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Role of lattice oxygen in oxidative steam reforming of toluene as a tar model compound over Ni/La_{0.8}Sr_{0.2}AlO₃ catalyst

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Catalytic steam reforming of tar with toluene as a model compound for production of synthesis gas (H₂ and CO) were studied using Ni/LaAlO₃, Ni/La_{0.8}Sr_{0.2}AlO₃, NL, and Ni/α-Al₂O₃ catalysts prepared using a wet impregnation method. Ni/La_{0.8}Sr_{0.2}AlO₃ catalysts demonstrated the most superior catalytic performance in terms of both catalytic activity and coke resistance in the steam reforming of toluene. The ¹⁰ presence of gas phase oxygen enhanced the catalytic performances of all four catalysts, with the extent of improvement being the greatest over Ni/La_{0.8}Sr_{0.2}AlO₃ catalyst. Catalyst characterization by x-ray diffraction (XRD), temperature-programmed reduction (TPR), x-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption of oxygen (TPD-O₂) revealed that the superior catalytic performance of Ni/La_{0.8}Sr_{0.2}AlO₃ catalyst was a result of lattice distortion caused by strontium doping, ¹⁵ that formed a higher concentration of oxygen vacancies on the catalyst surface. This lowered the activation energy of the migration of lattice oxygen, enhancing the mobility of lattice oxygen species, and also improved the adsorption abilities of gas phase oxygen species. Mobile lattice oxygen species (O_{lattice}) favored the direct partial oxidation of toluene, whereas gas-phase oxygen possessed stronger oxidative abilities and favored the complete oxidation of toluene. Both mobile lattice oxygen and gas phase oxygen ²⁰ species actively suppressed coke formation and oxidized coke deposited on the catalyst surface,

conferring coking resistance.

Introduction

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Biomass constitutes living species such as plants and animals that are alive or were alive some time ago. While conventional fossil ²⁵ fuels require millions of years to develop, biomass can readily

- reproduce. For this reason, it is considered renewable¹. In addition, biomass is said to be a "carbon-neutral" fuel as a majority of biomass take in CO_2 from the atmosphere for growth and reproduction. This CO_2 is subsequently released when the
- ³⁰ biomass is burnt. As such, biomass gasification is an increasingly popular area of research for the generation of energy or production of syngas for use in the synthesis of Fischer-Tropsch chemicals and methanol¹⁻⁴.
- However, tar formation as a by-product of biomass gasification ³⁵ remains a problem. Tar is a thick, black and highly viscous liquid comprising a complex mixture of 1- to 5-ring aromatic, as well as complex poly-aromatic hydrocarbons³. The condensation of tar in the low-temperature zones of gasifiers results in plugging and fouling. Typically, the amount of tar is reduced by steam ⁴⁰ reforming at high temperatures which cracks tar, producing
- lighter molecules such H_2 and CO^1 . Steam reforming of tar (C_nH_x) is illustrated by the following equation^{1, 5}:

$$C_n H_m + nH_2 O \rightarrow nCO + \left(n + \frac{m}{2}\right) H_2, \quad \Delta H_{298}^0 > 0$$

Reaction temperatures can be reduced through the use of catalysts. Various metal catalysts have been investigated such as Ni⁶⁻¹⁷, Co¹⁸⁻²¹, Fe^{6-10, 19, 22-23}, noble metal²⁵⁻²⁶ for steam reforming of biomass tar using toluene or benzene as the model compound. ⁵⁰ Recently, Li et al.²⁷ published a review on catalyst development for biomass tar reforming using either toluene, benzene, naphthalene, or phenol as model compounds. They concluded that Rh, Ni and Co are promising materials as catalyst for biomass tar reforming. Ni and Co are much cheaper than Rh, ⁵⁵ however, the improvement on catalytic activity and stability are needed to obtain the similar catalytic performance with the Rh catalyst.

It has been reported that coke formation can be minimized in various ways using catalyst modification. One of the modifications is to introduce oxygen property into the catalyst using few ways, such as forming perovskite structure²⁸⁻³⁰, promoting with elements having redox property³¹⁻³² or oxygen storage property³³⁻³⁴. Urasaki et al.²⁹ investigated the coking resistance as well as catalytic activities of several Ni/perovskite

Ni/LaAlO₃ and Ni/SrTiO₃ demonstrated high catalytic activities. Lattice oxygen in or on the support are believed to have played an active role in oxidizing CH_x adsorbed onto the nickel catalyst ⁵ surface. Stathopoulos et al.³⁰ also shed light on the high redox property of La_{0.8}Sr_{0.2}FeO_{3-x} catalyst support for the deNO_x reaction by H₂ and CH₄. Cu and Fe are popular elements having reduction-oxidation (redox) property which aids in the reduction of carbon deposition. Tomishige et al.^{18,31} reported the use of Fe 10 in Ni-Fe/α-Al₂O₃ catalyst in steam reforming of biomass tar and found that addition of Fe to Ni/a-Al2O3 catalyst enhanced catalytic activity by formation of Ni-Fe alloy and catalytic stability due to the presence of Fe on the catalyst surface which increases the oxygen storage/vacancy of the catalyst. Kawi et al.⁶ 15 reported that the addition of CeO₂ to the Ni/CaO-Al₂O₃ catalyst resulted in less carbon formation compared to the unpromoted catalysts. Another option for catalyst modification is using basic metal as promoter for the catalyst^{8-10, 35-42}. Our previous study⁸⁻⁹ showed that substitution of small amount of Sr with La in the 20 La_{0.8}Sr_{0.2}Ni_{0.8}Fe_{0.2}O₃ catalyst showed good catalytic activity and stability, especially at low amount of steam (Steam/Carbon=1) due to property of Sr in LSNFO catalyst to adsorb and desorb more water at higher temperature than La. The synergetic effect of Sr and La helps to enhance the catalyst stability. Choong et 25 al.⁴¹ also reported that addition of CaO to Ni catalyst promoted water adsorption and provided abundance of adsorbed OH groups to facilitate the C-C break in Ni catalyst, resulting in higher ethanol conversion in steam reforming of ethanol. Viinikainen et al.⁴² also reported that higher basicity of catalyst is a favorable 30 property for tar decomposition resulting in enhancement of catalyst stability. The last option to reduce coke deposition is by operating the reaction at high reaction temperatures and excess

catalysts in the steam reforming of methane. Of which,

steam-to-carbon ratio⁴³. Sekine et al.^{5,28,44.45} revealed that partially Sr-substituted
³⁵ catalyst support (Ni/La_{0.7}Sr_{0.3}AlO_{3-δ}) demonstrated higher catalytic activity and lower amounts of carbon deposition in the steam reforming of toluene as opposed to Ni/LaAlO₃ catalyst. This was attributed to the lattice distortion caused by partial Sr doping, resulting in the increase in amount of oxygen vacancies,
⁴⁰ which enhanced the mobility of lattice oxygen species. These were elucidated from XPS, XRD and transient isotopic H₂O¹⁸ analyses. Indeed, lattice oxygen is known to be capable of playing a significant role in promoting the catalytic activities of perovskite catalysts, but little research has uncovered the actual
⁴⁵ role of oxygen in these catalysts.

In this work, the role of lattice oxygen in the steam reforming of toluene would be elucidated through a series of comprehensive catalyst characterization methods. In addition, it can be postulated that the presence of oxygen vacancies formed by Sr-doping might

- ⁵⁰ enhance the effectiveness of minute amounts of gas-phase oxygen in the feed introduced to the toluene steam reforming reaction. Varied reforming temperatures and oxygen gas concentrations might also affect the roles of lattice and gas-phase oxygen. As an extension of the studies by Sekine et al.⁴⁴⁻⁴⁶, this study aims to
- ss reveal the actual roles of lattice and gas-phase oxygen in the steam reforming of toluene under varied oxygen gas concentrations.

60 Experimental

Catalyst synthesis

Ni catalysts supported on La_{0.8}Sr_{0.2}AlO₃, LaAlO₃, α-Al₂O₃ and La₂O₃ were prepared using conventional wet impregnation method with Ni loading amount of 10wt%. The molar ratio of 65 La:Sr of 8:2 in La_{0.8}Sr_{0.2}AlO₃ was chosen based on our previous results⁸. Catalyst supports La_{0.8}Sr_{0.2}AlO₃ and LaAlO₃ were prepared by a citric acid complex method. Firstly, metal nitrate precursors La(NO₃)₃.6H₂O, Sr(NO₃)₂ and Al(NO₃)₃.9H₂O (Sigma-Aldrich) were dissolved in water. Thereafter, an ⁷⁰ equimolar amount of citric acid C₆H₈O₇.H₂O (Sigma-Aldrich) to metal was added to the solution. The mixture was then evaporated at 55°C while stirring until it was dried. The dried powder was stored at 100°C overnight until a dome shape was formed. The sample was then crushed and calcined at 400°C for 75 30min, followed by further calcinations at 850°C for 7h. $La_{0.8}Sr_{0.2}AlO_3$, $LaAlO_3$, La_2O_3 and α -Al₂O₃ were then impregnated with a solution comprising nickel nitrate, Ni(NO₃)₂.6H₂O (Sigma-Aldrich). Likewise, the solution was evaporated at 55°C while stirring until it was dried. The dried ⁸⁰ powder was then stored at 100°C overnight. Finally, the samples were calcined at 850°C for 7h. The prepared catalysts are denoted as NLSAO, NLAO, NA, and NL for Ni/La_{0.8}Sr_{0.2}AlO₃, Ni/LaAlO₃, Ni/α-Al₂O₃, and NL.

85 Catalyst Characterization

X-ray Diffraction (XRD)

X-ray diffraction was carried out using monochromatised Cu K α radiation at 40kV and 30mA (XRD-6000; Shimadzu Corporation) for both fresh and reduced catalysts. The reduced 90 catalysts were treated in pure H₂ gas at 700°C for 30min. The samples were placed on a clear plastic slide and scanned from 2 θ of 10° to 80° at a rate of 2°/min. The receiving slit was 0.3mm, whereas the divergent and scattering slits were set to be 1mm.

95 Hydrogen temperature-programmed reduction (H2-TPR)

Temperature-programmed reduction (TPR-H₂) was conducted using Thermo Scientific TPDRO 1100 TPR/TPD system with a thermal conductivity detector (TCD). 50mg of fresh catalyst was used in the experiment. Prior to analysis, the sample was pretreated with helium gas at 300°C for 1h to remove impurities, and then heated from room temperature at 10°C/min to 1000°C with a 5% H₂/N₂ mixture. The TPR-H₂ profiles were generated through the monitoring of the changes in the signal of the temperature conductivity detector (TCD) against temperature.

X-ray Photon Spectroscopy (XPS)

105

X-ray photoelectron spectroscopy (XPS) was conducted in a spectrophotometer (AXIS Ultra DLD; Kratos Analytical) using mono-chromatized Al K α x-ray source with 1486.71eV photons,

at 15kV and 5mA, and with a constant dwell time of 100min. Prior to the analysis, the catalyst was ex-situ reduced at 700°C under H₂ for 30 mins which is the same as the reduction condition during reaction. The sample was then mounted on the standard s sample stub using double-sided adhesive tapes. The resulting

XPS peaks were fitted using XPSPeak fitting software. Binding energies were calibrated by referencing the C1 (C-C) bonds to 284.5eV.

10 Temperature programmed desorption of oxygen (TPD-O₂)

Temperature programmed desorption of oxygen (TPD–O₂) was conducted using Quantachrome ChemBET 3000 TPR/TPD system with a thermal conductivity detector (TCD). Prior to analysis, 100mg of each fresh catalyst was packed in a U-tube, *is in-situ* reduced at 700°C for 30min using pure H₂ gas, and flushed with oxygen at 300°C for 100min. The samples were then heated at a rate of 10°C/min to 1000°C in an atmosphere of helium gas. Desorption analyses were carried out by monitoring the signal readings of the thermal conductivity detector against the ²⁰ temperature of the sample. The TPD profile was recorded by a microcomputer.

TGA-DTA

The amounts of carbon deposition on spent catalysts were ²⁵ evaluated using a thermogravimetric analysis (TGA) (DTG-60 TG/DTA; Shimadzu). Around 10mg of spent catalysts were placed on an alumina pan under atmospheric pressure and heated at 10°C/min to 1000°C. The change in mass of the spent catalysts against temperature would be recorded. In addition, the ³⁰ differential peak temperature would be recorded to reveal the nature of the carbonaceous compounds present in the spent catalysts.

Field Emission Scanning Electron Microscopy (FESEM)

The morphologies of the spent catalysts were observed using a field emission scanning electron microscope (FESEM) (JSM-6700F; JEOL). A small amount of each spent catalyst was thinly dispersed on a copper stub, and thereafter coated with a layer of platinum using Pt-sputtering that was carried out for 60s at 40 20mA. Prepared samples were then analyzed with an electron

beam of 5 – 15kV, using a magnification of 25,000X.

Evaluation of Catalytic Activities

Catalytic activity tests were conducted at atmospheric pressure ⁴⁵ using a 60 cm fixed bed quartz tube reactor (I.D. 4mm) which was enclosed within a programmable furnace. 30mg of catalyst was utilized for each reaction, and held in the middle of the fixedbed reactor using quartz wool. Prior to the catalytic reaction at 650°C, the catalyst was reduced in 30 mL/min H₂ at 600°C for 30 ⁵⁰ mins, followed by purging in 120 mL/min helium while the

- temperature was increased to the reaction temperature. The feed of toluene and water was directed through a pre-heating coil held at a temperature of 300°C prior to entering the reactor to vaporize the inlet feed. The feed components, steam and toluene were spummed into the reactor at a steam/carbon (S/C) ratio of 1:1
- 55 pumped into the reactor at a steam/carbon (S/C) ratio of 1:1

molar ratio and GHSV 460,000 ml/g.h. Helium was selected as the carrier gas for the steam and toluene feed. The product gas exiting the reactor was connected to a condenser that was held at 5°C in to condense and remove unreacted toluene and water. 60 Non-condensable product gases were analyzed using gas chromatography. For reaction with oxygen, the flowrate of halium was adjusted so that the total flowrate of helium and

helium was adjusted so that the total flowrate of helium and oxygen is still 120 mL/min. The gas-chromatograph (HP 6890; Agilent) was equipped with

⁶⁵ a 15" column (I.D. 2.1mm) packed with 60/80 mesh Carboxen-1000 packing (Carboxen-1000; Sigma-Aldrich) and a thermal conductivity detector (TCD). The gas chromatograph was programmed to collect gas samples at 15-minute intervals. The chromatogram obtained for each reaction run showed peaks for

70 H₂, CO and CO₂ product species. The area of each peak was calculated using the integral function of the offline software coupled to the gas chromatograph. Based on the peak areas, the volume percentage of each product gases was obtained using the calibration curves that were previously determined. The 75 individual volumetric flow rate of the product gases was obtained based on their volume percentage and the total volumetric flow

$$X_{Toluene}(\%) = \frac{n_{CO} + n_{CO_2} + n_{CH_4}}{7 * n_{T,in}} x \, 100$$

rate of the product gases. The conversion of toluene was expressed in term of carbon conversion and calculated using the following formula:

80 where n is molar flow rate of each gas.

Results and discussion

XRD - Catalyst structure analysis

X-ray diffraction was carried out for freshly calcined and 85 reduced NLSAO, NLAO, NA and NL catalysts and depicted in Figures 1a and 1b. All XRD profiles were referenced with the Xray Powder Diffraction Database from the International Centre for Diffraction Data (ICDD) for characterization of the phases present. In Ni/Al₂O₃ catalyst, small NiAl₂O₄ spinel phase is 90 observed in addition to NiO peak. The presence of NiAl₂O₄ peak shows strong metal-support interaction in NA catalyst, resulting in enhanced difficulty for complete reduction of nickel to the Ni⁰ metallic state⁴⁷, even though the Al₂O₃ is α -Al₂O₃ which is very stable at high temperature. The NiO peak is observed strongly in 95 the XRD profile showing that this catalyst has quite big size of NiO particles. In contrast, the NiO peak is hardly not observed in fresh NL catalyst. Instead, LaNiO₃ perovskite and La₂NiO₄ spinel phases are observed well, showing that Ni has interaction between Ni and La2O3. Both NLSAO and NLAO fresh catalysts 100 show similar XRD patterns corresponding to the perovskite structure.

A comparison of the (110) perovskite peak for both freshly calcined NLSAO and NLAO catalysts reveals that the peak is observed at 20 of 33.62° for NLAO catalyst, but a lower angle at 20 of 33.54° for NLSAO catalyst. This shift is better illustrated in the magnified (110) peaks in Figure 1c. Furthermore, the full width at half maximum (FWHM) of both (110) perovskite peaks is calculated to be 0.54° for NLSAO catalyst as opposed to 0.40° for NLAO catalyst. The slight shift in peak angle and broader

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(110) perovskite peak for NLSAO catalyst demonstrated the distortion of the structure of perovskite due to the partial substitution with Sr, which can cause structural defects, resulting in oxygen nonstoichiometry i.e. lattice oxygen⁴⁸. This structural ⁵ distortion could lead to greater lattice oxygen of NLSAO catalyst as compared to the relatively stable NLAO catalyst. This enhanced lattice oxygen mobility of NLSAO catalyst could confer higher redox abilities, thereby resulting in improved catalytic activity and stability.



 $\begin{array}{l} \textbf{Fig 1a XRD of fresh catalysts} \left[\alpha: LaAlO_3, \beta: NiO, \delta: La_2O_3, \zeta: La_2NiO_4, \\ \epsilon: LaNiO_3, \kappa: NiAl_2O_4, \gamma: La(OH)_3, \lambda: Al_2O_3 \right] \end{array}$

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Fig. 1b XRD of reduced catalysts, $2\theta = 10^{\circ}$ to $2\theta = 80^{\circ}$ [α : LaAlO₃, η : Ni, δ : La₂O₃, κ : NiAl₂O₄, λ : Al₂O₃]



Fig. 1c Magnified (1 1 0) LaAlO₃ perovskite x-ray diffraction peaks of freshly calcined Ni/La_{0.8}Sr_{0.2}AlO₃ and Ni/LaAlO₃

TPR - catalyst reducibility analysis

As elucidated from Figure 2, the TPR profiles of NLAO and NLSAO catalysts both possessed a single peak at 457°C and 25 402°C, respectively. These reduction peaks correspond to the reduction of bulk NiO (Ni²⁺) to Ni^{0 49-50}. The partial substitution of lanthanum with strontium resulted in a shift of the reduction peak to a lower temperature. This is coherent with literature, which reported that the substitution of an A-site cation (La^{3+}) by ³⁰ another cation of lower valence (Sr^{2+}) could significantly reduce the stability of the perovskite structure, thereby increasing the mobility of lattice oxygen⁵¹⁻⁵². This facilitates its removal as water during reduction, therefore enhancing the reducibility of the perovskite⁵³. In order to maintain the stability of the 35 perovskite structure after such substitution, charge compensation is required. This could be achieved through either through the existence of Ni ions possessing valence states higher than 3+, or through the formation of an oxygen deficit perovskite, in the form ABO3-6 53



Finally, the TPR profile of NA catalyst demonstrated a strong so single peak at 425°C and a small shoulder peak at higher temperature. This single peak at lower temperature corresponds to the reduction of bulk NiO (Ni²⁺) to Ni⁰ ⁴⁹⁻⁵⁰, meanwhile the small shoulder peak at higher temperature can be attributed to the presence of NiAl₂O₄ phase, which can be confirmed by XRD so data. The presence of weak NiAl₂O₄ peak could indicate the presence of big Ni particle, which can be observed clearly from XRD of reduced NA catalyst.



30 catalyst.

XPS of reduced catalysts

The O 1s XPS profiles of reduced NLSAO, NLAO, NA and NL catalysts are presented in Figure 3. The XPS O 1s peak was reported to have a binding energy of 529.9eV^{55} . Based on curve s fitting analyses, the O 1s XPS profiles of reduced NL and Ni/Al₂O₃ catalysts both possessed a single peak at similar binding energies of 528.1 eV. Both of these peaks could be attributed to the O²⁻ oxidation state.

Doublet peaks are present in the O 1s XPS spectra of both ¹⁰ reduced NLSAO and NLAO catalyst. The peak with lower binding energy is attributed to lattice oxygen (O_{lattice}), whereas the peak with higher binding energy is attributed to adsorbed oxygen species onto the catalyst surface (O_{adsorbed})⁵. These could include adsorbed oxygen (O₂), hydroxyl (OH), carbonate (CO₃²⁻), and ¹⁵ water (H₂O) species⁵¹. The presence of these additional peaks indicates that the perovskite based catalysts possessed oxygen vacancies that were not present in NL or Ni/Al₂O₃.

The binding energies of both peaks of reduced NLSAO and NLAO catalysts are recorded in Table 1. Evident from Table 1, ²⁰ the binding energy of the lattice oxygen peak of reduced NLSAO catalyst is significantly lower than that of reduced NLAO catalyst. This could be explained by the partial substitution of lanthanum with strontium that is of lower valence. This oxidation state imbalance between lanthanum (La³⁺) and strontium (Sr²⁺) ²⁵ sites were reported to increase the amount of oxygen vacancies, thereby increasing the mobility of lattice oxygen species, allowing them to partake in oxidation as surface oxygen species of NLSAO catalyst is also lower than that of reduced NLAO



Fig. 3 XPS O 1s profiles of various reduced catalysts

Assuming the number of electrons recorded by XPS analysis is proportional to the number of atoms at a given state, the percentage atomic concentrations of each atom could be calculated. For the perovskite catalysts, the ratio of $O_{adsorbed}$ and $O_{lattice}$ species could be determined based on curve fitting analyses using XPSPeak software to calculate the concentration of surface oxygen vacancies (δ). For the defective perovskite present in the form of ABO_{3- δ}, O/(A+B) is equivalent to $(3-\delta)/2^5$. Therefore,

$$\delta = \frac{2[O_{lattice}]}{[La] + [Sr] + [Al]}$$

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- ⁴⁵ The concentration of surface oxygen vacancies for both reduced NLSAO and NLAO catalysts were calculated and tabulated in Table 1. Evidently, strontium substitution in La_{0.8}Sr_{0.2}AlO₃ catalyst support yielded a catalyst with higher concentrations of surface oxygen vacancies. This conferred ⁵⁰ NLSAO catalyst with better oxygen adsorption abilities. Furthermore, this also enhanced the mobility of lattice oxygen in
- Furthermore, this also enhanced the mobility of lattice oxygen in NLSAO catalyst to partake in oxidation as surface oxygen species⁵.

55	5 Table 1 Peak binding energies and concentration of surface of	oxygen
	vacancies (δ) on reduced NLSAO and NLAO	

Catalyst	Binding end	ergy of peak/ eV	Concentration of surface
Catalyst	Olattice	Oadsorbed	oxygen vacancies (δ)
Reduced NLSAO	525.62	528.12	2.16
Reduced NLAO	525.99	528.20	1.61

Temperature-Programmed Desorption of Oxygen (TPD-O₂)

TPD-O₂ was carried out for reduced NLSAO, NLAO, 60 Ni/Al₂O₃ and NL catalysts, in order to determine the extent of gas-phase oxygen uptake and the temperature of desorption of adsorbed oxygen species. The TPD-O2 results are illustrated in Figure 4. It can be observed that reduced NLSAO and NLAO catalysts demonstrated the largest extent of oxygen desorption 65 between the temperatures of 100°C and 1000°C, while no obvious peaks are observed for NL and NA catalysts, indicating that there is no lattice oxygen in these both catalysts, which is in agreement with XPS result. The presence of oxygen desorption peak shows the presence of oxygen vacancies in these perovskite 70 oxide catalysts, thereby allowing a greater extent of lattice and gas phase oxygen uptake onto the surface of these catalysts. Therefore, a larger amount of oxygen can also be desorbed eventually at higher temperatures. In addition, from the desorption peak formations illustrated in Figure 4, it was evident 75 that a majority of the oxygen on both NLSAO and NLAO catalysts desorbed at temperatures between 600°C to 800°C, which coincides with typical reaction temperatures used for the steam reforming of toluene. Therefore, oxygen would be expected to play a positive role in enhancing the catalytic 80 performances of NLSAO and NLAO catalysts in the steam reforming of toluene.



Fig. 4 TPD-O₂ profiles of various reduced catalysts

The TPD-O₂ profile of reduced NLSAO catalyst clearly ⁵ demonstrated two desorption peaks, one at a lower temperature of around 330°C and another at approximately 710°C. The lower temperature desorption peak is characteristic of oxygen species that were released from surface oxygen vacancies⁵⁶⁻⁵⁷. This is indicative that surface oxygen vacancies were present on the ¹⁰ surface of reduced NLSAO catalyst. In contrast, reduced NLAO catalyst also appeared to possess such a low temperature peak at a higher temperature of around 500°C, but the peak was less obvious. This may be indicative that there exists a lower concentration of such surface oxygen vacancies on the surface of ¹⁵ reduced NLAO catalyst.

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The higher temperature desorption peak of both reduced NLSAO and NLAO catalysts correspond to the migration of lattice oxygen in the bulk perovskite catalysts⁵⁹. Comparing the oxygen desorption profiles of reduced NLSAO and NLAO ²⁰ catalysts, the strontium doped perovskite catalyst possessed a slightly lower lattice oxygen desorption peak temperature of approximately 710°C, as opposed to a desorption peak of adsorbed oxygen and lattice oxygen desorption peaks of reduced

- ²⁵ NLSAO catalyst to a lower temperature as compared to NLAO catalyst are consistent with XPS results, where binding energies of both the adsorbed oxygen species and lattice oxygen species of NLSAO catalyst were found to be lower than that of reduced NLAO catalyst. Evidently, the partial substitution of lanthanum
- ³⁰ with strontium that resulted in oxidation state imbalance between lanthanum (La³⁺) and strontium (Sr²⁺) sites, creating oxygen vacancies that enhanced both the lattice oxygen and surface oxygen desorption abilities of reduced NLSAO catalyst.

35 Catalytic performances of prepared catalysts in absence of gas-phase oxygen

The catalytic performance of prepared catalysts in steam reforming of toluene in terms of toluene conversion is shown in Figure 5a and H₂ yield in Figure 5b. The catalytic activities of 40 those catalysts decrease in the following order: NL> NLSAO> NLAO> NA. Even though NL catalyst demonstrates the highest catalytic conversion, it has very high carbon deposition as the pressure of reactor system increased until the flow of He carrier gas could not pass through the catalyst bed and then the reaction 45 was stopped. In contrast, the other three catalysts demonstrate relatively stable carbon conversions throughout the entire duration of the reaction runs.

Table 2 tabulates the average results of the catalytic performance in terms of carbon conversion, production rate, and 50 H₂/CO. It can be seen in Table 2 that the H₂/CO ratios over NLAO, NA and NL are comparable at 3.03, 3.58 and 3.83 respectively, but that over NLSAO catalyst is significantly higher at 8.35. This enhancement of H₂/CO ratio could be attributed to the Sr substitution of the NLAO perovskite based catalyst. The 55 ideal steam reforming of toluene reaction with steam/carbon ratio of 1 should follow the reaction $C_7H_8 + 7H_2O \rightarrow 7CO+11H_2$, which result in H₂/CO ratio of 11/7. However, in reality, the water gas shift (WGS) reaction always occur simultaneously (CO + H₂O \rightarrow H₂ + CO). The combination of these two reaction will 60 give H₂/CO more than 11/7, depending on the contribution of WGS reaction. Furthermore, our previous study⁸⁻¹⁰ shows that combination of La₂O₃ and SrO is very good in water activation which provides more hydrogen to the whole reaction. Hence, the high H₂/CO ratio such as 8.35 is possible to be achieved. 65 Furthermore, carbon formation rate on NLSAO catalyst (which is explained later) is the lowest among other catalysts even though the conversion is quite high due to the presence of lattice oxygen which can oxidize the carbon species into CO and/or CO₂.

In addition, Table 2 also shows the average %-molar of ⁷⁰ product gases produced from the reaction. The H₂ %-molar of NLSAO catalyst is slightly higher than the one of NLAO catalyst, but the CO %-volume of NLSAO catalyst is much lower than NLAO catalyst. The low CO %-molar from NLSAO catalyst is due to very good water activation of combination between La₂O₃ ⁷⁵ and SrO as well as high contribution of WGS reaction, which can be confirmed with the high CO₂ %-molar. This result shows that WGS reaction has high contribution in this reforming reaction.

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Table 2 Summary of catalytic activity of various catalysts at 650°C

Catalant	Average		Average production rate (mol.gcat ⁻¹ .min ⁻¹)			Average % molar			H ₂ /CO	
Catalyst	(%)	H_2	СО	CH_4	CO ₂	H_2	СО	CH_4	CO_2	Ratio
NLSAO	20.03	501.6	60.3	0	192.2	66.51	8	0	25.49	8.35
NLAO	12.84	235.9	78.9	0	82.9	59.32	19.84	0	20.84	3.03
NA	5.31	65.1	18.3	0	48.6	49.32	13.86	0	36.82	3.58
NL	35.51	831.6	220.1	1.4	225.9	65.02	17.21	0.11	17.66	3.83

conversion and H₂ yield, respectively for all prepared catalysts. In the presence of 5 ml/min (223 µmol/min) of pure gas-phase 25 oxygen, both catalytic conversions and H₂ yield in steam reforming of toluene over all four catalysts increase. Gas-phase oxygen gas in the feed is found to have a positive role in enhancing the catalytic activities of all four catalysts in the steam reforming of toluene. Similar to catalytic performance in the 30 absence of gas-phase oxygen, catalytic activities of the four catalysts decrease in the following order: NL> NLSAO> NLAO> NA. Compared to Figure 5a and 5b, Figures 6a and 6b also reveal that catalytic activities over all four catalysts are more stable in the steam reforming reaction in the presence of 5ml/min of gas-35 phase oxygen. Likewise, it is apparent that amongst the four catalysts, NL catalyst demonstrates the lowest catalytic stability as evidenced by reactor blockage around 7.5h of steam reforming reaction.

A comparison of Tables 2 and 3 reveals that in steam ⁴⁰ reforming of toluene over NLSAO, NLAO, NA and NL catalysts in the presence of 5ml/min gas-phase oxygen, the following trends for are observed as compared to the corresponding reactions in the absence of gas-phase oxygen:

- 1. The average production rates of H₂, CO and CO₂ over all four catalysts increase.
- This resulted in a decrease in H₂/CO ratio over all four catalysts in the presence of gas-phase oxygen.

Specifically for NLSAO catalyst, the CO %-molar in the presence of oxygen is more than twice higher than the one in the absence 50 of oxygen while the H₂ and CO₂ %-molar in the presence of

oxygen are only slightly lower than those in the absence of oxygen. This result indicates that the oxygen helps to oxidize the deposited carbon to CO.

Fig. 5 (a) Carbon conversion and (b) H_2 yield of various catalysts at 650°C. Reaction condition: toluene 188 µmol/min; steam 1316 µmol/min; He 5357 µmol/min; W = 30 mg; reaction temperature 650°C; GHSV 460,000 ml/g.h

20 Catalytic performances of prepared catalysts in presence of gas-phase oxygen

Figure 6a and 6b show the catalytic activity in terms of toluene b 30 $^{-}$



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Figure 6 (a) Carbon conversion and (b) H_2 yield of various catalysts at 5 650°C. Reaction condition: toluene 188 µmol/min; steam 1316 µmol/min; O_2 223 µmol/min; He 5134 µmol/min; W = 30 mg; reaction temperature = 650°C; GHSV 460,000 ml/g.h



Table 3 Summary of catalytic activity of various catalysts in the presence of O2 at 650°C

Catalvat	Catalyst Average conversion (%)	Average production rate (mol.gcat ⁻¹ .min ⁻¹)			Average %molar			H ₂ /CO		
Catalyst		H_2	СО	CH_4	CO_2	H_{2}	СО	CH_4	CO_2	Ratio
NLSAO	67.5	1197.3	373.7	0	476.8	58.47	18.25	0	23.28	3.22
NLAO	31.65	348.7	152	0	246.9	46.64	20.33	0	33.03	2.29
NA	25.93	195.8	119.7	0	207.1	37.47	22.90	0	39.63	1.64
NL	75.12	1360.3	513.2	19.9	413.5	58.97	22.25	0.86	17.92	2.66

Catalytic performance of NLSAO catalyst at various O₂ flow rates

The results of the steam reforming reactions over NLSAO ²⁵ catalyst at 650°C in the presence of 5ml/min, 7.5ml/min, 10ml/min and 12.5ml/min gas-phase oxygen in the feed stream are illustrated in Figures 7a and 7b. It can be seen that as oxygen flow rate increases from 5ml/min to 12.5ml/min, the percentage carbon conversion and H₂ yield also increases. Therefore, overall ³⁰ catalytic activity increases as the oxygen flow rate was increases. In particular, this increase in catalytic activity is the most significant when O₂ flow rate increases from 5ml/min to 7.5ml/min. Thereafter, as O₂ flow rate further increases from 7.5ml/min through 12.5ml/min, the increment in catalytic activity ³⁵ is marginal.



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Fig. 7 (a) Carbon conversion and (b) H_2 yield of NLSAO catalyst at various O_2 flow rate. Reaction condition: toluene 188 µmol/min; steam 1316 µmol/min; O_2 223-557.5 µmol/min; He 4799.5-5134 µmol/min; W = 30 mg; reaction temperature = 650°C; GHSV 460,000 ml/g.h

Thermogravimetric Analysis (TGA)

Thermogravimetric analyses were conducted on spent NLSAO, NLAO, NL and NA catalysts after 8h of steam 10 reforming of toluene at 650°C in the absence and presence of 5ml/min gas-phase oxygen in the feed. The results are summarized in Table 4. The amount of carbon deposition on spent catalysts after 8h of steam reforming reaction in the absence of gas-phase oxygen followed the order: NL> NLAO> NA> 15 NLSAO. The low amounts of carbon deposition over NA catalyst could be related to low catalytic activities of the NA catalyst, whereas the high extent of carbon deposition over NL catalyst demonstrates that despite its high catalytic activity, it was not capable of conferring sufficient coke resistance in the steam 20 reforming of toluene. Therefore, the rate of production of coke via the Boudouard reaction and toluene and methane decomposition reactions far exceeded the rate at which carbon was removed.

25 Table 4 Amount of carbon deposition on spent catalysts after 8h reaction with and without 5ml/min gas phase oxygen in feed.

Catalyst	Coke format	tion (%wt)	Coke formation $(mg g-cat^{-1} h^{-1})$		
	Without O2	With O ₂	Without O2	With O ₂	
NLSAO	12.82	5.02	16.02	6.27	
NLAO	19.00	8.41	23.75	10.51	
NA	13.37	12.03	16.71	15.04	
NL	33.68	23.30	42.10	29.13	

Comparing the perovskite catalysts, the amount of carbon deposition over NLSAO catalyst was lower than that over NLAO ³⁰ catalyst due to strontium substitution of the LaAlO₃ perovskite, which led to greater mobility of lattice oxygen for the oxidation of carbon formed during the steam reforming of toluene. In addition to the amount of coke formation, Figure 8 shows the DTA profiles of coke produced from NLSAO and NLAO ³⁵ catalysts. The position of the peak can indicate the type of carbon and difficultness to be oxidized. The NLSAO catalyst shows two peaks of DTA profiles at 525°C and 605°C, while the NLAO catalyst only show one peak at 552°C. Wang et al.⁵⁸ classified the deposited carbon into 3 types, i.e. amorphous carbon, ⁴⁰ encapsulating carbon, and whisker/graphitic carbon, which has DTA peak at around 330, 460, and 650°C, respectively. The presence of whisker carbon is not a major issue as it can grow on top of the metal, hence, it will not affect the catalytic performance. In contrast, encapsulating carbon can cover the ⁴⁵ metal active sites, causing catalyst deactivation. According to these categories, the carbon on NLSAO and NLAO catalysts could be whisker carbon, which can be seen as carbon nanotubes in FESEM. Moreover, the peak is located at lower temperature compared to reaction temperature (650°C), which can indicate ⁵⁰ that the carbon can be easily reformed during reaction.



Fig. 8 TGA-DTA profiles of (a) spent NLSAO catalyst and (b) spent NLAO catalyst after 8 h reaction without oxygen

- In the presence of gas-phase oxygen, the amount of carbon formed over all four spent catalysts demonstrated a reduction. The extent of carbon deposition over the spent catalysts followed the order: NL> NA> NLAO> NLSAO. Evidently, the coking resistance of the NLSAO and NLAO perovskite catalysts we exceeded that of NA catalyst in the presence of gas-phase oxygen in the feed. The extents of reduction of the amounts of coke in the presence of gas-phase oxygen were calculated to be 75.4%, 63.1%, 11.2% and 30.8% for spent NLSAO, NLAO, NA and NL catalysts respectively.
- ⁶⁵ The extent of reduction was the greatest for the perovskite based catalysts, due to the presence of oxygen vacancies that is characteristic of perovskite catalysts. These oxygen vacancies allowed more oxygen species to be adsorbed onto the catalyst surface to partake in the oxidation of coke. The larger amounts of
- 70 oxygen vacancies formed by the strontium substitution in NLSAO catalyst resulted in its greater resistance to coke formation as compared to NLAO catalyst. Evidently, oxygen vacancies present in perovskite catalysts enhanced the effectiveness of oxygen.
- The results of thermogravimetric analyses of spent NLSAO catalyst after toluene steam reforming at 650°C in the presence of 5ml/min, 7.5ml/min, 10ml/min and 12.5ml/min gas-phase oxygen are presented in Table 5. As oxygen flow rate was increased, the carbon deposited on the spent catalyst surface after 100min of reaction decreased significantly. This elucidates that gas-phase
- oxygen played a positive and significant role in conferring coking resistance in the toluene steam reforming reaction.

Table 5 Carbon deposition and first dif nitial peak temperature of spent
NLSAO catalyst in various amount of oxygen.

O ₂ flow rate	Coke formation	Coke formation	Differential peak
(ml-min ⁻¹)	(%wt)	(mg g-cat ⁻¹)	temperature (°C)
5	9.09	90.91	595.73
7.5	6.63	66.34	601.33
10	5.34	53.38	602.32
12.5	2.67	26.73	495.94

Field Scanning Electron Microscopy (FESEM)

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FESEM measurement was conducted for all spent NLSAO, NLAO, NL and NA catalysts after 8h of steam reforming of toluene at 650°C in the absence and presence of 5ml/min gas phase oxygen in the feed to elucidate the morphology of the surface of spent catalysts and was depicted in Figure 9 (a) to (h). 10 For reaction in the absence of gas phase oxygen in the feed stream in Figure 8 (a)-(d), it was apparent that spent NL catalyst contained the largest surface concentration of carbon nanotubes. This was also evident during the steam reforming reaction, where a significant build-up of pressure within the reaction tube was 15 experienced. This suggests that NL catalyst possessed high activity. However, because of high carbon formation rate, there is no space left for the carbon nanotubes to grow causing pressure built-up in the system and blocking of the gas flow. Spent NA catalyst appeared to possess the lowest surface concentration of 20 carbon nanotubes. This could be attributed to the low catalytic activity of NA catalyst, therefore smaller amounts of carbon was formed as a side product via the Boudouard reaction and deposited on the catalyst surface.





Figure 9 (a) – (d): Spent NLSAO, NLAO, NL and NA catalysts after 8h of steam reforming of toluene at 650°C in the absence of gas phase oxygen. (e) – (h): Spent NLSAO, NLAO, NL and NA catalysts after 8h of steam reforming of toluene at 650°C in the presence of 5ml/min gas phase oxygen.

Perovskite catalysts prove to be a plausible solution to overcoming the shortcomings of both NL and NA. They 40 conferred relatively high catalytic activities, and low to moderate amounts of carbon deposition. This was due to the redox capabilities of perovskite catalysts⁵. Comparing the morphologies of two spent perovskite catalysts after 8 hours of toluene steam reforming without oxygen in the feed stream in Figure 8 (a) and 45 (b), it was apparent that spent NLSAO catalyst possessed a lower concentration of carbon nanotubes on its surface as opposed to spent NLAO catalyst. This was due to the doping of La by Sr which is of lower valance, resulting in oxidation state imbalance and thereby increasing the amount of oxygen vacancies in 50 NLSAO catalyst. This increased the mobility of lattice oxygen species, allowing them to react more quickly with carbon deposited on the catalyst surface during steam reforming of toluene, and therefore reducing the observed surface concentration of carbon nanotubes on the spent catalyst 55 morphology. All the above observations are consistent with TGA analyses.

For spent NLSAO, NLAO, NA and NL catalysts after 8h of toluene steam reforming in the presence of 5ml/min oxygen in the feed stream, it was evident that the presence of oxygen enhanced ⁶⁰ the coking resistance of all catalysts. Figures 8 (e)–(h) all showed a substantially lower amount of carbon present on the spent catalyst surface as opposed to the corresponding Figures 8 (a)–(d). Gas phase oxygen played a positive role in supressing carbon formation and removing deposited carbon in all four catalysts. ⁶⁵ This result is in-line with carbon deposition measurement from TGA.

Role of lattice oxygen in the catalytic steam reforming of toluene

The NLSAO catalyst demonstrated higher catalytic activity in terms of toluene conversion as well as H₂ production rate in the steam reforming of toluene at 650°C in the absence of gas phase oxygen compared to NLAO catalyst. XRD, TPR and XPS catalyst characterization analyses indicated that the partial ⁷⁵ substitution of lanthanum with strontium that is of lower valence in NLSAO catalyst resulted in oxidation state imbalance between lanthanum (La³⁺) and strontium (Sr²⁺) sites, thereby reducing the stability of the perovskite structure and conversely increasing the amount of oxygen vacancies in the perovskite catalyst. The ⁸⁰ presence of oxygen vacancies lowered the activation energy of the migration of lattice oxygen, enhancing the mobility of lattice

oxygen species. This enhanced lattice oxygen mobility of NLSAO catalyst allowed more lattice oxygen species to partake in oxidation as surface oxygen species, resulting in higher redox abilities and consequently improved catalytic activity and s stability.

It was found that the strontium substituted NLSAO catalyst not only demonstrated higher overall toluene conversion and percentage H_2 yield as opposed to NLAO catalyst, but also demonstrated lower CO yield. This resulted in a much higher

¹⁰ H₂/CO ratio over NLSAO catalyst (H₂/CO = 8.35) as compared to NLAO catalyst (H₂/CO = 3.03). However, the overall average production rates of H₂, CO and CO₂ over NLSAO catalyst were all higher than that over NLAO catalyst. This is indicative that the lattice oxygen of NLSAO catalyst that possessed enhanced ¹⁵ mobility was able to function as active oxygen partook in the partial oxidation of toluene:

 $C_7H_8 + 70_{lattice} \rightarrow 7C0_{lattice} + 4H_2, \ \Delta H^0_{298} = -824.18 kJ/mol$

Thereafter, some of the $\mathrm{CO}_{\mathrm{lattice}}$ underwent the water-gas shift $_{\mathrm{20}}$ reaction,

$$CO_{lattice} + H_2O \rightarrow CO_{lattice}O + H_2$$
, $\Delta H^0_{298} = -41.2 \text{kJ/mol}$

The oxygen vacancies were regenerated by steam. These mechanisms are consistent with transient response tests using ²⁵ H₂¹⁸O over NLAO and NLSAO catalysts conducted by Sekine et al.⁴⁵.

Additionally, thermogravimetric analysis (TGA) analysis elucidated that the amounts of carbon formed over NLSAO catalyst was lower than NLAO catalyst in the steam reforming of ³⁰ toluene at 650°C for 8h. This is indicative that lattice oxygen with enhanced mobility in NLSAO catalyst could also partake in the partial oxidation of carbon deposited on the catalyst surface as active oxygen species, increasing the overall coking resistance of the catalyst in the steam reforming of toluene.

 $C + O_{lattice} \rightarrow CO_{lattice}, \qquad \Delta H^0_{298} = -110.5 \text{kJ/mol}$

Role of gas phase oxygen in the catalytic steam reforming of toluene

In the presence of 5ml/min gas phase oxygen in the feed stream, the overall percentage carbon conversion and hydrogen ⁴⁰ yield over all four catalysts in the steam reforming of toluene at 650°C increased, as opposed to the reaction in the absence of gas phase oxygen. This is indicative that the presence of gas phase oxygen in the feed led to enhanced catalytic activities. Likewise, gas phase oxygen undertook the partial oxidation of toluene:

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$$C_7H_8 + 7/2 O_2 \rightarrow 7CO + 4H_2$$
, $\Delta H^0_{298} = -824.18 \text{kJ/mol}$

Based on catalytic performance trends observed in the presence of gas phase oxygen, it was apparent from these results that some of the adsorbed gas phase oxygen (O₂ species) possessed strong ⁵⁰ oxidative abilities, and were capable of completely oxidizing some of the carbon monoxide species:

 $CO + 1/2 O_2 \rightarrow CO_2$, $\Delta H^0_{298} = -283 \text{kJ/mol}$

55 Comparing the overall increase in average percentage carbon conversion and hydrogen yield over NLSAO and NLAO catalysts in the presence of gas phase oxygen, both improvements were greater for the reaction over NLSAO catalyst as opposed to that over NLAO catalyst. In particular, average percentage carbon 60 conversion increased from 20.0% to 67.5% (3.4 times) for NLSAO catalyst, but only 12.8% to 31.6% (2.5 times) for NLAO in the presence of gas phase oxygen. Whereas, the average percentage H₂ yield increased from 15.5% to 36.9% (2.4 times) for NLSAO catalyst, but only 7.3% to 10.8% (1.5 times) for 65 NLAO in the presence of gas phase oxygen. Such phenomena can be explained by the presence of a greater amount of oxygen vacancies present on the surface of NLSAO catalyst as opposed to NLAO catalyst as elucidated from XPS analyses. This allowed more gas phase oxygen to be adsorbed onto the oxygen vacancies 70 present on the NLSAO catalyst surface to partake in the oxidation of toluene, thereby enhancing the effectiveness of the 5ml/min gas phase oxygen introduced to the feed stream.

Additionally, through thermogravimetric analysis (TGA), the spent catalysts after 8h of steam reforming of toluene in the ⁷⁵ presence of 5ml/min gas phase oxygen all demonstrated a decrease in the amount of carbon formation as opposed to the spent catalysts after the reforming reaction in the absence of gas phase oxygen. This indicates that gas phase oxygen played a positive role in the oxidation of carbon deposited on the catalyst ⁸⁰ surface,

$$C + 1/2 O_2 \rightarrow CO$$
, $\Delta H^0_{298} = -110.5 \text{kJ/mol}$

In particular, the extents of reduction of the amounts of carbon nanotubes in the presence of gas phase oxygen were calculated to be 75.4%, 63.1%, 11.2% and 30.8% for spent NLSAO, NLAO, ⁸⁵ NA and NL catalysts respectively, as opposed to the reaction in the absence of gas phase oxygen. The extent of reduction was the greatest for the perovskite based catalysts, due to the presence of oxygen vacancies. The larger amounts of oxygen vacancies formed by the strontium substituted in NLSAO resulted in its

⁹⁰ greater improvement in coking resistance in the presence of gas phase oxygen as compared to NLAO catalyst.

As the flow rate of gas phase oxygen was increased from 5ml/min to 12.5ml/min at 650°C, the overall percentage carbon conversion and H₂ yield for the steam reforming of toluene over ⁹⁵ NLSAO catalyst also increased. This increase in catalytic activity was the most significant when O₂ flow rate was increased from 5ml/min to 7.5ml/min. Thereafter, as O₂ flow rate was further increased from 7.5ml/min through 12.5ml/min, improvements in catalytic activity were increasingly marginal. This may be ¹⁰⁰ indicative that 7.5ml/min O₂ is optimal given the existing toluene steam reforming conditions.

At low O₂ flow rates, the surface oxygen vacancies on NLSAO were unsaturated, therefore an increase in oxygen flow rates from 5ml/min to 7.5ml/min allowed more gas phase oxygen species to ¹⁰⁵ be adsorbed onto the oxygen vacancies present on the catalyst surface, enhancing the oxidation of toluene. As O₂ flow rates were continually increased, the oxygen vacancies present on the catalyst surface became increasingly saturated, therefore any increase in oxygen flow rates would only result in a less than ¹¹⁰ proportionate increase in catalytic activities at high oxygen flow

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rates.

In addition, thermogravimetric analysis (TGA) revealed that as the flow rates of gas phase oxygen were increased from 5ml/min to 12.5ml/min, the extent of carbon deposition on spent NLSAO 5 catalyst after the toluene steam reforming reaction decreased. This is consistent with the preceding postulation that gas phase oxygen oxidized carbon deposited on the catalyst surface, resulting in enhanced coke resistance. In excess of gas phase oxygen, more of the carbon deposited would be oxidized, leading 10 to lower amounts of carbon deposition.

Conclusion

Four Ni-based catalysts: Ni/LaAlO₃ (NLAO), Ni/La_{0.8}Sr_{0.2}AlO₃ (NLSAO), Ni/La₂O₃ (NL), and Ni/Al₂O₃ (NA) 15 were developed for the steam reforming of tar using toluene as a model compound. NLSAO catalyst demonstrated the best catalytic performance in terms of both catalytic activity, as well as coke resistance. As evident from XRD, TPR-H₂ and XPS catalyst characterization analyses, the partial replacement of ²⁰ lanthanum (La³⁺) with strontium that is of lower valence (Sr²⁺) resulted in oxidation state imbalance in NLSAO catalyst, thereby reducing the structural stability of the perovskite oxide catalyst, and increasing the number of oxygen vacancies present in the catalyst. The presence of oxygen vacancies in NLSAO catalyst 25 lowered the activation energy of the migration of lattice oxygen (Olattice), enhancing their mobility and allowing them to function as surface oxygen species. For the steam reforming of toluene at 650°C, mobile lattice oxygen partook in the direct partial oxidation of toluene, forming CO_{lattice} and H₂.

³⁰ In addition, the formation of oxygen vacancies also allowed more gas phase oxygen species (O₂) introduced in the feed stream to be adsorbed onto the catalyst surface of NLSAO catalyst to partake in the oxidation of toluene. This enhanced the improvement in catalytic activity of NLSAO catalyst in the ³⁵ presence of gas phase oxygen as compared to undoped NLAO catalyst. Gas phase oxygen species possessed strong oxidative

abilities and were capable of completely oxidizing some of the feed toluene gas to form CO₂. As elucidated from TGA spent catalyst characterization techniques, both mobile lattice and gas ⁴⁰ phase oxygen species played positive roles in oxidizing deposited carbon on the catalyst surface during the steam reforming of toluene.

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50 Notes and references

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