_{0.3}AlO_{3-\delta}$, $LaAlO_3$, Sr/$LaAlO_3$, $LaAl_{0.7}Zn_{0.3}O_{3-\delta}$, $SrTiO_3$, $SrTi_{0.7}Fe_{0.3}O_{3-\delta}$, $SrZrO_3$ and $SrCe_{0.5}Zr_{0.5}O_{3-\delta}$). Figure 1 presents the time course of catalytic activities of toluene steam reforming over these catalysts. $Co/La_{0.7}Sr_{0.3}AlO_{3-\delta}$ catalyst showed the highest toluene steam reforming activity stably among these catalysts.

To evaluate its high catalytic activity on $Co/La_{0.7}Sr_{0.3}AlO_{3-\delta}$, structures of various catalysts were observed with STEM measurements. STEM measurements and XPS measurements indicated the coexistence of La ion and lattice oxygen defects might contribute to fine dispersion of Co metal particles. For confirmation of the anchoring effect between Co particles and supports, STEM measurements after reduction at 1073 K for 30 min and oxidation at 1073 K for 30 min, followed by second reduction at 1073 K for 30 min, were conducted. As a result, a major part of Co particles remained small on the support in which La ion and lattice oxygen defects coexisted. These results ensured that Co particles were anchored on the support possessing La ions and lattice oxygen defects.

Next, the redox property for these catalysts was investigated. $H_2{}^{18}O$ steady-state isotopic transient kinetic analysis was conducted on each catalyst. As a result, a linear correlation was found between the toluene conversion rate and the lattice oxygen release rate. In addition, $Co/La_{0.7}Sr_{0.3}AlO_{3-\delta}$ catalyst showed a higher lattice oxygen release rate than that of either $Co/La_{0.7}Ca_{0.3}AlO_{3-\delta}$ or $Co/La_{0.7}Ba_{0.3}AlO_{3-\delta}$. This tendency was the same as that found for the mobile oxygen ratio. From these data, it can be inferred that the Co catalyst supported on $La_{0.7}Sr_{0.3}AlO_{3-\delta}$ can decompose toluene using mobile oxygen well if the supported metal particles are highly dispersed. In the redox mechanism, it is important that circulation of the release and regeneration of oxygen species in/on support. Lattice oxygen must be filled by water dissociation. Therefore, the water dissociation rate was analyzed using isotopic ^{18}O. As a result, all substituted perovskite supports showed higher water dissociation rates than the unsubstituted one, so it can be inferred that water dissociation occurs on the lattice oxygen defect. Considering the release and regeneration rates of lattice oxygen, the redox property is connected to the catalytic activity.

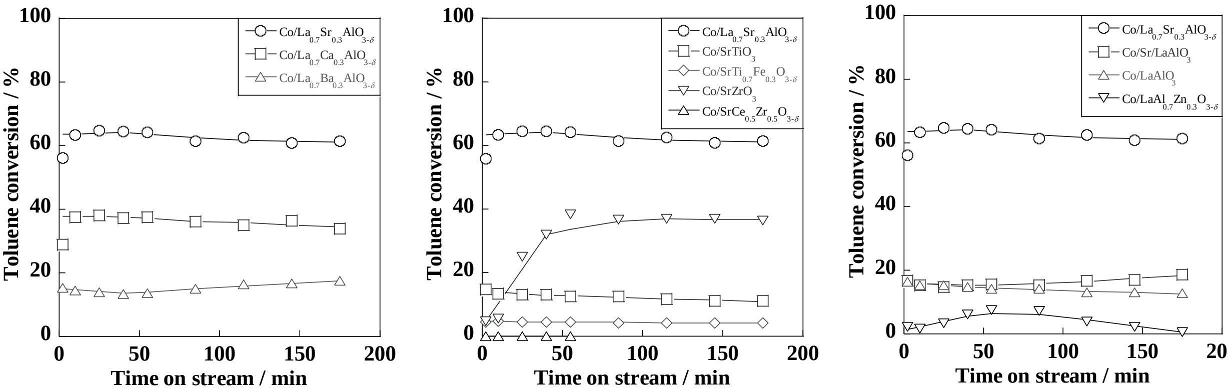

Figure 1. Results of activity tests on various Co supported perovskite-type oxide catalysts. Co loading amount: 10 wt%. Reaction conditions: 873 K reaction temperature, S/C = 2.0 [3].

4. Conclusions

$Co/La_{0.7}Sr_{0.3}AlO_{3-\delta}$ catalyst showed the highest toluene steam reforming activity stably among various Co supported perovskite catalysts. This high activity was attributable to the Co metal anchoring effect and the high redox property over $Co/La_{0.7}Sr_{0.3}AlO_{3-\delta}$. STEM measurement revealed that the coexistence of La ion and lattice oxygen defect were both important for Co metal dispersion on perovskite. $H_2{}^{18}O$ steady-state isotopic transient kinetic analysis and OH dissociation rate analysis using ^{18}O revealed that the redox property is connected to the catalytic activity.

References

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