Selective Adsorption of Toluene on Perovskite-type Oxide

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Organic chemical hydrides are one of the most promising methods for hydrogen storage, but aromatic compound remains unreacted after the hydrogenation process due to equilibrium limitations. We attempted to develop a solid-state absorbent which could selectively absorb toluene from methylcyclohexane (MCH)-toluene mixture. Several La-based oxides were tested and La$_{0.8}$Ba$_{0.2}$CoO$_3$ (LBCO) was found to exhibit high adsorption and selectivity for toluene. Analyses of the electronic state and adsorption state of toluene found part of the Co ions in the LBCO lattice were Co$^{4+}$. Co$^{4+}$ in the lattice and surface lattice oxygen are important for the selective adsorption of toluene.

Keywords
Perovskite oxide, Organic hydride, Hydrogen storage, Selective adsorption, DFT calculation, XANES spectra

1. Introduction

Hydrogen has high potential as a carbon-free secondary energy source for the future, but hydrogen has low volumetric energy density under atmospheric pressure, which makes its transportation and storage difficult. Consequently, safe and efficient methods are required for transportation and storage of hydrogen. Several methods have been proposed such as liquid hydrogen, compressed hydrogen, ammonia, and so on, but almost all involve disadvantages in safety, efficiency and cost$^{[1]}$.

Organic chemical hydride has high hydrogen density, so is a good candidate for hydrogen transportation and storage. In this approach, naphthenic compounds such as methylcyclohexane (MCH) are used as the hydrogen carrier, and hydrogen is produced by reversible dehydrogenation. The naphthenic compounds used in this method are liquid at ambient temperature, and can be easily stored like gasoline. The MCH-toluene system is one of the proposed systems for the organic hydride method, which has low toxicity and remains liquid under most conditions. For these reasons, the MCH-toluene system is considered as the most promising candidate for the hydrogen carrier$^{[2,3]}$.

The reaction formula of toluene hydrogenation, which occurs in a hydrogen storage process, is shown in Eq. (1)

$$C_7H_8 + 3H_2 \rightarrow C_7H_{14} \quad \Delta H^o = -205 \text{ kJ mol}^{-1} \quad (1)$$

Hydrogenation of aromatics has been studied for several decades. This reaction is often performed in the gas phase$^{[4-8]}$ or the liquid phase$^{[9]}$. Recently, new aromatic hydrogenation processes have been studied for application to organic chemical hydride methods such as electrochemical hydrogenation$^{[10,11]}$. Although these technologies exhibit high conversion and selectivity for the hydrogenated product, unreacted aromatic compound remains in the hydrogenated product because of equilibrium limitations, and so causes energy efficiency loss in the organic hydride method. Therefore, purification after hydrogenation of aromatics is necessary for efficient hydrogen energy transportation. However, separation of benzene/cyclohexane or toluene/MCH mixtures by conventional distillation is difficult because these compounds form close boiling point mixtures$^{[12]}$. Other separation methods have been studied, such as membrane separation$^{[13-16]}$, but no adequate method to remove unreacted aromatic compound is available because the concentration in hydrogenated products is very low. Therefore, we evaluated adsorption processes for further separation of toluene.

Few studies have investigated the separation of toluene and MCH by selective adsorption, so we focused on the adsorption properties of solid state oxides. Toluene temperature programmed desorption (TPD) IR measurements revealed that adsorbed toluene remained on Ni/La$_{0.5}$Sr$_{0.5}$AlO$_{3-\delta}$ (LSAO) even at high tempera-
tures (～873 K)\(^1\). Consequently, La-based complex oxides such as LSAO are likely to have high toluene adsorption. In this study, selective adsorption of toluene was evaluated for La-based complex oxides, and their properties were studied.

2. Experimental

2.1 Preparation of Samples

La-based complex oxides were prepared using the Pechini method with metal nitrate (Kanto Chemical Co., Inc.). A stoichiometric mixture of metal nitrate precursors was dissolved in distilled water. 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 348 K for 16 h. The product was dried on a hot plate until the sample powder was obtained. This obtained powder was pre-calced at 673 K for 2 h, and then calcined at 1123 K for 10 h.

2.2 Pulsed-dosing Adsorption Test

The adsorption properties of the oxides for hydrocarbons were investigated using pulsed dosing adsorption tests of MCH-toluene (Kanto Chemical Co., Inc.) mixed gas. The synthesized sample as the adsorbent was sieved to 250-500 mm and 200 mg or 600 mg of adsorbent was filled in a quartz tube (6 mm o.d., 4 mm i.d.). Pre-treatment for the adsorbent was conducted at 773 K in Ar flow for 30 min. After pre-treatment, the adsorbent bed was cooled and maintained at 363 K. The feed gas composition and conditions were as follows: MCH 4 %; toluene 4 % with balanced Ar, and each dose amount for adsorbate was 0.4 mL. The outlet gas from the adsorbent bed after each pulse was analyzed using online FID gas chromatograph (GC-14B; Shimadzu Corp.) with a BX-10 column (GL Sciences Inc.). Pulsed doses were continued until the detected adsorbate in the outlet gas was considered to have reached a steady state. Adsorption tests were also conducted for other hydrocarbons: benzene, cyclohexane, xylene, and 2,2,4-trimethylpentane (Kanto Chemical Co., Inc.). In these tests, the feed gas composition was hydrocarbon 4 % with balanced Ar. Other conditions were the same as above.

2.3 Temperature Programmed Desorption (TPD)

The adsorption state of toluene was investigated by TPD analyzed with a Fourier transform infrared spectrometer (IR, FT/IR-6100; JASCO Corp.). For IR measurement, adsorbent was diluted with α-\(\text{Al}_2\)O\(_3\) so that the adsorbent concentration was 5 wt%. \(\alpha-\text{Al}_2\)O\(_3\) was obtained by calcination of \(\gamma-\text{Al}_2\)O\(_3\) (JRC-ALO-6). Diluted samples were pressed and shaped into a 10 mm (dia.) disk. Pre-treatment was conducted at 773 K in Ar flow for 30 min. After pre-treatment, the disk was cooled and maintained at 323 K in Ar, then the background spectrum was measured. Toluene was introduced into the IR cell for 30 min and purged with Ar for 30 min. Toluene flow was passed under saturated vapor pressure at room temperature with total flow rate of 40 mL min\(^{-1}\) (SATP). Then, the IR cell was heated to 373, 473, 573, 673, 773 and 873 K, and maintained at each temperature for 30 min. The IR spectrum was measured after the disk was cooled to 323 K.

2.4 Characterization of Adsorbent

Crystalline structures of adsorbents were observed using a powder X-ray diffractometer (XRD, SmartLab 3; Rigaku Corp.) operating at 40 kV and 40 mA with Cu \(K\alpha\) radiation. The 2θ angle was scanned at 10° min\(^{-1}\) for the range of 10° < 2θ < 90°. BET specific surface areas of adsorbents were measured using N\(_2\) adsorption at 77 K (Gemini VII; Micromeritics Instrument Corp.) after purge at 573 K in N\(_2\) flow for 2 h.

To investigate the reduction behavior of adsorbents, temperature programmed reduction (TPR) was conducted using TG (TGA-50; Shimadzu Corp.). After pre-treatment, the sample was cooled to 323 K and TPR was conducted from 323 to 1073 K at 10 K min\(^{-1}\) in 20 vol% of H\(_2\) flow balanced with Ar.

The electronic states of adsorbents were observed using an X-ray photoelectron spectroscopy (XPS, PHI-5000 VersaProbe II; Ulvac-Phi Inc.), with 25 W Al \(K\alpha\) emission as an X-ray source. Binding energies were calibrated with a Cls peak at 284.8 eV. X-ray absorption near-edge structures (XANES) were also observed at the BL14B2 station at SPring-8 (Hyogo, Japan) using a transmission method. Adsorbents were diluted with BN (Kojundo Chemical Laboratory Co., Ltd.) for XANES measurements. The sample was pressed and shaped into a 7 mm (dia.) disk. Obtained spectra were analyzed with the Athena software (Demeter 0. 9. 24)\(^{18}\).)

2.5 Theoretical Calculations

Plane wave basis pseudopotential calculations were implemented in the CASTEP code\(^{9}\) to simulate the XANES spectra and Mulliken\(^{20}\) population analysis. The exchange correlation function used the Perdew-Burke-Ernzerhof (PBE) function derived from the generalized gradient approximation (GGA). Ultrasoft pseudopotentials were used. The plane wave cutoff energy (\(E_{\text{cut}}\)) was taken as 600 eV. The k-point separation in the Monkhorst-Pack reciprocal space was set as 0.07 Å\(^{-1}\) (1 Å = 10\(^{-10}\) m). For comparison with the experimental spectra, the theoretical spectra were broadened using Gaussian and Lorentzian parameters set as 0.2 eV and 1.33 eV, respectively. Details of spectrum calculation were given previously\(^{21}\). In the pseudopotential method, the transition energy cannot be obtained in cases where only valence electrons are considered in all energy. The core electron contribution must also be considered. Details of transition energy calculations are described in an earlier
tivity for toluene. XRD showed La0.8Ba0.2NiO3 and La0.8Ba0.2CoO3 as the best substitution metal at the A site. The relationship between the adsorption of toluene and Ba ratio was studied. Adsorption tests on various perovskite-type oxides, La1−xMxCO3−δ (M: alkaline earth metal except for Ba, x = 0, 0.2, 1) were conducted to clarify which elements in the structure of LBOC caused selective toluene adsorption (Table 1), but only BaCO3 adsorbed toluene selectively. Therefore, coexistence of Ba and Co in the oxide lattice is important for the selective adsorption of toluene. Part of the Co ions in La1−xBaxCoO3−δ (x = 0.2, 1) is considered to be in the low-spin state (S = 1/2), as expected for Co4+ ions. Therefore, Co4+ stabilized by Ba2+ was assumed to be the selective adsorption site for toluene. However, part of the Co ions in the lattices in La0.8Sr0.2CoO3−δ and La0.8Ca0.2CoO3−δ, which did not adsorb either toluene or MCH, also contains ions in the 4+ oxidation state. The difference in the adsorption of hydrocarbons between the tested oxides presumably depended on the ionic radii of the A site substitution metals. The ionic radius of Co4+ (0.4 nm) is smaller than that of Co3+ (0.61 nm). Therefore, a larger ion is necessary to stabilize large amounts of Co4+ in the perovskite-type lattice. Among the tested alkaline earth metals, Ba was the best substitution metal at the A site for toluene adsorption, and might stabilize the Co4+ ion in the structure.

### Table 1 Adsorption Tests for MCH/Toluene Mixture on Various Oxides at 363 K

| Oxide                | Amount of adsorption [μmol g−1] | BET s. a. [m2 g−1] |
|----------------------|---------------------------------|--------------------|
| LaAlO3               | 0.00                            | 2.7                |
| LaMnO3               | 0.00                            | 7.9                |
| LaFeO3               | 0.00                            | 7.9                |
| LaFe0.6Mn0.4O3−δ     | 0.00                            | 7.9                |
| La0.9Sr0.1CoO3−δ     | 0.00                            | 7.9                |
| La0.9Ba0.1CoO3−δ     | 0.00                            | 7.9                |
| La0.9Ba0.1MnO3−δ     | 0.00                            | 7.9                |
| La0.9Ba0.1FeO3−δ     | 0.00                            | 7.9                |
| La0.9Ba0.1MgO3−δ     | 0.00                            | 7.9                |
| La0.9Ba0.1CuO3−δ     | 0.00                            | 7.9                |
| La0.9Ba0.1ZnO3−δ     | 0.00                            | 7.9                |
| La0.9Ba0.1NiO3−δ     | 0.00                            | 7.9                |
| La0.9Sr0.1FeO3−δ     | 0.00                            | 7.9                |
| La0.9Sr0.1CoO3−δ     | 0.00                            | 7.9                |
| La0.9Sr0.1MnO3−δ     | 0.00                            | 7.9                |
| La0.9Sr0.1CuO3−δ     | 0.00                            | 7.9                |
| La0.9Sr0.1ZnO3−δ     | 0.00                            | 7.9                |
| La0.9Sr0.1NiO3−δ     | 0.00                            | 7.9                |
| La0.9Sr0.1FeO3−δ     | 0.00                            | 7.9                |
| La0.9Sr0.1CoO3−δ     | 0.00                            | 7.9                |
| La0.9Sr0.1MnO3−δ     | 0.00                            | 7.9                |
| La0.9Sr0.1CuO3−δ     | 0.00                            | 7.9                |
| La0.9Sr0.1ZnO3−δ     | 0.00                            | 7.9                |
| La0.9Sr0.1NiO3−δ     | 0.00                            | 7.9                |

For density of state (DOS) calculations, DFT all-electron calculation was performed using DMol3 code. The exchange correlation function was the PBE function derived from the GGA. The wave functions were expanded in terms of a double-numerical with polarization functions basis set. In all calculations, spin-polarization was examined.

### 3. Result and Discussion

#### 3.1. Screening Tests for Selective Toluene Adsorption

Pulse-dosing adsorption tests were performed on various samples at 363 K to identify selective adsorbents of toluene from MCH–toluene mixed gas as shown in Table 1. La0.8Ba0.2CoO3−δ (LBCO) and La0.8Ba0.2NiO3−δ exhibited high adsorption and selectivity for toluene. XRD showed La0.8Ba0.2NiO3−δ consisted of mixed phase with unstable structure. In contrast, XRD of LBCO showed single phase. LBCO consisted of mixed phase with unstable structure. In all calculations, spin-polarization was examined.

#### 3.2. Effect of A Site Substitution by Ba on La1−xBaxCoO3−δ

To confirm the activity of the Co4+ site stabilized by Ba as the adsorption site, adsorption tests for toluene were conducted on La1−xBaxCoO3−δ (x = 0, 0.05, 0.1 and 0.2). The relationship between the adsorption of toluene and doped Ba ratio x is presented in Fig. 1. Oxides with higher Ba-substitution ratio exhibited higher adsorption, suggesting that Co4+ stabilized by Ba2+ was the selective adsorption site for toluene. However, oxide with substitution ratio x of 1 (i.e. BaCoO3, shown in Table 1) did not show high adsorption, presumably because of the variability of valence. All Co ions in the lattice of stoichiometric BaCoO3 perovskite oxide are ideally expected to be Co4+. However, both Co4+...
ion and Co$^{4+}$ ion are present in the lattice of LBCO. Coexistence of Co$^{3+}$ and Co$^{4+}$ was assumed to form active surface lattice oxygen. Stoichiometric BaCoO$_3$ perovskite oxide was obtained after calcination at 973 K, and the lattice oxygen was released and perovskite BaCoO$_{2.74}$ was formed after calcination at 1273 K$^{29}$. On the other hand, La$_{0.5}$Ba$_{0.5}$CoO$_{2.96}$ started releasing lattice oxygen at about 530 K and average valence of Co$^{n+}$ decreased from 3.4 (530 K) to 2.98 (1173 K)$^{30}$. Therefore, the oxygen releasing temperature of LBCO is lower than that of BaCoO$_3$. Oxygen release capacity of LBCO is presumably higher than that of BaCoO$_3$. Co$^{4+}$ ion in LBCO can be reduced to Co$^{3+}$ without affecting the perovskite crystalline structure as La$^{3+}$ acts as the receptor of trivalent Co ion. In the process of such reduction, the lattice oxygen is released to neutralize the electronic state of the oxide. The released oxygen is important as an active oxygen species for anchoring adsorbed toluene on the surface of LBCO. Therefore, the high toluene adsorption might depend on the amount of active lattice oxygen of LBCO.

3.3 Adsorption State of Toluene on La$_{1-x}$Ba$_x$CoO$_{3-\delta}$ for Various Values of $x$; adsorbent weight: 200 mg; feed gas composition; Ar : toluene = 96 : 4; dose amount: 0.4 mL; adsorbent bed temperature: 363 K

![Fig. 1 Adsorption Tests on La$_{1-x}$Ba$_x$CoO$_{3-\delta}$ for Various Values of $x$](image)

Table 2 Adsorption Tests for Various Hydrocarbons on LBCO at 363 K

| Hydrocarbon     | Amount of adsorption [μmol g$^{-1}$] |
|-----------------|--------------------------------------|
| Toluene         | 3.74                                 |
| Methylocyclohexane | 1.07                               |
| Benzene         | 0.00                                 |
| Cyclohexane     | 0.76                                 |
| p-Xylene        | 4.82                                 |
| m-Xylene        | 4.42                                 |
| o-Xylene        | 3.76                                 |
| 2,2,4-Trimethylpentane | 0.00                           |

![Fig. 2 IR Spectra during Temperature Programmed Desorption of Toluene over La$_{0.8}$Ba$_{0.2}$CoO$_{3-\delta}$](image)
or partial oxidation\(^{17}\)). According to the peak assignment, toluene was adsorbed and retained mediated by the surface lattice oxygen of LBCO.

### 3.4. Electronic State of La\(_{0.8}\)Ba\(_{0.2}\)CoO\(_{3-\delta}\)

#### 3.4.1. Effect of Oxidation State of La\(_{0.8}\)Ba\(_{0.2}\)CoO\(_{3-\delta}\) on Adsorption

Recycling adsorption test on LBCO after regeneration was conducted to investigate the effect of surface lattice oxygen of LBCO on toluene adsorption. Regeneration (i.e. surface cleaning) of LBCO after saturated adsorption of toluene was based on heating in Ar flow at 773 K. Table 3 shows that LBCO adsorbed neither MCH nor toluene in the second cycle after regeneration. However, toluene adsorption was regenerated in the third cycle by re-oxidation of the surface at 773 K. Presumably Co\(^{4+}\), which is supposed to be the adsorption site for toluene, was reduced during the first adsorption cycle, and re-oxidation of the surface of LBCO regenerated selective adsorption of toluene. XRD patterns were observed to investigate the crystalline structure of LBCO during these tests. Figure 3 presents the XRD patterns of LBCO as prepared and after heating in Ar flow at 773 K. The crystalline structure of LBCO was retained even after heating. Therefore, the LBCO structure was stable under these conditions.

In addition to the recycling test, adsorption tests with pre-reduction were conducted to investigate the effect of surface oxygen of LBCO on the selective adsorption of toluene. Prior to the test, TPR was conducted to determine the appropriate condition for reduction of the surface of LBCO. Figure 4 presents the TPR profile of LBCO, which shows three reduction peaks. Based on the TPR profile, pre-reduction of the surface oxygen of LBCO was conducted at 573 K. Subsequently, toluene was not adsorbed at all as presented in Table 4. The reduced LBCO was re-oxidized, and the selective toluene adsorption of LBCO was regenerated. The results of pre-reduction and re-oxidation tests showed that high oxidation state of LBCO (i.e. Co\(^{4+}\)) and surface lattice oxygen together with the Co\(^{4+}\) cation are necessary for selective toluene adsorption.

#### 3.4.2. Direct Measurement of Electronic State of La\(_{1-x}\)Ba\(_{x}\)CoO\(_{3-\delta}\)

The electronic state of LBCO was observed with XANES and XPS spectroscopy. The Co K-edge XANES spectra of La\(_{1-x}\)Ba\(_{x}\)CoO\(_{3-\delta}\) are presented in Fig. 5. The normalized absorbance in the range from 7725 to 7728.5 eV increased with higher Ba substitution, suggesting that the electronic state of Co became similar to Co\(^{4+}\) in BaCoO\(_3\). Co K-edge XANES spectra for La\(_{1-x}\)Ba\(_{x}\)CoO\(_{3-\delta}\) were simulated by calculation. The periodic boundary condition (PBC) models of LaCoO\(_3\) and BaCoO\(_3\) were quoted from Atomwork, which is the inorganic materials database developed by J. Jpn. Petrol. Inst., Vol. 61, No. 5, 2018
Space groups of LaCoO$_3$ and BaCoO$_3$ were $R3c$ and $P63/mmc$, respectively. The procedure used to create the model for La$_{0.8}$Ba$_{0.2}$CoO$_3$ was partial replacement of La sites in LaCoO$_3$ with Ba. The computational composition of La$_{1-x}$Ba$_x$CoO$_3$ was La$_{5/6}$Ba$_{1/6}$CoO$_3$. The model is shown in Fig. 6. In the model unit cell of La$_{5/6}$Ba$_{1/6}$CoO$_3$, three electronic states of Co were determined by the Mulliken charge method.

The XANES spectra were simulated for each type of Co and presented in Fig. 7. In these spectra, Co closer to Ba had higher normalized absorbance in the range from 7752 to 7756 eV. However, the order of the electronic states of Co calculated by the Mulliken charge method was not the same as the order in the XANES spectra. The oxidation state of Co closest to that of Ba was the lowest among the Co types in the model lattice. Presumably this disorder derived from the overlap of the Ba and Co orbitals. Some electrons originally derived from Ba were apparently considered to belong to Co in the Mulliken charge method, so that the model oxidation state of Co was lower than the actual state. Therefore, the actual oxidation state of Co closest to Ba was expected to be the highest. These results demon-
strated that the normalized absorbance of the XANES spectra in the range mentioned above increased with higher oxidation number of Co. From the measured and simulated XANES spectra, the oxidation number of Co was increased by adding Ba to LaCoO$_3$. These results and the previous section indicate that Co$^{4+}$ is important for selective adsorption of toluene.

The XANES spectra of LBCO and La$_{0.8}$Sr$_{0.2}$CoO$_{3-\delta}$ were also compared as shown in Fig. 8. From these spectra, almost all Co ions in the lattice of La$_{0.8}$Sr$_{0.2}$CoO$_{3-\delta}$ are expected to be in the state of Co$^{3+}$. Therefore, Sr cannot stabilize Co$^{4+}$ ion enough to adsorb and retain toluene on the surface of the oxide. Consequently, Ba is expected to be the only available substitution metal to stabilize Co$^{4+}$ ion.

Detailed quantitative analyses were based on XPS spectra of La$_{1-x}$Ba$_x$CoO$_{3-\delta}$. The Ba4$d$ spectrum overlapped with the main Co spectrum (i.e., Co2$p$). Therefore, Co3$p$ spectra were observed instead of Co2$p$ spectra. The Co3$p$ spectra are shown in Fig. 9. Two peaks were observed in all Co3$p$ spectra. The peak at higher binding energy was considered to be a shake-up satellite peak.$^{36}$ The other peak (main peak) was decomposed into two components. The main peak is reported to broaden toward higher binding energy with more Co$^{4+}$ ions.$^{36}$ In the Co2$p$ spectrum, the peaks derived from Co$^{4+}$ appear at higher binding energy than those of Co$^{3+}$.$^{37,38}$ However, direct assignment of Co$^{4+}$ in the Co3$p$ spectrum has not been reported. To confirm the assignment of Co$^{4+}$ in Co3$p$ spectrum, the local density of states (DOS) for LaCoO$_3$ and BaCoO$_3$ in the range of the Co3$p$ orbital were calculated as shown in Fig. 10. In the DOS for BaCoO$_3$, which was expected to be Co$^{4+}$, two peaks appeared and one
of these peaks overlapped with the peak in DOS for LaCoO$_3$, which was expected to be Co$^{3+}$. The other peak appeared at definitely higher binding energy. According to the DOS, the component at higher binding energy of the main peak in Fig. 9 can be assigned to Co$^{4+}$. The area ratios of Co$^{4+}$ peak against Co$^{3+}$ peak were calculated for each spectrum, and the relationships between Ba substitution and the Co$^{4+}$ ratio and toluene adsorption are presented in Fig. 11. The ratio of Co$^{4+}$ increased and toluene adsorption increased with greater Ba substitution. This trend for the electronic state at the near surface was similar to the result observed in XANES measurement for the bulk material. The Co$^{4+}$ ratio decreased significantly after heating at 773 K in the saturated state and LBCO could not adsorb toluene. These phenomena show that Co$^{4+}$ is important for the selective adsorption of toluene. The interaction between the B site ion and the electron rich aromatic ring, which is donated electrons by the methyl group, resulted in the high selectivity for toluene. The active lattice oxygen of LBCO was important in the high toluene adsorption.

4. Conclusion

The present study investigated selective toluene adsorption from MCH–toluene mixed gas with La-based complex oxides. LBCO exhibited high adsorption and selectivity for toluene. Coexistence of Ba and Co and electron donation to the aromatic ring from the methyl group were important for selective adsorption of
toluene. Co$^{4+}$ ion in the LBCO and surface lattice oxygen were important for the selective adsorption of toluene. XANES and XPS analyses revealed that only LBCO among the tested oxides had high oxidation state and part of the Co ion in the LBCO lattice was expected to be Co$^{4+}$. XANES observation suggested that Ba was the optimal substitution metal for stabilizing Co$^{4+}$ ion. The high oxidation state of Co$^{4+}$ in the LBCO lattice and surface lattice oxygen mediates the selective adsorption of toluene.

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要  旨

ベロブスカイト酸化物によるトルエンの選択吸着

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有機ハイドライド法は湿素貯蔵法の一つとして知られる。この際に芳香族の水素化において平衡制約のため、未反応の芳香族が残存することが問題となる。そこで本研究では、未反応トルエンのみを選択的に吸着分離できる複合系酸化物材料の探索を行った。いくつかのLa系複合酸化物を検討した結果,

La_{0.8}Ba_{0.2}CoO_3 (LBCO) 酸化物が高い吸着量とトルエン選択吸着性を示すことを見出した。電子状態ならびに吸着状態を各種実験ならびに計算化学によって検討した結果, LBCO中のCoイオンがCo^{4+}の状態を取り、格子内のCo^{4+}イオンと表面酸素の協奏がトルエン選択吸着に対して重要な役割を果たしていることを見出した。