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## Title

Steam reforming of aromatic hydrocarbon at low temperature in electric field

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## **Graphical abstract**



## Highlights

- Catalytic toluene steam reforming was investigated over Ni/La<sub>0.7</sub>Sr<sub>0.3</sub>AlO<sub>3- $\delta$ </sub> catalyst.
- Reaction was promoted by an electric field drastically even at 473 K.
- Low apparent activation energy of 26.1 kJ/mol was observed in the electric field.
- SSITKA and TPD-IR revealed the electric field promoted redox of surface lattice oxygen.

• Electric field achieved high activity and low carbon deposition at low reaction temperature

#### Abstract

Toluene steam reforming was conducted over Ni-supported La<sub>0.7</sub>Sr<sub>0.3</sub>AlO<sub>3.6</sub> (LSAO) perovskite oxide at 473 K in an electric field, and high toluene conversion was achieved even at such low temperature. Steam reforming is generally done at higher temperatures because of the endothermic nature of this reaction and coke prevention, which requires the contribution of heat energy in great amounts. Reportedly, water activation is particularly difficult to achieve at lower temperatures. Results of kinetic analyses such as Arrhenius plots and partial pressure dependence have revealed that imposing an electric field promotes water activation over Ni/LSAO catalyst. According to steady state isotopic kinetic analysis (SSITKA) and temperature programmed desorption infrared (TPD-IR) measurements, such water activation was accelerated via a redox mechanism using surface lattice oxygen of LSAO. The stimulated mobile lattice oxygen oxidized the adsorbed toluene and formed coke precursor in the electric field. The electric field achieved a lowered reaction temperature for efficient hydrogen production and coke suppression with redox property of LSAO support during toluene steam reforming.

#### Keywords

Coke suppression; Hydrogen production; Ni catalyst; Perovskite-type oxide; Redox mechanism; Toluene steam reforming

#### Main text

#### 1. Introduction

Hydrogen production has been attracting much attention because hydrogen is demanded for use in various chemical industries and is anticipated for use as clean secondary energy for combustion or fuel cell utilization. Currently, the typical method used for producing hydrogen is catalytic steam reforming using light hydrocarbons such as methane or naphtha [1,2], but steam reforming of aromatic hydrocarbons is also investigated extensively because it enables the use of biomass or brown-coal-derived materials [3–19]. These aromatic hydrocarbons are less reactive and tend to form coke during such catalytic reactions, deriving coverage of active sites and plugging of the reactor in the worst case. Certainly, suppressing coke formation and lowering the reaction temperature are extremely important for the steam reforming of aromatic hydrocarbons.

To investigate coke formation suppression, many studies have been conducted to assess the inhibition of coke deposition during steam reforming. Dilution of an active metal such as Ni might be an effective means of suppressing coke by-production [20–23]. For instance, Anjaneyulu *et al.* reported that using a synthesized Ni-Zn alloy supported Al<sub>2</sub>O<sub>3</sub> catalyst improved coke resistance

during ethanol steam reforming [20]. In this case, Zn played important roles in dilution of Ni metal and in the enhancement of hydrogen spillover to form adsorbed water to suppress coking [20]. Similarly, the presence of alkali or magnesia-based catalyst can enhance steam adsorption to depress coke formation [21,24]. Additionally, lattice oxygen in/on support oxides can contribute to coke resistance [25–35]. Marinho *et al.* stated that the formed coke was calcined by transferred oxygen from perovskite-type oxide, LaNiO<sub>3</sub>/CeSiO<sub>3</sub> catalyst under water presence during ethanol steam reforming [25]. In an earlier study, we demonstrated that lattice oxygen of La<sub>0.7</sub>Sr<sub>0.3</sub>AlO<sub>2.85</sub> (LSAO), a perovskite-type oxide, drastically decreased the amount of coke formation during toluene steam reforming [36–41]. Furthermore, such lattice oxygen promoted toluene decomposition with a redox mechanism. Consequently, LSAO support achieved both high activity and stability during steam reforming of aromatic hydrocarbons.

Lowering the reaction temperature of steam reforming is beneficial for removing coke oxidatively and for achieving high-efficiency hydrogen production, simultaneously utilizing lowgrade heat. Various approaches have been inspected for lowering the reaction temperature, for example auto thermal reforming (ATR) [42–45]. Electric field addition to the catalyst bed can also lower the reaction temperature of endothermic reactions such as steam reforming [46–49]. Manabe *et al.* reported that steam reforming of methane in an electric field proceeded with high activity even at temperatures lower than 473 K [50]. In this reaction, the adsorbed water promoted proton transfer and a collisional reaction between accelerated protons and methane over Pd-supported CeO<sub>2</sub> [50,51]. Vayenas *et al.* suggested that electric current promoted oxygen mobility in metal oxides and their catalytic oxidation through NEMCA (Non-Faradaic Electrochemical Modification of Catalytic Activity) [53-55]. Accordingly, ion transfer or activation might be promoted in an electric field during a steam reforming reaction. For this study, toluene steam reforming was conducted at 473 K in an electric field over Ni-supported LSAO catalyst, which showed high activity and stability because of redox ability: lattice oxygen mobility.

#### 2. Experimental

### 2.1 Catalyst preparation

Perovskite-type oxide,  $La_{0.7}Sr_{0.3}AlO_{3-\delta}$  (LSAO) for catalyst support was synthesized using the citric acid complex method. The crystalline structure was confirmed by XRD as shown in supporting information figure S1, and we could observe only for LSAO perovskite peaks and no other peaks for impurity phases were confirmed. Earlier reports explained additional details related to the citric acid complex method [36, 38, 40, 41]. After powdered LSAO was impregnated with a solution of nickel (II) nitrate (Kanto Chemical Co. Inc.), the LSAO was soaked in 25 mL of water for 2 h. Then Ni nitrate was added with 15 mL of water and was dissolved for 2 h using an evaporator. Concentration of nickel nitrate was adjusted for each loading amount i.e., 1, 3 and 5 wt% of Ni. Later, it was dried and calcined at 773 K for 2 h. The obtained catalyst size was adjusted to 355–500 µm with sieving.

#### 2.2 Activity tests with/without the electric field

Catalyst activity tests were conducted using a tubular reactor in which 200 mg of catalyst was charged into a fixed bed as shown in supporting information figure S2. Two stainless steel electrodes were set contiguously on the upper side and bottom side of the fixed catalysts to charge an electric field. The same setup was used for steam reforming without the electric field. Toluene steam reforming was conducted for 60 min in each condition after pre-reduction at 873 K. For reaction with an electric field, 3 mA of constant current was applied between the two electrodes. The reaction gas composition was  $C_7H_8$  :  $H_2O$  : Ar = 3 : 42 : 155 (mL min<sup>-1</sup>). The steam to carbon ratio (S/C) was 2.0. Also, the weight flow ratio was 3.14 g-cat h mol<sup>-1</sup>. We confirmed that the condition is in the kinetic region and that diffusion is not a rate determining factor. Results demonstrate that the effect of mass transportation was negligible in such a condition. The product gas of the reaction was measured using GC-FID (GC-8A; Shimadzu Corp.) and GC-TCD (GC-8A; Shimadzu Corp.). Toluene conversion and hydrogen yield were defined with a toluene feed rate (mmol s<sup>-1</sup>) and the following formation rate of products:  $r_{CO}$  (mmol s<sup>-1</sup>) for CO,  $r_{CH4}$  (mmol s<sup>-1</sup>) for CH<sub>4</sub>,  $r_{CO2}$  (mmol s<sup>-1</sup>) for CO<sub>2</sub>, and  $r_{H2}$  (mmol s<sup>-1</sup>) for hydrogen.

Toluene conversion (%) =  $(r_{\rm CO} + r_{\rm CH4} + r_{\rm CO2}) / (C_7 H_8 \text{ feed rate } \times 7) \times 100$  eq. 1

Toluene steam reaction is described as  $C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2$ 

And sequential water gas shift reaction is described as  $CO + H_2O \rightarrow CO_2 + H_2$ 

By combining these two reactions, the total reaction can be described as

 $C_7H_8 + 14H_2O \rightarrow 7CO_2 + 18H_2$ 

So, the hydrogen yield can be calculated as follows;

Hydrogen yield (%) =  $r_{\text{H2}}$  / (C<sub>7</sub>H<sub>8</sub> feed rate × 18) × 100 eq. 2

After reaction for 60 min, the amount of deposited coke was measured with a gas chromatograph using temperature programmed oxidation (TPO) measurements to estimate CO or CO<sub>2</sub> from coke. The temperature was increased from 298 K to 1173 K at 10 K min<sup>-1</sup> for the gas composition of  $O_2$ : He = 10 : 90 (mL min<sup>-1</sup>). The resultant ratio of produced gas components and coke formation amounts was confirmed based on the carbon balance, which was almost 1.

#### 2.3 Catalytic structure analysis

The obtained perovskite-type structure of LSAO support was confirmed from X-ray diffraction measurements (XRD: Ultima III; Rigaku Corp.) using Cu Kα X-ray radiation of 40 kV at 40 mA. The average particle diameter of the supported Ni metal was estimated using CO pulse measurements (BELCAT II; MicrotracBEL Corp.). Furthermore, the obtained particle diameter was confirmed with images and EDX mapping results obtained using scanning transmission electron microscopy (STEM; HF-2210; Hitachi Ltd.).

2.4 Kinetic analysis of Ni supported LSAO catalyst

Arrhenius plots were obtained over 5 wt% Ni/LSAO catalyst to evaluate the apparent active energy of toluene steam reforming in each condition: (1) at 473 K with the electric field and (2) at 698 K without the electric field. Reaction rates were evaluated in terms of kinetic control. The reaction rates were defined from the formation rate of CO, CO<sub>2</sub>, and CH<sub>4</sub> in the same manner as that used for activity tests. In the case of reaction with an electric field, catalyst temperatures were increased with Joule heat by charged electricity. Thermocouples detected the temperature on the catalyst. Those data were then used to ascertain the temperature rise.

To elucidate reaction mechanisms, partial pressure dependences of the reaction rates were confirmed for toluene and steam pressure in each reaction condition: (1) at 473 K with the electric field and (2) at 698 K without the electric field. The feed gas compositions were modified as  $C_7H_8$ :  $H_2O$  : Ar = (1, 2, 3) : 42 : (157, 156, 155) (mL min<sup>-1</sup>) and  $C_7H_8$  :  $H_2O$  : Ar = 3 : (30, 42, 54) : (167, 155, 143) (mL min<sup>-1</sup>), respectively, for toluene and steam pressure. Reaction rates were calculated from the formation rates of CO, CO<sub>2</sub>, and CH<sub>4</sub> analyzed using GC-FID (GC-8A; Shimadzu Corp.).

2.5 Evaluation of the lattice oxygen release rate with steady state isotopic transient kinetic analysis (SSITKA)

Lattice oxygen release rates were estimated over the 5 wt% Ni/LSAO catalyst, in the following three conditions: (1) at 473 K with the electric field, (2) at 698 K without the electric field and (3) at 473 K without the electric field. Detailed procedures for SSITKA have been described elsewhere [25, 27–29]. For this experiment, the first reaction was conducted with gas including isotopic water i.e.  $1.5\%C_7H_8$ :  $6.3\%H_2^{16}O$ :  $14.7\%H_2^{18}O$ : 5%Ar: 72.5%He vol% (total flow rate: 200 mL min<sup>-1</sup>) to replace lattice oxygen in/on the LSAO support by <sup>18</sup>O. After helium purging treatment for 120 min, sequential reactions were conducted in the following gas composition:  $1.5\%C_7H_8$ :  $21\%H_2^{16}O$ : 5%Ar: 72.5%He vol% (total flow rate:  $21\%H_2^{16}O$ : 5%Ar: 72.5%He vol% (total flow rate:  $21\%H_2^{16}O$ : 5%Ar: 72.5%He vol% (total flow rate:  $21\%H_2^{16}O$ : 5%Ar: 72.5%He vol% (total flow rate: 200 mL min<sup>-1</sup>). Products of the second reaction were measured using a quadrupole mass spectrometer (Q-Mass, HPR20; Hiden Analytical Ltd.). The observed signals of m/e were  $2(H_2)$ , 4(He),  $15(CH_4)$ ,  $18(H_2O)$ ,  $20(H_2^{18}O)$ , 28(CO),  $30(C^{18}O)$ , 40(Ar),  $44(CO_2)$ ,  $46(C^{16}O^{18}O)$ ,  $48(C^{18}O_2)$ ,  $78(C_6H_6)$ , and  $91(C_7H_8)$ . We found the effect of  $Ar^{2+}$  (m/z = 20) signal to  $H_2^{18}O$  is negligible [38–41]. The lattice oxygen release rate was defined as formation rates of  $30(C^{18}O)$ ,  $46(C^{16}O^{18}O)$ , and  $48(C^{18}O_2)$ .

### 2.6 Temperature programmed desorption infrared (TPD-IR) measurements in an electric field

Diffuse reflectance infrared spectrometry was applied to observe adsorbed species on Ni/LSAO catalyst using a Fourier transform infrared spectrometer (FT/IR-6100; Jasco Corp.). Additionally, the measurement apparatus was assembled for applying the electric field on the samples as described elsewhere in the literature [51]. Sieved catalyst was used in this experiment. Two stainless steel electrodes were set on the catalyst. An earlier report described the temperature program scheme for this measurement [38]. After pre-reduction at 873 K and background measurement at 323 K, diluted toluene gas was flowed into a measurement chamber for 30 min with 2 mL min<sup>-1</sup> of the toluene feed

rate. Subsequently, argon gas was introduced to remove gas-state toluene before the temperature rise. Without the electric field, the IR cell was heated and kept at 373, 473, 573, 673, 773, and 873 K for 10 min independently in Ar gas. For reaction with an electric field, the temperature was raised to 373, 473, 573, and 673 K because of thermotolerance of the Teflon cell. Also, an electric field was charged for 10 min at each temperature. After each heating operation, the cell was cooled to 323 K. Then the IR spectrum was measured. Figures presented in an earlier report present a comprehensive view of the relevant spectra [38].

### 3. Results and Discussion

3.1 Catalytic activity and coke deposition during toluene steam reforming in an electric field

Toluene steam reforming was conducted over supported metal catalyst with 5 wt% of active metal i.e. Ni, Co, Fe or Cu supported on LSAO, in a tubular reactor at 473 K with an electric field. Figure 1 shows the time courses of the catalytic activities and hydrogen yields for these catalysts. Results indicate that Ni/LSAO catalyst showed the highest activity among these catalysts in this condition during toluene steam reforming. Consequently, toluene steam reforming was also conducted over Ni/LSAO catalyst without an electric field at 473 K for better comparison. However, Ni/LSAO showed no activity at such a low reaction temperature. To elucidate the effects of the electric field over Ni/LSAO catalyst, catalytic activity was investigated at each reaction temperature from 473 K to 873 K. The results of activity testing at each reaction temperature with and without the electric field are presented in Figure 2, in which filled plots and open plots respectively represent the activities with (ER: reaction with an electric field) and without (SR: steam reforming without an electric field) the electric field. In the case of ER, the catalyst bed was heated by Joule heating of about 100 K, so filled plots are shifted to higher temperatures than the original furnace temperature. The reaction temperature was measured using a thermocouple on the catalyst bed inside of a tubular reactor. Results show that the catalytic activity of ER was much higher than that of steam reforming at the same temperature: for example, ER, 44.7% at 573 K vs. SR, 1.3% at 573 K. The electric field effect is greater at temperatures lower than 773 K. We confirmed the waveform of response voltage during electric field addition using an oscilloscope, and no plasma was found. Also no emission spectra can be observed. Therefore, the electric field promotes some catalytic reaction steps effectively at lower temperatures, at which toluene steam reforming does not generally proceed.

Effects of Ni loading amounts on the coke deposition activity were investigated using LSAO support in the electric field. Figure 3 and supporting information Tables S1 and S2 depict the respective toluene conversion, hydrogen yields and other products including deposited coke over three catalysts, i.e. 1, 3 and 5 wt%Ni/LSAO, during steam reforming with and without the electric field. Results demonstrated that 5 wt%Ni/LSAO showed higher activity than other catalysts in both cases. As for ER, the catalyst attained better stability. The catalytic activity was very low without supported Ni metal as shown in supporting information figure S3. Table 1 shows the catalytic

activities and the amounts of formed coke over these Ni/LSAO catalysts at 473 K with the electric field and at 698 K without the electric field because conversion showed similar values in these conditions. In the case of ER, the amounts of formed coke were very small over 1, 3 and 5 wt%Ni/LSAO as shown in supporting information figure S4. These values were below 10 mg g-cat<sup>-1</sup>. In the case of SR, the amounts of coke increased considerably from 39.2 mg g-cat<sup>-1</sup> to 525.8 mg g-cat<sup>-1</sup> as the Ni loading amounts and catalytic activities increased. Steam reforming was promoted with Ni loading, simultaneously causing coke by-production without the electric field. To confirm coke suppression effects of the electric field, an activity test was conducted over 5 wt% Ni/LSAO catalyst at 473 K for 60 min after toluene steam reforming at 698 K for 60 min. After all these treatments, the amount of formed coke was decreased to 253.4 mg g-cat<sup>-1</sup> compared to 525.8 mg g-cat<sup>-1</sup> as shown in supporting information figure S5. In the lower temperature region, it was described that more reactive coke such as C $\alpha$  and C $\beta$  tended to deposit [56,57]. This experiment suggests that some reactive coke is formed, but such coke can be removed by electric field charging. These results revealed that the electric field promoted endothermic steam reforming at lower temperature, and that it strongly suppressed coke formation during toluene steam reforming.

#### 3.2 Active site specification and kinetic analysis for toluene steam reforming in an electric field

Catalytic activities were improved by the increase of Ni metal loading. Actually, Ni metals played important roles as reactive sites for progression of the steam reforming reaction. Consequently, the Ni-specific area dependency of activities was evaluated over 1, 3 and 5 wt% Ni/LSAO catalysts with/without the electric field. Table 2 and supporting information figure S6 present turnover frequencies (TOF) of two kinds, as determined by the Ni specific surface area (TOF-s) and Ni-support perimeter (TOF-p), STEM image of supported Ni is shown in supporting information figure S7 and Ni particle size was evaluated by CO adsorption as shown in Table S3. Regarding ER, the value of TOF-p was constant over each Ni catalyst. The toluene steam reforming activity was determined by the Ni-support perimeter. However, both TOF-s and TOF-p values were increased as the Ni particle diameter increased in the case of steam reforming without an electric field. Generally, adsorbed water was regarded as activated on metal oxide supports rather than on supported active metal. Additionally, it is difficult to activate water in the lower temperature region [40]. Consequently, the water activation rate over LSAO support affects the total reaction rate of steam reforming. According to reports of earlier studies, catalytic activity is affected strongly by the Ni-support perimeter when the adsorbed water is dissociated rapidly, for example via redox mechanism [37, 39-41]. The electric field possibly promoted water activation over Ni/LSAO catalyst.

Kinetic analysis was performed over 5 wt% Ni/LSAO catalyst to elucidate the electric field effects of more specifically. Figure 4 shows the resultant Arrhenius plots over Ni/LSAO catalyst with and without the electric field. These results show that the apparent active energy was 26.1 kJ mol<sup>-1</sup> for ER and 78.9 kJ mol<sup>-1</sup> for SR. The evaluation was conducted in a kinetic region, confirmed

by changing the contact time as shown in figure S8, and the Arrhenius plot for higher temperature in a diluted condition is shown in figure S9. The apparent active energy decreased drastically by electric field application, meaning that the electric field promoted a specific reaction path. Subsequently, as shown in Figure 5, partial pressure dependences for toluene and steam were analyzed over Ni/LSAO catalyst in each condition: ER at 473 K and SR at 698 K. The reaction rate of toluene steam reforming ( $r_{SR}$ ) is defined as shown below.

$$r_{\rm SR} = k[{\rm C}_7{\rm H}_8]^a[{\rm H}_2{\rm O}]^b$$
 eq. 3

For steam reforming without the electric field, the reaction rate depended predominantly on the steam partial pressure i.e., a = 0.23 and b = 0.93. As described above, the adsorbed water is difficult to dissociate at a low temperature such as 698 K [37, 39–41]. Regarding ER, the reaction rate more reliant on toluene partial pressure i.e., a = 0.95 and b = 0.29. Apparently, the electric field facilitated dissociation of adsorbed water, even at a low temperature such as 473 K, which achieved acceleration of steam reforming in the lower temperature region and coke resistance. This partial pressure tendency was also observed when the redox mechanism was expressed over LSAO support [37, 39–41]. It is typically affirmed that redox mechanism occurs at higher temperatures above approximately 800 K without any special treatment such as an electric field [37, 40]. For this reason, further experiments were conducted to clarify water activation mechanisms and the conduction species over LSAO support in an electric field.

As for the energy balance for this reaction, energy balance was calculated with the following equation;

Energy balance (%) = Converted toluene (mol sec<sup>-1</sup>) ×  $\Delta H$  for the reaction (kJ mol<sup>-1</sup>) / Input power (W) × 1000 eq. 4

 $\Delta H$ : Required enthalpy for C<sub>7</sub>H<sub>8</sub> + 14H<sub>2</sub>O  $\rightarrow$  7CO<sub>2</sub> + 18H<sub>2</sub> (828.6 kJ mol<sup>-1</sup>)

Accordingly, resulted energy balance was 18.3%. Therefore, there is a room for improvement *in status quo*. Faraday efficiency was 29.4 (one electron promoted the conversion of 29.4 times of toluene). This reaction was not electrochemical reaction, and promising for reducing required electric power by controlling the bulk electron conductivity (to decrease wasted Joule heat).

3.3 Lattice oxygen redox property over LSAO support in an electric field

Steady state isotopic transient kinetic analysis (SSITKA) was applied over Ni/LSAO catalyst during toluene steam reforming with and without the electric field because LSAO support was regarded to accelerate water activation with its redox property. Figure 6 and Table 3 present lattice oxygen release rates over 5 wt% Ni/LSAO catalyst in the following conditions: (a) at 473 K with the electric field, (b) at 698 K without the electric field, and (c) at 473 K without the electric field. Lattice oxygen release rates were estimated with isotopic <sup>18</sup>O release after surficial purge treatment,

after which <sup>18</sup>O exists only inside of LSAO lattice and defects [39–41]. The results of Figures 6(b) and 6(c) showed that the lattice oxygen release rates were 0.59 and 0.03 µmol s<sup>-1</sup> at 698 K and 473 K during steam reforming without the electric field. Regarding the ER, the lattice oxygen release rate was 1.77 µmol s<sup>-1</sup> at 473 K. The lattice oxygen release rate was remarkably faster with the electric field. Even catalytic activities were similar between the two conditions: (a) at 473 K with the electric field and (b) at 698 K without the electric field. Furthermore, this oxygen mobility was not observed over the catalyst without redox ability such as Ni/LaAlO<sub>3</sub>, on which the electric field was not stable and generated blue-white plasma with discharging. Consequently, results suggest that the redox ability of LSAO support promoted water activation at low temperatures, and that mobile oxygen ions and their vacancies play an important role in toluene steam reforming in an electric field.

Water activation was accelerated with redox ability of LSAO in the electric field. However, it remains unclear that toluene steam reforming proceeded with a redox mechanism. Therefore, temperature programmed desorption infrared (TPD-IR) measurements were conducted over Ni/LSAO with/without the electric field. Figure 7 shows results of TPD-IR measurements conducted with and without the electric field, respectively. At low temperatures, typical ring C-C vibration was detected at wavenumbers 1500 and 1600 cm<sup>-1</sup> in the respective conditions [38,40]. Symmetric and asymmetric COO vibrations started to appear at 673 K in the case of steam reforming without the electric field, as shown in Figure 7(B) [38,40]. By contrast, those peaks were detected at a lower temperature, 473 K in the case of ER. In earlier studies, adsorbed toluene was converted to oxygenate intermediates on LSAO support before sequential oxidation to CO or CO<sub>2</sub> over Ni particles. Then, such formation of oxygenates facilitates decomposition of toluene [38,40]. These results suggest that the redox mechanism is predominant over Ni/LSAO catalyst in the electric field, which is important for coke resistance and processes of steam reforming.

#### 4. Conclusion

We investigated catalytic steam reforming of toluene as a model compound of aromatic hydrocarbons at low temperatures in an electric field. Even at 473 K, Ni/LSAO showed high catalytic activity during toluene steam reforming in an electric field. Without the electric field, almost no activity was observed at 473 K. The coke deposition amount was 10 mg g-cat<sup>-1</sup> for ER at 473 K and 525.8 mg g-cat<sup>-1</sup> for SR at 698 K, although the toluene conversion was almost identical for these two conditions. The formed coke can be removed by the imposition of an electric field because more reactive coke such as C $\alpha$  and C $\beta$  tended to be produced in the low temperature region. The apparent active energy was lowered from 78.9 kJ mol<sup>-1</sup> to 26.1 kJ mol<sup>-1</sup> by application of the electric field. The steam partial pressure dependence changed simultaneously. The lattice oxygen release rate was considerably higher. Oxygenate intermediates were formed at lower temperature in the electric field. Therefore, we infer that the redox mechanism is predominant over Ni/LSAO

catalyst in the electric field. These results indicate that the electric field promoted activation of water using lattice oxygen ion and its vacancy, which is important for oxidation of surficial reactive coke and adsorbed toluene.

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### Captions to figures

### Figure 1

Toluene conversion and hydrogen yield during toluene ER over metal-supported LSAO catalyst: Ni/LSAO, Co/LSAO, Fe/LSAO, or Cu/LSAO. Metal loading amount: 5 wt%. Reaction conditions: 473 K reaction temperature; S/C = 2.0; W/F = 3.14 g-cat h mol<sup>-1</sup>; 3 mA current charged for filled plots; no current charged for open plots.

## Figure 2

Temperature dependence of catalytic activity on 5 wt% Ni/LSAO with or without the electric field. Filled plots for ER and open plots for SR. Reaction conditions: 473–873 K reaction temperature; S/C = 2.0; W/F = 3.14 g-cat h mol<sup>-1</sup>; 3 mA current charged.

### Figure 3

Toluene conversion and hydrogen yield on Ni/LSAO catalyst, 1, 3 and 5 wt% Ni/LSAO, (A) for ER at 473 K and (B) for SR at 698 K. Reaction conditions: 473 K reaction temperature; S/C = 2.0; W/F = 3.14 g-cat h mol<sup>-1</sup>; 3 mA current applied for ER.

### Figure 4

Arrhenius plots of 5 wt% Ni/LSAO catalyst for ER and SR. Reaction conditions: S/C = 2.0; W/F = 3.14 g-cat h mol<sup>-1</sup>; 3 mA current charged for ER.

## Figure 5

Partial pressure dependences of (a) toluene and (b) steam on 5 wt% Ni/LSAO catalyst for ER at 473 K and SR at 698 K. Reaction conditions: S/C = 2.0; W/F = 3.14 g-cat h mol<sup>-1</sup>; 3 mA current charged for ER.

## Figure 6

Formation rate of <sup>18</sup>O containing C<sub>1</sub> products standing for lattice oxygen release on 5 wt% Ni/LSAO in each condition: (a) 473 K for ER, (b) 698 K for SR. and (c) at 473 K for SR. Symbols: **•**, C<sup>18</sup>O; **•**, C<sup>16</sup>O<sup>18</sup>O; **•**, C<sup>18</sup>O<sub>2</sub>;  $\circ$ , H<sub>2</sub><sup>18</sup>O. Reaction conditions: S/C = 2.0; W/F = 3.14 g-cat h mol<sup>-1</sup>; 3 mA current applied for ER.

## Figure 7

Spectrum of TPD-IR measurement on 5 wt% Ni/LSAO (A) with the electric field charging (ER) and (B) without the electric field (SR): 323–673 K temperature region; 3 mA applied current for ER.







Figure 2



Figure 3



Figure 4



Figure 5



Figure 6





Catalyst	El	lectric Field	l at 473	3 K	Heated at 698 K			
	Toluene conv.	H <sub>2</sub> yield	carbon deposition / mg g-cat <sup>-1</sup>		Toluene conv.	H <sub>2</sub> yield	carbon deposition	
	/ %	/ %			/ %	/ %	/ mg g-cat <sup>-1</sup>	
1wt%Ni/LSAO	10.9		14.0	7.5	7.2	5.	5 39.2	
3wt%Ni/LSAO	29.1		26.7	9.1	25.3	26	3 322.8	
5wt%Ni/LSAO	44.7		33.3	10.0	42.9	40.	0 525.8	

Table 1 Catalytic activity and amount of carbon deposition during steam reforming on Ni/LSAO catalysts.

Table 2 Ni structure and TOF determined by Ni specific surface area (TOF-s) and Ni-support perimeter (TOF-p)

Catalyst	Ni particle diameter Ni surface area		Ni-support perimeter TOFs / sec <sup>-1</sup>				TOF <sub>p</sub> / sec <sup>-1</sup>	
	/ nm	$/ m^2 g^{-1}$	$/ 10^8 \text{ m g}^{-1}$	EF	heated	EF	heated	
1wt%Ni/LSAO	8.9	0.56	1.27	0.41	0.27		9.29	6.15
3wt%Ni/LSAO	9.5	1.58	3.32	0.39	0.34		9.44	8.20
5wt%Ni/LSAO	9.9	2.55	5.16	0.37	0.36		9.34	8.95

 $\begin{tabular}{|c|c|c|c|}\hline Table 3 Release rates of lattice oxygen over Ni/LSAO in various conditions. \\ \hline O_{lat} release rate & O_{lat} release amount \\ \hline / \ \mu mol sec^{-1} & / \ \mu mol \\ \hline with EF (473 \ K) & 1.77 & 42.9 \\ \hline without EF (698 \ K) & 0.59 & 14.3 \\ \hline without EF (473 \ K) & 0.03 & 0.8 \\ \hline \end{tabular}$ 

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