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Effect of Hydrocarbon Structure on Steam Reforming over Ni/perovskite Catalyst

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Ni/perovskite-type oxide catalyst (Ni/La_{0.7}Sr_{0.3}AlO_{2.85}:LSAO) shows high catalytic activity and low carbon formation during the steam reforming of aromatic hydrocarbons because of the high mobility of lattice oxygen in the support. The reaction mechanisms of the catalyst were investigated by characterizations and catalytic activity tests for steam reforming of various hydrocarbons including toluene, methylcyclohexane, and *n*-heptane. The catalytic performance was affected by the reactant structure, as revealed by Arrhenius plots and FT-IR analyses. Adsorption state and stability of reaction intermediates were very important factors in the catalytic activity for steam reforming.

Keywords

Hydrocarbon steam reforming, Nickel catalyst, Hydrogen production, Adsorption state, SSITKA

1. Introduction

Hydrogen production by steam reforming of hydrocarbons has been extensively investigated^{1)–7)}. Steam reforming of hydrocarbon has been commercialized on a large scale, but is very energy intensive. Moreover, the catalyst is deactivated by coking. Recently, hydrogen has attracted increasing attention as a clean energy carrier and biomass utilization has become important as an energy source. Biomass gasification for hydrogen or syngas production requires the removal of biomass tar, which causes plugging of the reactor or fouling. Steam reforming of biomass tar, which contains aromatic compounds, is an effective method.

Nickel catalyst is widely regarded as a promising catalyst for the steam reforming of biomass tar because of its low cost. However, nickel catalyst suffers from some crucial problems associated with carbon deposition, such as decreased catalytic activity and coke accumulation. Coke deposits are especially caused by the reaction of aromatic compounds^{6),8)–10)}. Most carbon is gasified, but some is converted to less active compounds. Formation of whisker carbon will separate the nickel from the catalyst surface^{11),12)}. To improve the carbon resistance, alkali metals (K, Ca)¹³⁾ and transition metals (Mo, W)^{14),15)} have been added as carbon

inhibitors. Addition of a small amount of platinum as a second metal to the nickel catalyst enabled the formation of a bimetallic structure between Pt and Ni, and suppression of carbon deposition¹⁶⁾.

Perovskite type oxide (ABO₃) was investigated as the support for nickel catalyst in the steam reforming of CH₄¹⁷⁾. LaAlO₃ (LAO) had high activity and inhibited carbon deposition. Perovskite-type oxides have lattice oxygen conductivity which may have promoted the oxidation of CH₄ and inhibited carbon deposition. Our previous studies revealed that perovskite-type oxides are an effective catalyst support for the steam reforming of aromatic compounds (toluene), as Ni/La_{0.7}Sr_{0.3}AlO_{2.85} (LSAO) showed high activity and carbon resistance^{18),19)}. Isotope exchange experiments (H₂¹⁸O) revealed that the lattice oxygen mobility was improved by partial substitution of La³⁺ with Sr²⁺²⁰⁾.

In this study, various hydrocarbons, including aromatics, alkanes, and naphthene, were used as reactants to compare catalytic activity and the involvement of lattice oxygen to assess the reaction mechanism of steam reforming of toluene over Ni/LSAO catalyst.

2. Experimental

Perovskite-type oxides (LSAO and LAO) were prepared using a citric acid complex method with metal nitrate. Metal nitrate precursors (Kanto Chemical Co., Inc.) were dissolved in water. Then, excess citric acid and ethylene glycol (Kanto Chemical Co., Inc.) were

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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 348 K for 16 h. The product was dried on a hot plate with stirring for 1 h and dried in an oven at 393 K for 14 h. The dried powder was pre-calcined at 673 K for 2 h, then calcined at 1123 K for 10 h. Support for the reference catalyst (Ni/ α -Al₂O₃), α -Al₂O₃, was obtained by calcination of γ -Al₂O₃ (JRC-ALO-8) at 1623 K for 3 h. Perovskite and α -Al₂O₃ were impregnated with a solution of nickel nitrate precursors (Kanto Chemical Co., Inc.), dried and calcined at 1073 K for 1 h. Structures of catalysts were observed using X-ray diffraction (XRD, RINT-2000; Rigaku Corp.). The BET-specific surface area was measured using N₂ adsorption at 77 K (Autosorb-1; Quantachrome Instruments). Metallic dispersion of nickel was measured using CO adsorption (BEL-CAT-55; Bel Japan Inc.).

Three C₇ hydrocarbons were used as reactants: *n*-heptane (Kanto Chemical Co., Inc.) as an alkane, methylcyclohexane (Kanto Chemical Co., Inc.) as a naphthene, and toluene (Kanto Chemical Co., Inc.) as an aromatic compound. Catalytic activity tests for steam reforming of hydrocarbons were conducted in a fixed bed quartz reactor at atmospheric pressure. Catalysts were sieved to 250–500 μ m and diluted with SiO₂. SiO₂ was confirmed to be inert under this condition by preliminary experiments. The standard feed gas composition and conditions were as follows: reactant 1.5 %; H₂O 21 %; Ar 5 %; He 72.5 %, total flow rate of 200 mL min⁻¹ (SATP) and GHSV about 6000 h⁻¹. Limitation for mass transport was negligible under this condition, as confirmed by our preliminary experiments. Pre-reduction was conducted in H₂ 10 % : Ar 90 %, with total flow rate of 200 mL min⁻¹ (SATP) at 1073 K for 0.5 h. Formation rates of products were analyzed using quadrupole mass spectroscopy (Q-mass, HPR20; Hiden Analytical Ltd.) and gas chromatograph hydrogen-flame ionization detector (GC-FID, GC-8A; Shimadzu Corp.) Ar was added as an internal standard gas for detection by the Q-mass. The analyzed *m/e* was 2(H₂), 4(He), 15(CH₄), 18(H₂O), 28(CO), 40(Ar), 44(CO₂), 78(C₆H₆), 91(C₇H₈), 98(C₇H₁₄), and 100(C₇H₁₆). Hydrocarbon conversion and selectivity for products were defined as shown below.

$$\text{Hydrocarbon conversion (\%)} = \frac{r_{\text{CO}} + r_{\text{CH}_4} + r_{\text{CO}_2}}{7 \times \text{hydrocarbon feed}} \times 100 \quad (1)$$

$$\text{Selectivity to product (\%)} = \frac{\text{formation rate of each product}}{r_{\text{CO}} + r_{\text{CH}_4} + r_{\text{CO}_2}} \times 100 \quad (2)$$

In this equation, *r* denotes the formation rate of each product. The amount of carbon deposition on the catalysts was determined by detecting CO and CO₂ formation during the temperature-programmed oxidation (TPO). The feed gas composition was N₂ 90 % : O₂ 10 %, and the total flow rate was 100 mL min⁻¹ (SATP).

The rate of temperature increase was 10 K min⁻¹.

Transient response tests using H₂¹⁸O (steady state isotopic transient kinetic analyses, SSITKA method^{21),22}) were conducted to assess the reactivity of lattice oxygen in the perovskite oxides. After pre-reduction at 1073 K for 30 min, SSITKA tests were conducted in the following steps. The first reaction for the replacement of lattice oxygen with isotope used reactant 1.5 % : H₂¹⁸O 6.3 % : H₂¹⁶O 14.7 % : Ar 5 % : He 72.5 %; total flow rate of 200 mL min⁻¹ (SATP) for 30 min, after 2 h purge with He to remove surface adsorbate. The second reaction used reactant 1.5 % : H₂¹⁶O 21 % : Ar 5 % : He 72.5 %; total flow rate of 200 mL min⁻¹ (SATP).

The adsorption state of the adsorbate on the catalyst was observed using a Fourier transform infrared spectrometer (FT/IR-6100; Jasco Corp.). The calcined catalyst was pressed and shaped into a 20 mm ϕ disk. Pre-reduction was conducted in H₂ 10 % : N₂ 90 %, with total flow rate of 50 mL min⁻¹ (SATP), at 1073 K for 30 min. The disk was cooled to 323 K in N₂. Then the background spectrum was measured. The reactant was introduced into the IR cell for 10 min and purged with N₂ for 30 min. The reactant feed was adjusted to 2 mL min⁻¹ (SATP) and was diluted with Ar. Then, IR cells were heated to 373, 473, 573, 673, 773, and 873 K, and maintained at each temperature for 10 min. The IR spectrum was measured after the disk was cooled to 323 K.

3. Results and Discussion

3.1. Catalyst Performance and Reactivity for Steam Reforming

Steam reforming of various C₇ hydrocarbons including toluene, methylcyclohexane, and *n*-heptane was performed over Ni/LSAO, Ni/LAO, and Ni/ α -Al₂O₃ catalysts. **Table 1** presents the results of the activity test and amount of carbon deposition on the catalyst after reaction for 180 min. Ni/LSAO catalyst had high activity and low coke accumulation for all reactants, whereas Ni/LAO and Ni/ α -Al₂O₃ showed low activity and high coke accumulation. Differences in the catalytic activity and coke formation were found for alkane, naphthene, and aromatic compounds. The effects of the catalyst structure on the catalytic activity and coke formation were evaluated by measuring the BET-specific surface area, Ni dispersion from CO pulse measurement, and mean particle size of Ni metal from scanning transmission electron microscope (STEM) images as shown in **Table 2**. The Ni metal particles on LSAO were much smaller than those on LAO or α -Al₂O₃. Furthermore, the Ni particle size on LSAO remained stable before and after the reforming reaction, but the Ni particles on LAO and α -Al₂O₃ were enlarged and aggregated. Such findings indicate that Ni metal on LSAO has a stable dispersed structure²³) because of the

Table 1 Catalytic Activities of Ni/La_{0.7}Sr_{0.3}AlO_{2.85}, Ni/LaAlO₃ and Ni/ α -Al₂O₃ for Steam Reforming of Three Reactants, and Carbon Deposition after Reaction for 180 min: W/F = 3.4 g h mol⁻¹, S/C = 2.0, Reaction Temperature: 873 K, and Ni Loading: 5 wt%

Reactant	Catalyst	Initial conversion	Selectivity			Amount of carbon deposition [mg g cat ⁻¹]
			CO	CH ₄	CO ₂	
Heptane	Ni/La _{0.7} Sr _{0.3} AlO _{2.85}	77.8	43.9	5.3	50.8	1
	Ni/LaAlO ₃	50.8	36.4	2.9	60.6	324
	Ni/ α -Al ₂ O ₃	25.5	29.0	0.83	70.2	713
Methylcyclohexane	Ni/La _{0.7} Sr _{0.3} AlO _{2.85}	76.6	40.8	7.7	51.5	6
	Ni/LaAlO ₃	63.9	36.5	7.7	55.7	489
	Ni/ α -Al ₂ O ₃	18.1	34.5	0.39	65.1	455
Toluene	Ni/La _{0.7} Sr _{0.3} AlO _{2.85}	73.0	40.8	7.4	50.8	37
	Ni/LaAlO ₃	35.9	42.1	0.17	57.7	278
	Ni/ α -Al ₂ O ₃	9.1	76.3	0	23.7	43

Table 2 BET Specific Surface Area of Supports, and Dispersion and Particle Size of Supported Ni

Support/catalyst	BET surface area [m ² g ⁻¹]	Ni dispersion [%]	Ni mean particle size [nm]
La _{0.7} Sr _{0.3} AlO _{2.85} (LSAO)	13.4	-	-
Ni/LSAO	-	5.8	9
LaAlO ₃ (LAO)	6.3	-	-
Ni/LAO	-	3.0	22
α -Al ₂ O ₃	3.6	-	-
Ni/ α -Al ₂ O ₃	-	2.4	15

interaction between the LSAO support and the Ni metal particles.

Less carbon deposition on Ni/LSAO after steam reforming for all reactants probably resulted from the higher lattice oxygen mobility in perovskite oxide caused by partial displacement of La³⁺ with Sr²⁺ which increased the carbon removal activity^{17,18}. The coking rate is well known to increase with olefin and aromatic reactants^{6,12}, but on Ni/LAO and Ni/ α -Al₂O₃, the amount of carbon deposition was greater even with alkane and naphthene. This finding might depend on the balance between the decomposition rate of hydrocarbon to form an intermediate (C _{α}) and the reaction rate of C _{α} on the catalyst surface.

3.2. Apparent Activation Energy and Lattice Oxygen

Arrhenius plots for steam reforming of alkane, naphthene, and aromatic compounds were constructed to elucidate the difference in the reactivity for three hydrocarbons (toluene, methylcyclohexane, *n*-heptane). The apparent activation energies were calculated to assess the reaction pathway, and the reaction was conducted within the kinetic region (*i.e.* lower conversion). **Figure 1** shows the Arrhenius plots for steam reforming of alkane (*n*-heptane), naphthene (methylcyclohexane), and aromatic compound (toluene) over Ni/LSAO and Ni/LAO catalysts. The apparent activation energy changed between high and low temperatures in a specific temperature range of around 800-1000 K¹⁹, *i.e.* the apparent activation energy changed at 803 K on Ni/LSAO, and at 936 K on Ni/LAO. This change in apparent activation energy reflects the change in the rate

limiting step. The reaction mechanism changed from the Langmuir-Hinshelwood (L-H) model at low temperature to the redox model (using lattice oxygen) at high temperature, which resulted from the higher lattice oxygen mobility^{18,19}. The partial pressure dependencies of steam and aromatic compound were measured to identify the rate limiting step. Activation of steam was the rate limiting step in the L-H model at low temperatures, and activation of aromatic compounds was the rate limiting step in the redox model at high temperatures²⁰. Steam reforming was promoted by higher lattice oxygen mobility, and adsorption and cracking of aromatic compounds were the rate limiting steps at high temperatures. Changes in the apparent activation energy between high and low temperatures were also confirmed for only alkane and naphthene over Ni/LSAO, which is similar to the findings for aromatic compounds. The switching temperature was at 833 K for alkane, at 819 K for naphthene, and at 803 K for the aromatic compound. These similar temperatures indicate that the change in reaction mechanism apparently depends on the lattice oxygen mobility of Ni/LSAO. Furthermore, the apparent activation energies for alkane and naphthene were lower than that for aromatic compounds in the low temperature range because of the structure of the hydrocarbons, *i.e.* alkane and naphthene are easier to decompose than toluene.

The Arrhenius plots showed different trends over Ni/LAO compared to Ni/LSAO. The apparent activation energy changed at around 940 K for steam reforming of aromatic compound, but did not change between high and low temperatures for alkane and naphthene. The

Fig. 1 Arrhenius Plots for *n*-Heptane Steam Reforming over (a) $Ni/La_{0.7}Sr_{0.3}AlO_{2.85}$ and (b) $Ni/LaAlO_3$, for Methylcyclohexane (MCH) Steam Reforming over (c) $Ni/La_{0.7}Sr_{0.3}AlO_{2.85}$ and (d) $Ni/LaAlO_3$, and for Toluene Steam Reforming over (e) $Ni/La_{0.7}Sr_{0.3}AlO_{2.85}$ and (f) $Ni/LaAlO_3$

values were 61.6 kJ mol^{-1} for alkane and 52.9 kJ mol^{-1} for naphthene, respectively, which are intermediate between the values of 48 kJ mol^{-1} at high temperatures

and 121 kJ mol^{-1} at low temperatures for the aromatic compound.

To investigate the role of the lattice oxygen in the

Fig. 2 Formation of ^{18}O Products over $\text{Ni/La}_{0.7}\text{Sr}_{0.3}\text{AlO}_{2.85}$ during Steam Reforming (SR), Steady State Isotopic Transient Kinetic Analyses (SSITKA) for Various Reactants: S/C = 2.0

perovskite, lattice oxygen mobility was confirmed by H_2^{18}O isotope exchange transient experiments during steam reforming of the hydrocarbons. The production rates of ^{18}O species including H_2^{18}O , C^{18}O , $\text{C}^{16}\text{O}^{18}\text{O}$,

and C^{18}O_2 were measured by SSITKA over Ni/LSAO (Fig. 2) and Ni/LAO (Fig. 3). In these experiments, the ^{18}O products originated from the lattice oxygen in the perovskite. Large amounts of ^{18}O species were

Fig. 3 Formation of ^{18}O Products over Ni/LaAlO₃ during Steam Reforming (SR), Steady State Isotopic Transient Kinetic Analyses (SSITKA) for Various Reactants: S/C = 2.0

detected from Ni/LSAO at 873 K (corresponding to high temperature in the Arrhenius plot) for alkane, naphthene, and aromatic compound. The formation of $\text{C}^{16}\text{O}^{18}\text{O}$ and C^{18}O species indicates that the reaction proceeds *via* the redox mechanism using lattice oxygen of the perovskite support. Furthermore, lower ^{18}O release was detected at 748 K (corresponding to low temperature in the Arrhenius plot) over Ni/LSAO,

which indicates that the main reaction path has changed from the redox mechanism at high temperatures to the L-H mechanism at low temperatures. This phenomenon coincided with the change of apparent activation energy from low temperatures to high temperatures.

Release of ^{18}O species was observed on Ni/LAO only at 973 K (high temperatures in Arrhenius plot) for toluene, but not at 823 K (low temperatures in Arrhenius

Fig. 4 IR Spectra during Temperature Programmed Desorption of Various Reactants over $\text{Ni/La}_{0.7}\text{Sr}_{0.3}\text{AlO}_{2.85}$

plot), as depicted in **Fig. 3**. Therefore, lattice oxygen release directly affects the reaction mechanism, changing the apparent activation energy even on Ni/LAO in the case of aromatic compounds. However, no ^{18}O species was detected at 973 K or at 823 K for alkane and naphthene over Ni/LAO, which indicates lattice oxygen is not involved in the reaction at temperature and no change in the mechanism occurs between high and low temperatures. These phenomena might depend on the interaction between the reactant and the lattice oxygen release behavior. Steam reforming of aromatic compounds on Ni/LAO at high temperatures involves

lattice oxygen, and the apparent activation energy becomes lower (48 kJ mol^{-1}) than that of other reactants ($61.6, 52.9 \text{ kJ mol}^{-1}$). The low value of the apparent activation energy for aromatic compound at high temperature might depend on the adsorption state of the reactant on the catalyst surface and the interaction between the adsorbate and lattice oxygen.

3.3. Adsorption of Reactants and Reaction Mechanism on the Ni/LSAO

3.3.1. Relationship between Reactant Adsorption and Catalytic Activity

We examined whether the catalytic activity recovers or not after Ar purge over these three catalysts. Deactivation was not irreversible (*i.e.*, no sintering or migration of Ni) which might depend on strong adsorption of reactant or intermediate on the catalyst surface (results not shown). Therefore, the adsorption state of hydrocarbon on these catalysts was investigated. The adsorption state of the reactant is extremely important to ascertain the surface properties of highly active Ni/LSAO catalyst. Adsorption of *n*-heptane (alkane), methylcyclohexane (naphthene), and toluene (aromatic compound) on Ni/LSAO, Ni/LAO, and Ni/ α - Al_2O_3 was investigated using *in-situ* IR measurement. The IR spectra obtained after adsorption of reactant, and heating and cooling the catalyst are shown in **Fig. 4** (Ni/LSAO), **Fig. 5** (Ni/LAO), and **Fig. 6** (Ni/ α - Al_2O_3). Three peaks were observed for *n*-heptane temperature-programmed desorption (TPD) on Ni/LSAO (**Fig. 4**) at 1573, 1466, and 1406 cm^{-1} . The peak at 1466 cm^{-1} is assigned to the C-C vibration, and 1406 cm^{-1} to the COO asymmetric stretching vibration²⁴). In addition, adsorption peaks were observed for methylcyclohexane TPD at 1516, 1469, and 1396 cm^{-1} , and for toluene at 1478 cm^{-1} and 1400 cm^{-1} . Peaks at around 1470 cm^{-1} and 1400 cm^{-1} were observed for all reactants. Peaks for *n*-heptane TPD on Ni/LAO (**Fig. 5**) were observed around 1556–1587 cm^{-1} and 1348 cm^{-1} . Peaks for methylcyclohexane were observed at 1564 cm^{-1} and 1347 cm^{-1} , similar to the case of *n*-heptane. However, peaks for toluene²⁴) were observed at 1594, 1546, and 1401 cm^{-1} , in contrast to the other catalysts. These differences in the spectra indicate different conditions for the reaction intermediate and variations in the apparent activation energies, as described in section 3.2.

We can assess the stability of the adsorbate on these catalysts from these spectra. The adsorption peaks became larger with increasing temperatures from 373 to 773 K despite the active molecular vibration on Ni/LSAO catalyst (**Fig. 4**). After increasing the temperature to 873 K, the absorption decreased and the molecules were decomposed and desorbed. The adsorption peaks disappeared at 573 K for *n*-heptane and methylcyclohexane (**Fig. 5**), and at 773 K for toluene on Ni/LAO catalyst²⁴). The reactants did not strongly adsorb onto the catalyst, or rapidly desorbed because no peak

Fig. 5 IR Spectra during Temperature Programmed Desorption of *n*-Heptane and MCH over Ni/LaAlO₃

Fig. 6 IR Spectra during Temperature Programmed Desorption of *n*-Heptane and MCH over Ni/α-Al₂O₃

change was detected from low temperatures to high temperatures on Ni/α-Al₂O₃ (Fig. 6). These results revealed that adsorption stability was correlated with catalytic activity. This phenomenon indicates that the affinity between reactants and catalyst support is important in determining the reaction pathway and catalytic activity.

3.3.2. Adsorption State of Reactant and Reaction Intermediate

The stability of adsorbate on the catalyst depended both on the hydrocarbon structure and on the characteristics of the catalyst support surface as shown above. The LSAO support showed strong interaction with various reactants. The adsorption intermediate on LSAO was investigated by *in-situ* TPD-IR using various reactants including *n*-heptane, methylcyclohexane, and toluene. Furthermore, the interactions between LSAO and other organic compounds (for alkane: *n*-hexane, *n*-pentane and 2,2-dimethylbutane, for cycloalkane: methylcyclopentane) were investigated by *in-situ* TPD-IR to characterize the structure of the reaction intermediate.

Figure 7 shows the temperature-programmed desorption of various hydrocarbons on the LSAO support.

Specific desorption temperatures were 873 K for *n*-heptane, and 573 K for *n*-hexane. Pentane was only slightly adsorbed onto the surface of LSAO in this experiment. These results revealed that the interaction between reactants and LSAO surface varied between *n*-C₇, C₆ and C₅ hydrocarbons, and that *n*-C₇ hydrocarbon was strongly adsorbed but *n*-C₅ was not adsorbed on LSAO. Such a difference might depend on the intermediate structure, *i.e.* *n*-C₇ hydrocarbon can be converted into a stable cyclic intermediate structure, but not *n*-C₅. Such cyclization is a stabilization path for linear alkane on the LSAO support. However, the multi-branched hydrocarbon, 2,2-dimethylbutane, had a strong interaction with the surface.

The absorption of linear alkane and cycloalkane were compared as follows. Peaks were observed at 1503, 1470, and 1399 cm⁻¹ for *n*-heptane, and very similar peaks were observed at 1521, 1469, and 1403 cm⁻¹ for methylcyclohexane. In addition, peaks were observed at 1555 cm⁻¹ and 1340 cm⁻¹ for *n*-hexane, and very similar peaks at 1563, 1400, and 1340 cm⁻¹ for methylcyclopentane. These results indicate that *n*-heptane is

Fig. 7 IR Spectra during Temperature Programmed Desorption of Various Reactants over Bare $\text{La}_{0.7}\text{Sr}_{0.3}\text{AlO}_{2.85}$

adsorbed and stabilized as a six-membered ring structure on LSAO, and that *n*-hexane is adsorbed and stabilized as a five-membered ring structure on the LSAO

surface. These findings are consistent with the result for *n*-pentane (almost no adsorption) because *n*-pentane is hard to stabilize on the LSAO surface as a five-

Fig. 8 IR Spectra during Temperature Programmed Desorption of Toluene

membered ring due to the carbon number and does not form an unstable four-membered ring. The peak at 1550 cm^{-1} was probably a derivative of naphthene compounds, and reflects the difference between linear alkanes and cycloalkanes.

3. 3. 3. Adsorption Sites on LSAO Support

To elucidate the involvement of lattice oxygen and incorporation of Sr in perovskite, toluene TPD-IR spectra were observed on Sr/LAO and pre-oxidized LSAO support (Fig. 8), and compared with the spectra of pre-reduced LSAO (Fig. 7) to identify the adsorption sites of toluene on the LSAO support. LSAO and LAO are differentiated by the presence of lattice defects, which carry positive charge, and electron deficient sites caused by distortion of the lattice and surface Sr^{2+} sites. The desorption peaks on Sr/LAO (*i.e.* Sr^{2+} was not incorporated but supported on LAO) appeared at 1509 cm^{-1} and 1393 cm^{-1} , which were different to the peaks for toluene on LAO²⁴⁾. Therefore, the peaks observed for Sr/LAO adsorption are attributable to the adsorption of toluene on Sr^{2+} sites. However, the peaks on pre-oxidized LSAO (1073 K, 30 min) were observed at 1521 cm^{-1} and 1391 cm^{-1} , which were greatly different from the spectrum of pre-reduced LSAO containing lattice defects, but were just consistent with the peaks on Sr/LAO. These findings indicate that the toluene

Fig. 9 Reaction Pathway of Steam Reforming over Ni/La_{0.7}Sr_{0.3}AlO_{2.85} Catalyst

adsorption site is located at surface Sr^{2+} on LSAO support. Based on these results, we summarized the reaction pathway of toluene steam reforming on Ni/LSAO as shown in Fig. 9.

4. Conclusion

Perovskite-type oxide La_{0.7}Sr_{0.3}AlO_{2.85} (LSAO) has higher activity and lower carbon deposition as a support of nickel catalyst for steam reforming of various C₇ reactants compared to LaAlO₃ and alumina support. The Arrhenius plot of Ni/LSAO catalyst showed a

kinked curve, indicating that the apparent activation energy and reaction path changed between the low-temperature and high-temperature ranges because of the involvement of lattice oxygen in the reaction of any C₇ reactant. This result demonstrates that the reaction proceeds *via* a redox mechanism, and that the lattice oxygen is active in the suppression of carbon formation. However, distinct differences in lattice oxygen release were observed between aromatic and other compounds over Ni/LAO catalyst, which indicates that the structure of reactants is closely related to the ability of lattice oxygen release. FT-IR analyses indicated that C₇ reactants have high adsorption stability at the Sr²⁺ site on the LSAO surface, because of the formation of six-membered rings.

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要 旨

Ni/ペロブスカイト触媒を用いた水蒸気改質における炭化水素の構造の影響

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Ni/ペロブスカイト型酸化物触媒 (Ni/La_{0.7}Sr_{0.3}AlO_{2.85}) は、その担体の格子酸素易動性によって、芳香族炭化水素の水蒸気改質において高い転化率と低い炭素析出を示す。この触媒の反応メカニズムを詳細に解析するために、触媒のキャラクタリゼーションを行うとともに、トルエン、メチルシクロヘキサ

ン、*n*-ヘプタンの3種の炭化水素の水蒸気改質について比較した。結果として、アレニウスプロットやFT-IR解析から、これらの反応活性は構造と深い相関があることが分かった。反応中間体の表面への吸着とその安定性は、活性に対して重要な因子となることが分かった。