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Catalytic reforming of tar model compound over $La_{1-x}Sr_x$ - $Co_{0.5}Ti_{0.5}O_{3-\delta}$ dual perovskite catalysts: Resistance to sulfide and chloride compounds



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ARTICLE INFO ABSTRACT Keywords: Sr-containing La1.0-Co0.5Ti0.5O3 as dual perovskite materials were investigated for the steam reforming of the Biomass tar model reforming toluene (SRT) reaction. The impact of Sr-doping on tolerance towards tar contaminants (chloride & H₂S) for the Chloride tolerance SRT reaction was also studied. Overall, an optimum catalyst composition of La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ gave superior Reversible H₂S poisoning reforming activity than others. At 700 °C (S/C = 2), La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ exhibited ~ 90 % of toluene con-Dual perovskites version and stable for 21 h. La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ also displayed 80 % and 65 % of toluene conversion in the H₂-rich syngas presence of 0.1 % and 1% of trichloroethylene (TCE) at 700 °C. XRD analysis revealed the formation of dual perovskite structures for calcined Sr doped La1.0-Co0.5Ti0.5O3 materials and negligible Co agglomeration during SRT reaction. TGA analysis revealed that the formation of carbon was insignificant during the SRT reaction at 700 °C. Finally, the superior catalytic performance of La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ catalyst over others is attributed to the availability of surface Co species (H₂ chemisorption), mobile O₂ species, and an optimum basic character.

1. Introduction

Tar is a complex mixture of largely aromatic hydrocarbons (like benzene, toluene, phenols, naphthalene, etc.), which is generated from thermal reaction of organic compounds with steam or limited supply of oxygen causing sequential pyrolysis and partial oxidation of organic compounds [1-4]. Biomass and, recently, refuse-derived fuel from municipal solid waste are some of the most commonly available renewable organic compounds. Converting these organic compounds to energy via gasification processes is a promising waste-to-energy technology in recent times [5]. However, the main concern for the potential commercialization of this technology is the complete conversion or removal of tar generated during the gasification process. Though tar is rich in hydrocarbon energy, it often causes major operational challenges due to fouling and blocking at a colder section of the gasifier, and interfering with downstream catalytic processes. Thus, efficient conversion of tar not only solves the above operational problems but also significantly improves the quality of synthesis gas generated. Moreover, catalytic conversion via steam reforming is one of the striking approaches for complete tar conversion in the gasification process, as it generates more valuable H₂ rich syngas [6-9].

In the steam reforming of tar reaction, the role of the catalyst is pivotal. The catalyst has to exhibit high catalytic activity concerning tar conversion, H₂ yields, and stability. Several types of catalysts such as natural minerals [10-13], bio-char [14,15], supported metal oxides [16-22], promoted metal catalysts [23-27], zeolites [28], structured catalysts (hydrotalcite, perovskites, and phyllosilicates) have been reported for steam reforming of tar reaction [29-35]. Among all, nickel and cobalt-based catalysts are the choices of priority due to their promising steam reforming activity and availability. These metal catalysts have been in monometallic forms [36,37], alloyed with other transition metals [38–40], and promoted with base metal oxides [20,33, 41,42]. Among them, Ni-based catalysts were extensively explored for steam reforming of tar reaction, especially in the absence of poisoning compounds such as sulfur. Whereas, cobalt-based catalysts have been investigated for various reforming reactions in the presence of sulfur-like compounds. Due to high oxophillic and redox nature, Co-based systems showed enhanced catalytic performance for resistance towards coke deposition, sulfur and NOx like compounds compared to Ni-based catalysts [43,44].

In order to adopt these catalyst systems for the gasification process of biomass and municipal solid waste (MSW) feedstocks, the catalysts must be active and resistant to natural inorganic trace compounds such as S, Cl, and N-compounds present in biomass and MSW feedstocks [45–47]. During steam reforming of tar reaction, catalysts tend to lose their activity due to the poisoning effect of coke deposition, sulfide, and chloride

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species, resulting in a slow decline of tar reforming efficiency. The content of Cl^- and sulfur compounds is highly dependent on the nature of the feedstock. Sulfur compounds are the major poisonous compounds present in biomass feedstocks. For MSW, it is possible to have a high quantity of chloride compounds both in inorganic (NaCl) and organic (PVC) form [48–50]. The sulfur poisoning of metal catalysts is caused by the formation of stable and inactive metal sulfide compounds, making metal species unavailable for reforming reaction. Similarly, poisoning due to chloride compounds is due to the formation of metal chlorides, which can potentially leach to downstream, depleting the metal from the catalyst due to sulfur and chloride compounds is serious, and few instances of it are irreversible. Therefore, it is required to develop efficient tar reforming catalysts which can resist deactivation by sulfur and Cl^- like poisonous compounds.

Our previous report, CeO2 promoted Co-based perovskites were investigated for steam reforming of toluene (SRT) reaction and its stability against coke deposition, H₂S, and NO poisoning [51]. Various types of Ni-based mono and bi-metallic perovskite materials were also reported for the steam reforming of the toluene reaction. In all the cases, the unique properties of perovskite materials such as high oxygen mobility, basicity, and redox property play a crucial role in promoting tar conversion activity and suppressing coke deposition during tar reforming reaction [16,36,52-56]. In a work, well-dispersed Rh sites on the LaCoO₃ perovskite layer showed improved H₂S tolerance during reforming reaction [57]. Given the above works, herein, we have reported La_xSr_{1-x}Co_{0.5}Ti_{0.5}O₃ materials for SRT application, where toluene was used as a model for the biomass-derived tar compound. The role of Sr-doping to Lax-Co0.5Ti0.5O3 perovskite materials characteristics and their influence towards toluene reforming activity was investigated with and without S and Cl⁻ compounds. A mixture gas of 50 ppm H₂S balance He gas is used for sulfur tolerant experiments, and trichloroethylene (TCE) is used as a model compound for Cl⁻ tolerant studies. TCE is a nonflammable liquid; upon decomposition at high temperature, 1 mol of TCE releases 03 mol of Cl⁻ ions. Finally, a structure-activity relation was elucidated using various characterization of reduced and spent catalysts.

2. Experimental

2.1. La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ perovskites synthesis

A series of La_xSr_{1-x}Co_{0.5}Ti_{0.5}O₃ perovskite materials were synthesized using ethylene glycol (EG) assisted sol gel method as reported elsewhere. In this synthesis method, the metal nitrate precursors of La, Sr and Co elements, and Ti(OC₃H₇)₄ of the required quantity were first dissolved in 10 mL of solvent mixture (DI water = 5 mL, EG = 2 mL and ethanol = 3 mL). At 60 °C, the solution was then stirred to get a gel-like mixture. The gel solution was then dried at 100 °C in an oven for 24 h. The oven-dried sample was air calcined in a box furnace at 400 °C/1 h, followed by 800 °C/3 h. The obtained powdered sample was ground into a fine powder with a particle size of < 125 µm. The synthesized samples were labeled as La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ perovskites, where x represents the strontium (Sr) molar ratio. About 06 materials were prepared with changing nominal contents of La and Sr compositions to understand the influence of Sr doping in La_{1.0}-Co_{0.5}Ti_{0.5}O₃ materials for steam reforming performance.

2.2. Characterization techniques for $La_{1-x}Sr_x$ -Co_{0.5}Ti_{0.5}O₃ materials

The surface area of the freshly calcined La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials were measured using Micromeritics ASAP 2020 analyzer by adopting the Brunauer-Emmett-Teller (BET) method. Powdered X-ray diffraction (XRD) patterns for La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials were obtained using Shimadzu XRD-6000 X-ray diffractometer. The samples were scanned between 20° and 80° with a scan rate of 2°/min. Thermo Scientific TPDRO 1100 series system (with TCD detector) was used to

measure H₂ temperature-programmed reduction (H₂–TPR), H₂ pulse chemisorption, and O₂/CO₂ temperature-programmed desorption (O₂/CO₂–TPD) experiments for all the materials. X-ray photoelectron spectra (XPS) of the reduced and spent La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials were measured using a Kratos AXIS spectrometer with a spatial resolution of 30 µm equipped with an Al K α (h ν = 1486.6 eV; 1 eV = 1.6302 × 10⁻¹⁹ J) X-ray source. The amount and nature of coke deposited during the SRT reaction are measured using the Shimadzu DTG-60 analyzer (TG/DT analysis). The detailed description for the above characterization techniques was provided in supplementary material and also reported elsewhere [31].

2.3. Steam reforming activity over $La_{1-x}Sr_x$ - $Co_{0.5}Ti_{0.5}O_3$ materials in H_2S and TCE compounds

Steam reforming of toluene activity over La1-xSrx-Co0 5Ti0 5O3 materials with and without H₂S and TCE compounds was carried out in a fixed-bed reactor (Fig. S1) [31,51]. The testing conditions for SRT reaction in the absence of any poisonous compounds were catalyst weight = 0.1 g, toluene flow rate = 188 µmol/min, steam-to-carbon (S/C) ratio = 2, reaction temperature = 700 $^{\circ}$ C and reduction temperature = 750 °C/1 h. In addition to above-operating conditions, for chloride tolerance tests, TCE concentration of 0.1 and 1% was fed with toluene. For sulfur compounds, tolerance tests, reaction temperature of 800 °C, and H₂S concentration of ~ 50 ppm was used. The 50 ppm of H_2S concentration was achieved by co-feeding 10 sccm of 500 ppm of H_2S/He and 90 sccm of pure He gas. Before the SRT reaction, all the catalysts were reduced in 30 sccm flow of H₂ gas at 750 °C/1 h. After reduction, the temperature was to the desired reaction temperature in He gas (100 sccm). Water and toluene were preheated at 250 °C, mixed with He gas and fed onto the catalyst. The unconverted reactants and liquid products were removed while the product mixture is passing through a ice cold trap from the reforming reaction. The gaseous product was analyzed using a GC with a TCD detector. Using a calibration curve and considering the total flow rate, the molar flow of each gas will be calculated. The % toluene conversion was calculated using Eq (1):

$$X_{\rm T} (\%) = (n_{\rm CH4} + n_{\rm CO} + n_{\rm CO2}) * 100 / (7*n_{\rm r in})$$
(1)

where X is toluene conversion percentage, and n is the molar flow rate of CH₄, CO, and CO₂ gases.

3. Results and discussion

3.1. Characteristics of fresh and reduced $La_{1-x}Sr_x$ -Co_{0.5}Ti_{0.5}O₃ perovskite materials

The powdered XRD patterns for calcined and reduced La1-xSrx- $Co_{0.5}Ti_{0.5}O_3$ materials are displayed in Fig. 1(A) and (B), respectively. XRD pattern for La1.0- Co0.5Ti0.5O3 material, as in Fig. 1(A) has diffractions corresponding to cubic perovskite structure ($2\theta = 32.4^{\circ}$, 39.9° , 46.4°, and 57.6°). Upon replacing La with Sr in $La_{1-x}Sr_x$ - $Co_{0.5}Ti_{0.5}O_3$ material, new diffractions are observed in addition to the cubic structure, which corresponds to the presence of tetragonal perovskite structure. This phase is more evident in high Sr-containing materials. Similar dual perovskite structures are also reported in high Sr containing Sr_2TiO_4 materials [58]. Additionally, the impurity phase of $SrCO_3$ is barely observed for the $\mathrm{Sr}_{1.0}\text{-}\mathrm{Co}_{0.5}\mathrm{Ti}_{0.5}\mathrm{O}_3$ catalyst. The absence of diffractions corresponding to cobalt oxide species suggests that cobalt species are either well mixed within the catalyst material or in the perovskite structure. Furthermore, the diffractions corresponding to various perovskite phases remain intact even after treating the La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials in H₂ gas (Fig. 1(B)). However, there is a change in the intensity of the diffractions between different catalysts. The persistence of perovskite structures in the reduced form of La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ is due to the dominance of species such as La, Sr, and Ti



Fig. 1. XRD patterns of (A) air calcined at 800 °C and (B) H₂ reduced at 750 °C for (a) $La_{1.0}$ - $Co_{0.5}Ti_{0.5}O_3$, (b) $La_{0.8}Sr_{0.2}$ - $Co_{0.5}Ti_{0.5}O_3$, (c) $La_{0.6}Sr_{0.4}$ - $Co_{0.5}Ti_{0.5}O_3$, (d) $La_{0.4}Sr_{0.6}$ - $Co_{0.5}Ti_{0.5}O_3$, (e) $La_{0.2}Sr_{0.8}$ - $Co_{0.5}Ti_{0.5}O_3$ and (f) $Sr_{1.0}$ - $Co_{0.5}Ti_{0.5}O_3$ perovskite materials.

oxides, these are known to be barely reducible or un- reducible oxides. Though Co oxides can be reduced to form metallic Co species, the diffractions corresponding to metallic Co species are scarecely observed in Fig. 1(B). Overall, from XRD analysis, it can be inferred that cubic perovskite structure is the dominant phase for La_{1.0}-Co_{0.5}Ti_{0.5}O₃ and low Sr containing catalysts. In contrast, both tetragonal and cubic perovskite structures exist in high Sr containing La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials, and these perovskite structures are stable in reducing environment.

H₂-TPR analysis was adopted to check the reducibility of La_{1,x}Sr_x-Co_{0.5}Ti_{0.5}O₃ perovskite materials up to 950 °C. The obtained H₂ consumption profiles were depicted in Fig. 2, and the total H₂ uptakes were provided in Table 1. From Fig. 2, it is clear that all the catalysts have multiple reduction centers between 250 °C and 900 °C; however, the H₂ consumption varies between the materials. As per previous reports, the H₂ consumption in La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ perovskite materials is from a multi-stage reduction of Co oxides (Co $_3O_4 \rightarrow CoO \rightarrow Co^{\circ}$) and mobile oxides $(ABO_3 \rightarrow ABO_{3-\delta})$ available in the perovskite structure. Other oxides present in La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ perovskites such as La, Sr, and Ti oxides are known to be un-reducible [51,59]. In Fig. 2, for La₁-Co_{0.5-} Ti_{0.5}O₃ material, a broad dual-stage H₂ consumption behavior has appeared between 250 and 850 °C. The H₂ consumption in La_{1.0}-Co_{0.5-} Ti_{0.5}O₃ material is mainly attributed to the multi-stage reduction of Co and mobile oxygen species available in the material. Similar reduction behavior is also observed for Sr-containing $La_{1-x}Sr_x$ -Co_{0.5}Ti_{0.5}O₃ perovskite materials. By correlating this result with XRD patterns of reduced



Fig. 2. H_2 -TPR profiles of calcined (a) $La_{1.0}$ -Co_{0.5}Ti_{0.5}O₃, (b) $La_{0.8}Sr_{0.2}$ -Co_{0.5}Ti_{0.5}O₃, (c) $La_{0.6}Sr_{0.4}$ -Co_{0.5}Ti_{0.5}O₃, (d) $La_{0.4}Sr_{0.6}$ -Co_{0.5}Ti_{0.5}O₃, (e) $La_{0.2}Sr_{0.8}$ -Co_{0.5}Ti_{0.5}O₃ and (f) $Sr_{1.0}$ -Co_{0.5}Ti_{0.5}O₃ perovskite materials.

Table 1

BET surface area, H₂ uptakes, O₂ desorption, CO₂ desorption and surface Co content for La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ catalysts.

Catalyst	BET- SA (m ² / g)	^a H ₂ uptakes (μmol/ g)	Total O ₂ desorbed (μmol/g)	Total CO ₂ desorbed (µmol/g)	^b Surface Co content (μmol/g)
La _{1.0} - Co _{0.5} Ti _{0.5} O ₃	15.8	1473.5	9.9	16.8	41.2
La _{0.8} Sr _{0.2} - Co _{0.5} Ti _{0.5} O ₃	16.1	2248.0	54.5	42.7	82.3
La _{0.6} Sr _{0.4} - Co _{0.5} Ti _{0.5} O ₃	6.8	2475.9	39.2	26.9	80.4
La _{0.4} Sr _{0.6} - Co _{0.5} Ti _{0.5} O ₃	3.4	2233.9	39.0	46.3	54.8
La _{0.2} Sr _{0.8} - Co _{0.5} Ti _{0.5} O ₃	1.8	2560.4	44.5	76.5	42.5
Sr _{1.0} - Co _{0.5} Ti _{0.5} O ₃	1.0	2736.9	47.1	73.9	31.8

^a Calculated from H₂-TPR results.

 $^{\rm b}$ Measured from H₂ chemisorption experiments at 35 °C.

samples, it can be inferred that the persistent nature of perovskite structures in La1-xSrx-Co0.5Ti0.5O3 catalysts is due to the high-temperature reducibility behavior. The La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials required about 850 °C for complete reduction of reducible species. The total reducible species measured for La1.0-Co0.5Ti0.5O3, La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃, La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃, La_{0.4}Sr_{0.6}-Co_{0.5}Ti_{0.5}O₃, La_{0.2}Sr_{0.8}-Co_{0.5}Ti_{0.5}O₃ and Sr_{1.0}-Co_{0.5}Ti_{0.5}O₃ materials are 1473.52, 2248.04, 2475.92, 2233.88, 2560.42 and 2736.93 µmol.g⁻¹, respectively. Furthermore, the Co-based reducibility at 750 °C for La_{1.0}-Co_{0.5}Ti_{0.5}O₃, La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃, La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃, $La_{0.4}Sr_{0.6}-Co_{0.5}Ti_{0.5}O_3$, $La_{0.2}Sr_{0.8}-Co_{0.5}Ti_{0.5}O_3$ and $Sr_{1.0}-Co_{0.5}Ti_{0.5}O_3$ materials are 71.2 %, 92.5 %, 109.3 %, 104.4 %, 94.1 % and 78.8 %, respectively. From TPR results, it can be inferred that at 750 °C, the majority of the Co oxide species in La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ can be reduced to catalytically active lower oxidation states.

The CO₂-TPD experiments were conducted to monitor the change in the basicity of La₁-Co_{0.5}Ti_{0.5}O₃ material by replacing La with Sr oxides. The obtained CO₂ curves with desorption temperature were displayed in Fig. 3. Overall, three types of CO₂ desorption centers were observed for La_{1-x}Sr_x-CTO materials. The first desorption peak is observed between 100 °C and 200 °C, which is mainly allocated to either basic sites with low-strength or physisorbed sites [60,61]. This type of CO₂ desorption



Fig. 3. CO₂-TPD profiles for reduced (a) $La_{1.0}$ -Co_{0.5}Ti_{0.5}O₃, (b) $La_{0.8}Sr_{0.2}$ -Co_{0.5}Ti_{0.5}O₃, (c) $La_{0.6}Sr_{0.4}$ -Co_{0.5}Ti_{0.5}O₃, (d) $La_{0.4}Sr_{0.6}$ -Co_{0.5}Ti_{0.5}O₃, (e) $La_{0.2}Sr_{0.8}$ -Co_{0.5}Ti_{0.5}O₃ and (f) $Sr_{1.0}$ -Co_{0.5}Ti_{0.5}O₃ perovskite materials.

peak is dominating in both La_{1.0}-Co_{0.5}Ti_{0.5}O_3 and La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O_3 and is almost negligible in high Sr-containing materials. The second peak is between 350 °C and 600 °C, which is assigned to basic sites with moderate strength. The intensity of this CO_2 desorption peak seems to be increased with the Sr oxide content in the material. The third CO₂ desorption peak is observed at above 850 °C and is obvious in Sr-containing catalysts only. This peak corresponds to the decomposition of stable carbonates, possibly SrCO₃ species. In general, the strength of the basic centers is correlated with the temperature at which CO₂ is desorbed, and the number of basic centers is measured as the area under the desorption peak. Furthermore, the basicity of $La_{1,v}Sr_v$ -Co_{0.5}Ti_{0.5}O₃ perovskite determined by considering the CO₂ desorbed peak area up to 700 °C, as in Fig. 3. The basicity was measured to be 16.42, 26.63, 15.748, 36.61, 67.91 and 68.40 $\mu mol.g^{-1}$ for $La_{1.0}\text{-}Co_{0.5}\text{Ti}_{0.5}\text{O}_3,$ $La_{0.8}Sr_{0.2}\text{-}Co_{0.5}Ti_{0.5}O_3,\ La_{0.6}Sr_{0.4}\text{-}Co_{0.5}Ti_{0.5}O_3,\ La_{0.4}Sr_{0.6}\text{-}Co_{0.5}Ti_{0.5}O_3,$ La_{0.2}Sr_{0.8}-Co_{0.5}Ti_{0.5}O₃ and Sr_{1.0}-Co_{0.5}Ti_{0.5}O₃ materials, respectively. This result shows, except La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃ material, the amount of CO2 desorbed was seemed to be increasing trend with higher Sr-amount in the material. Moreover, it can be established that the basicity strength of the La_{1.0}-Co_{0.5}Ti_{0.5}O₃ material is significantly improved by adding Sr oxide species, which helps the Sr-containing material to activate the steam easier and enhance the reaction between steam and carbon, which ultimately results in an enhancement in toluene conversion and suppression of coking during SRT reaction.

Next, O2-TPD experiments were conducted to know the availability of mobile oxygen species in La1-xSrx-Co0.5Ti0.5O3 materials reduced at 750 °C. And the obtained O2-desorption profiles were displayed in Fig. 4. From the figure, it can be observed that there are two O₂desorption peaks for high Sr-containing materials i.e., Sr_{1.0}-Co_{0.5}Ti_{0.5}O₃ and La_{0.2}Sr_{0.8}-Co_{0.5}Ti_{0.5}O₃ catalysts - a minor low-temperature desorption peak below 400 °C and a major high-temperature desorption peak above 750 °C. The amount of O_2 desorbed is measured to be 9.85 μ mol/ g, 54.52 µmol/g, 39.23 µmol/g, 38.98 µmol/g, 44.48 µmol/g and 47.11 μ mol/g for La_{1.0}-Co_{0.5}Ti_{0.5}O₃, La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃, La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃, La_{0.4}Sr_{0.6}-Co_{0.5}Ti_{0.5}O₃, La_{0.2}Sr_{0.8}-Co_{0.5}Ti_{0.5}O₃ and Sr_{1.0}-Co_{0.5}Ti_{0.5}O₃ materials, respectively. From this result, it can be concluded that the amount of mobile O species is higher for La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ material than others. For the steam reforming reaction, the crucial role of mobile oxygen species is either to enhance the reaction between carbon and oxygen species or reaction of steam to generate active hydroxyl groups. In either case, it ultimately promotes the toluene reforming activity with reduced carbon deposition.

The BET surface area (SA) for the calcined $La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O_3$ materials were presented in Table 1. From Table, it is observed that the



Fig. 4. O_2 -TPD profiles for reduced (a) $La_{1.0}$ - $Co_{0.5}Ti_{0.5}O_3$, (b) $La_{0.8}Sr_{0.2}$ - $Co_{0.5}Ti_{0.5}O_3$, (c) $La_{0.6}Sr_{0.4}$ - $Co_{0.5}Ti_{0.5}O_3$, (d) $La_{0.4}Sr_{0.6}$ - $Co_{0.5}Ti_{0.5}O_3$, (e) $La_{0.2}Sr_{0.8}$ - $Co_{0.5}Ti_{0.5}O_3$ and (f) $Sr_{1.0}$ - $Co_{0.5}Ti_{0.5}O_3$ perovskite materials.

SA for La_{1.0}-Co_{0.5}Ti_{0.5}O₃ material is 15.8 m²/g. Upon replacing La with 0.2Sr species, the SA was slightly increased to reach 16.1 m²/g, and a further increase in doping of Sr in La_{1.0}-Co_{0.5}Ti_{0.5}O₃ led to a drastic reduction in SA. By considering XRD patterns (as in Fig. 1) of calcined materials, it can be inferred that the SA reduction for high Sr-containing materials is possibly due to the presence of a new perovskite phase, which might be deposited in the pores of parent cubic perovskite phase.

3.2. Steam reforming of biomass tar model

Fig. 5 depicted the SRT activity for La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials without poisonous compounds. The SRT performances were performed at a reaction temperature of 700 °C and at a relatively lower steam-to-carbon of 2. The time-dependent toluene conversion and product formation rate for La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials were displayed in Figs. 5 and S1, respectively. In this study, H₂, CO, CO₂, and trace amounts of CH₄ (<1%) the main gaseous product were detected, which is consistent with the previous report [51]. In Fig. 5, La_{1.0}-Co_{0.5}Ti_{0.5}O₃ gave a toluene



Fig. 5. SRT activity over reduced (a) La_{1.0}-Co_{0.5}Ti_{0.5}O₃, (b) La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃, (c) La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃, (d) La_{0.4}Sr_{0.6}-Co_{0.5}Ti_{0.5}O₃, (e) La_{0.2}Sr_{0.8}-Co_{0.5}Ti_{0.5}O₃ and (f) Sr_{1.0}-Co_{0.5}Ti_{0.5}O₃ perovskite materials. Condition: W =100 mg; toluene flow rate =188 µmol/min; H₂O flow rate = 2632 µmol/min, S/C = 2; reduction temperature =750 °C/1 h and reaction temperature =700 °C.

conversion between 75 % and 85 % within the testing period of 21 h. Upon replacing 0.2La with Sr in La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃, the toluene conversion reached a maximum of 90 % and gave nearly stable conversion throughout the testing period. With the further replacement of La with Sr, the toluene conversion was reduced. Overall, the catalytic performance are in the decreasing order of La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ > $La_{1,0}\text{-}Co_{0,5}\text{Ti}_{0,5}\text{O}_3>La_{0,6}\text{Sr}_{0,4}\text{-}Co_{0,5}\text{Ti}_{0,5}\text{O}_3>La_{0,4}\text{Sr}_{0,6}\text{-}Co_{0,5}\text{Ti}_{0,5}\text{O}_3>$ ${\tt La}_{0.2}{\tt Sr}_{0.8}{\rm -Co}_{0.5}{\tt Ti}_{0.5}{\tt O}_3~>~{\tt Sr}_{1.0}{\rm -Co}_{0.5}{\tt Ti}_{0.5}{\tt O}_3$ catalyst. It can also be observed from Figures that the decrease in the toluene conversion is minimal at these experimental conditions. In general, the initial steam reforming activity greatly influenced by the availability of surface Co sites, and the long term stability of the material was determined by oxygen mobility, basicity, and structural stability of the material during SRT reaction. Moreover, the deactivation of Co-based catalysts is caused by the accumulation of carbon, active metal sintering, and oxidation of active metal centers in the steam environment.

In this study, the amount of surface Co sites was measured using H₂ pulse chemisorption at 35 °C for all the reduced La_xSr_{1.0-x}-Co_{0.5}Ti_{0.5}O₃ materials. The amount of surface Co sites are calculated to be 41.2, 82.3, 80.4, 54.8, 42.5 and 31.8 µmol/g-cat correspondingly for La_{1.0}-Co_{0.5}Ti_{0.5}O₃, La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃, La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃, La_{0.4}Sr_{0.6}-Co_{0.5}Ti_{0.5}O₃, La_{0.2}Sr_{0.8}-Co_{0.5}Ti_{0.5}O₃ and Sr_{1.0}-Co_{0.5}Ti_{0.5}O₃ materials. The Co particle size was also calculated using H₂ chemisorption values. It is calculated to be 35.3, 18.0, 18.5, 27.2, 34.9, and 46.7 nm, respectively for La_{1.0}-Co_{0.5}Ti_{0.5}O₃, La_{0.4}Sr_{0.6}-Co_{0.5}Ti_{0.5}O₃, La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃, La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃, materials co_{0.5}Ti_{0.5}O₃, La_{0.6}Sr_{0.6}-Co_{0.5}Ti_{0.5}O₃, La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃, materials. The Co particle size was also calculated using H₂ chemisorption values. It is calculated to be 35.3, 18.0, 18.5, 27.2, 34.9, and 46.7 nm, respectively for La_{1.0}-Co_{0.5}Ti_{0.5}O₃, La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃, La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃, materials reduced at 750 °C. The result shows that the surface Co content is significantly increased with replacing 0.2Sr with La species in La_{1.0}-Co_{0.5}Ti_{0.5}O₃ catalyst. However, a further increase in Sr content caused a decrease in surface Co species' availability and

increased Co particle size. It is reported that the surface Co sites in lower oxidation state are responsible for activating C—C and C—H bonds present in the toluene molecule. And the toluene conversion is further enhanced by other characteristics of the material such as basicity and O mobility, which promotes the reaction between steam and carbon of toluene. This result indicates the highest toluene conversion for La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ material is possibly due to Co sites available on the catalyst surface. Furthermore, by considering other characteristics, it can also be inferred that the stable catalytic performances of these catalysts are due to the structural stability of the La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ perovskite materials and enhanced basicity nature obtained by doping with Sr oxides.

As highlighted before, for the catalysts to be applied for steam reforming of tar derived from MSW, it should be resistant to the poisonous compounds such as chlorides and sulfides. Here, we have chosen two best compositions of La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ and La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃ materials for further evaluating their catalytic performance in the presence of poisonous compounds. Tetrachloroethylene (TCE) is used as a model for chloride compound, and 50 ppm of H₂S is used as a sulfur compound. Fig. 6 depicted the steam reforming of toluene for $La_{0.8}Sr_{0.2}$ -Co_{0.5}Ti_{0.5}O₃ and $La_{0.6}Sr_{0.4}$ -Co_{0.5}Ti_{0.5}O₃ materials at 700 °C in the presence of 1000 ppm and 1% of TCE. By comparing the activity profiles in Fig. 5 with Fig. 6, it is observed that for La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ material, the initial toluene conversion was 85 % in the absence of TCE, whereas it is decreased to \sim 70 % in the presence of 1000 ppm of TCE and is further reduced to below 60 % with 1% TCE. On the other hand, the La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃ catalyst showed continuous deactivation behavior and reached below 20 % of toluene conversion from 80 % within 12 h of the testing period. The deactivation behavior is more severe in the presence of 1% TCE.



Fig. 6. SRT activity over (A) $La_{0.8}Sr_{0.2}$ -Co_{0.5}Ti_{0.5}O₃ and (B) $La_{0.6}Sr_{0.4}$ -Co_{0.5}Ti_{0.5}O₃ catalysts in the presence of 0.1 % of TCE, and (C) $La_{0.8}Sr_{0.2}$ -Co_{0.5}Ti_{0.5}O₃ and (D) $La_{0.6}Sr_{0.4}$ -Co_{0.5}Ti_{0.5}O₃ catalysts in the presence of 1% of TCE. Condition: W =100 mg; toluene flow rate =188 µmol/min; H₂O flow rate = 2632 µmol/min, TCE concentration = 0.1 and 1.0 %; reduction temperature =750 °C/1 h and reaction temperature =700 °C.

These catalysts are further tested for sulfur tolerance ability during SRT reaction at 800 °C. The change in the catalytic performance as product distribution upon exposure of 50 ppm of H₂S is presented in Fig. 7. In Fig. 7, the SRT performance for the initial 3 h time is before H₂S exposure, and the performance between the dotted lines is in the presence of 50 ppm of H₂S. In both tests, H₂S was introduced for about 6 h. The change in the toluene conversion after stopping H₂S was monitored for both the catalysts. It was reported that the deactivation behavior of Co-based catalysts for sulfur-containing hydrocarbon reforming reaction is because of the formation of cobalt sulfide compounds (Co $^\circ$ + H_2S \rightarrow $CoS + H_2$). The formed sulfide compounds are inert and catalytically inactive for hydrocarbon reforming reactions. However, the catalytic activity can be regenerated by making these sulfide compounds to decompose or oxidize to generate Co sites and SO_x compounds. Thus, the activity of Co-based materials is highly influenced by the stability of the sulfide compounds in the reaction environment.

In Fig. 7(A), La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ gave toluene conversion of above 90 % before H₂S exposure, and while upon exposure to H₂S, it decreased to nearly 20 %. The activity was recovered to the original level of toluene conversion in the post-H₂S exposure region. On the other hand, for the La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃ catalyst, though the initial toluene conversion is the same as La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ material, in the presence of H₂S the toluene conversion decreased to ~15 % and the catalytic performance could not come back to the original level in the post-H₂S exposure zone. From this result, it can be deduced that the poisoning



Fig. 7. SRT activity over (A) $La_{0.8}Sr_{0.2}$ -Co_{0.5}Ti_{0.5}O₃ and (B) $La_{0.6}Sr_{0.4}$ -Co_{0.5}Ti_{0.5}O₃ perovskite materials in the presence 50 ppm of H₂S. Condition: W =100 mg; toluene flow rate =188 µmol/min; H₂O flow rate = 2632 µmol/min, H₂S =50 ppm for 5 h; reduction temperature =750 °C/1 h and reaction temperature =800 °C.

effect due to sulfur compound exposure in lower Sr-containing materials is temporary. Finally, the better performance for $La_{0.8}Sr_{0.2}$ - $Co_{0.5}Ti_{0.5}O_3$ material is due to its enhanced O lability and basicity nature. These properties promote the conversion of cobalt sulfides to SO_x and Co oxide species in the presence of H₂, H₂O, and CO_x at the post H₂S exposure region.

3.3. XRD analysis of spent materials

The stability of the perovskite structural phase before and after the SRT reaction for La1-xSrx-Co0.5Ti0.5O3 catalysts was analyzed using XRD analysis. The XRD patterns for La1-xSrx-Co0.5Ti0.5O3 catalysts after the reforming activities, as in Fig. 5 was provided in Fig. 8. In the figure, all the catalysts have diffractions at $2\theta = 32.4^{\circ}$, 39.9° , 46.4° , and 57.6° , which correspond to the availability of cubic perovskite structure. This phase is also observed in reduced La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ catalysts (Fig. 1 (B)), indicating the stability of the perovskite phase during SRT reaction at 700 °C. A stark difference in Fig. 8 compared to Fig. 1(B) is the absence of diffractions corresponding to the tetragonal perovskite structure. This could be due to either conversion of the tetragonal perovskite to cubic structure or its decomposition to form corresponding metallic and metal oxide phases. Furthermore, all the spent La_{1-x}Sr_x- $Co_{0.5}Ti_{0.5}O_3$ materials have diffraction at $2\theta \sim 44.5^\circ$, corresponds to the availability of the Co° phase. Moreover, the intensity of this peak is much stronger for high Sr containing La1-xSrx-Co0.5Ti0.5O3 materials, indicating the possibility of agglomeration of Co species during reforming reaction. The presence of the cubic perovskite structure and metallic Co phase is also observed for La1-xSrx-Co0.5Ti0.5O3 materials tested in the presence of H₂S and TCE compounds (Fig. S3). Overall, from XRD analysis, it can be concluded that the cubic perovskite structure of $La_{1-x}Sr_x$ -Co_{0.5}Ti_{0.5}O₃ materials is quite stable in the highly reductive environment of toluene reforming, and crystallite size of metallic Co is smaller for low Sr-containing catalysts. This could be one of the reasons for the better SRT activity of La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ than other catalysts.

3.4. FE-SEM images of reduced and spent catalysts

Fig. 9 presents the FE-SEM images of La $_{1.0}$ -Co $_{0.5}Ti_{0.5}O_3$, La $_{0.8}Sr_{0.2}$ -Co $_{0.5}Ti_{0.5}O_3$ and Sr $_{1.0}$ -Co $_{0.5}Ti_{0.5}O_3$ catalyst obtained after reduced at 750 °C for 1 h and after SRT reaction at 700 °C.

The micrograph of $La_{1.0}\text{-}Co_{0.5}Ti_{0.5}O_3$ as in Fig. 9(a) shows the irregular sized gains fused together with clear boundary. The mean grain



Fig. 8. XRD patterns of (a) $La_{1.0}$ - $Co_{0.5}Ti_{0.5}O_3$, (b) $La_{0.8}Sr_{0.2}$ - $Co_{0.5}Ti_{0.5}O_3$, (c) $La_{0.6}Sr_{0.4}$ - $Co_{0.5}Ti_{0.5}O_3$, (d) $La_{0.4}Sr_{0.6}$ - $Co_{0.5}Ti_{0.5}O_3$, (e) $La_{0.2}Sr_{0.8}$ - $Co_{0.5}Ti_{0.5}O_3$ and (f) $Sr_{1.0}$ - $Co_{0.5}Ti_{0.5}O_3$ catalysts after steam reforming of toluene activity at 700 °C as in Fig. 5.



Fig. 9. FE-SEM images of (a) $La_{1.0}$ - $Co_{0.5}Ti_{0.5}O_3$, (b) $La_{0.8}Sr_{0.2}$ - $Co_{0.5}Ti_{0.5}O_3$, (c) $Sr_{1.0}$ - $Co_{0.5}Ti_{0.5}O_3$ catalysts reduced at 750 °C, and (d) $La_{1.0}$ - $Co_{0.5}Ti_{0.5}O_3$, (e) $La_{0.8}Sr_{0.2}$ - $Co_{0.5}Ti_{0.5}O_3$, (f) $Sr_{1.0}$ - $Co_{0.5}Ti_{0.5}O_3$, (g) $Sr_{1.0}$ - $Co_{0.5}Ti_{0.5}O_3$, (g) $Sr_{1.0}$ - $Co_{0.5}Ti_{0.5}O_3$, (g) $Sr_{1.0}$ - $Co_{0.5}Ti_{0.5}O_3$, (h) $Sr_{1.0}$ - $Sr_{1.0}$ -S

size is in nanoscale range, approximately 80 nm for the sample reduced at 750 °C for 1 h. Moreover, a bright spot on each grain could be attributed to the metallic Co or partially reduced Co species, which are still in present in the perovskite structure. Comparatively, the image after SRT reaction at 700 °C shows the agglomeration of the particles and highly irregular sizes. Also, filament like structures are observed in the images, indicates the formation of filamentous carbon during SRT reaction at 700 C. Similar grain size and bright spots for each grains for reduced La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ catalyst is observed (in Fig. 9(b)). There is slight agglomeration is observed for the catalyst after SRT reaction at 700 °C. For Sr_{1.0}-Co_{0.5}Ti_{0.5}O₃ catalyst, irregularly shaped particles are separated among each other is observed. And, upon SRT reaction, much sever agglomeration of particles observed for this catalyst.

3.5. XPS analysis of reduced and spent catalysts

The nature of surface elements presents in freshly reduced and spent La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials were analyzed using the XPS study. The binding energy (BE) profiles for O 1s and Co 2p species before and after SRT reaction at 700 °C of La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials are depicted in Figs. 10 and 11, respectively. The Sr 2p BE profiles before and after SRT reaction were provided in Fig S4. In Fig. 10(A), the reduced La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials have O 1s BEs corresponding to lattice oxygen (O_L) at 529.4 \pm 0.3 eV and adsorbed oxygen species (O_{Ads}) at 531.2 \pm 0.3 eV. In the figure, moving from Sr_{1.0}-Co_{0.5}Ti_{0.5}O₃ materials, it was observed that the surface O_L/O_{Ads} species were increased with the decrease in Sr content in the material. And La_{0.8}Sr_{0.2}-CTO has higher O_L/O_{Ads} species than La_{1.0}-Co_{0.5}Ti_{0.5}O₃ materials is attributed to the presence of surface carbonates. Furthermore,

the amount of O_L/O_{Ads} in La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials can also be related to their steam reforming performance. This result indicates that the mobility of O species (OL) in La1-xSrx-Co0.5Ti0.5O3 is enhanced with the replacement of La with 0.2Sr species in the catalysts, supporting the observations made in O₂-TPD results (Fig. 4). Next, Fig. 10(B) has O 1s BEs of La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials after the SRT reaction at 700 $^\circ\text{C}.$ In Fig. 10(B), in addition to above O species observed for reduced materials, they have BE at 533.9 \pm 0.5 eV, which is attributed to O species from adsorbed OH groups. This kind of O species can be expected in the spent catalysts because the catalysts are exposed to the steam environment during SRT reaction. Finally, this result indicates the role of Sr doping in enhancing O species mobility of La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ material and its involvement in the SRT reaction at 700 °C. By combining this result with the H₂ chemisorption result, it can be concluded that the better reforming activity of La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ is possibly due to the presence of high surface Co species and enhanced O₂ mobility during SRT reaction.

Next, Fig. 11 shows the Co 2p binding energy profiles for reduced and spent La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ perovskite materials. In Fig. 11A, the Co 2p_{3/2} BEs are at ~781.9 eV and ~ 780.2 eV, which are assigned to Co²⁺ and Co³⁺ species [62,63]. The BE peak at around 786 eV is assigned to oxidized species. It is also observed that comparatively, the Co 2p BEs of spent catalyst were shifted slightly to higher values than reduced materials. This shift to higher BE values in spent catalyst indicates that the interactions between Co species and support species were significantly enhanced during the reforming reaction. Furthermore, The peak at ~ 786 eV, corresponding to oxidized species, seems to be significantly enhanced for all the spent catalysts except for the La₀₈Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ catalyst. This result indicates a certain degree of Co oxidation during steam reforming of toluene reaction at 700 °C; as a result, there could be



a decrease in the surface Co active species during reforming reaction. However, this oxidation is almost negligible for La₀₈Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ catalyst. It could be one of the reasons for the stable performance of the La₀₈Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ catalyst over others. The absence of BE corresponding to Co° species in both reduced and spent catalysts is possibly due to the existence of strong Co metal to SrOx/LaOx support interaction in the perovskite structure.

Furthermore, the Sr 3d BE profiles for reduced and spent La1-xSrx- $Co_{0.5}Ti_{0.5}O_3$ are deconvoluted to two types of species (Fig. S4). The BE at \sim 132.3 eV is assigned to SrO species, and BE at \sim 133.1 eV is assigned to SrCO3 or SrTiO3 species. It is also observed that comparatively, the BE for spent catalysts are slightly shifted to higher values than reduced catalysts, indicates the possibility of conversion of SrO into SrCO₃ like species during SRT reaction. Besides, the presence of stable chloride species after SRT reaction in the presence of 1% TCE is verified using XPS analysis. Fig. S5 has Cl 2p_{3/2} BE at around 781.3 is corresponding to the presence of inorganic chloride species. When considering the elements present in the perovskite materials, these chlorides be the formation of SrCl₂ species. According to the previous report, Sr species in the perovskite structure promoted steam activation during the SRT reaction. As a result, it enhanced toluene reforming activity and suppress carbon formation during SRT reaction. By considering the above results, the slight decrease in the performance of perovskite materials in TCE presence could be formation of inert inorganic chloride species. This could be one of the possible reasons for the enhanced coke deposition during SRT reaction in the presence of TCE compounds. Furthermore,



Fig. 11. Co 2p binding energies of (A) reduced at 750 °C and (B) spent at 700 °C (a) La_{1.0}-Co_{0.5}Ti_{0.5}O₃, (b) La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃, (c) La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃, (d) La_{0.4}Sr_{0.6}-Co_{0.5}Ti_{0.5}O₃, (e) La_{0.2}Sr_{0.8}-Co_{0.5}Ti_{0.5}O₃ and (f) Sr_{1.0}-Co_{0.5}Ti_{0.5}O₃ catalysts.

the formation of stable sulfide species is also verified using XPS analysis over perovskite materials after the SRT reaction, as in Fig. 7. The S 2p binding energy profiles as in Fig. S6 shows that the presence of stable surface sulfide species is almost negligible. The absence of surface sulfide species could be the reason for the recovery of the perovskite materials to it's original level of toluene reforming activity.

3.6. Carbon analysis

The nature and amount of coke deposited during SRT reaction over La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ materials were determined using TGA/DTA analyses. The TGA and DTA profiles of La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ after SRT reaction at 700 °C (as in Fig. 5) are presented in Fig. S7. The result shows that carbon formation during pure SRT reaction at 700 °C is almost negligible, supporting these catalysts' stable SRT performances. Also, it indicates the crucial role of Sr species in La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ catalyst in activating steam to promote the reaction between carbon and steam during SRT reaction at 700 °C. Furthermore, the TGA and DTA profiles of La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ and La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃ catalysts after SRT reaction in the presence of TCE and H₂S are presented in Fig. 10. The TG/DT profiles in Fig. 10(A) shows an intense weight loss associated with an exothermic differential thermal peak between 400 °C and 600 °C. This weight loss is due to the oxidation of carbon species deposited

during the SRT reaction. The amount of carbon deposited is highly dependent on the concentration of TCE present during the SRT reaction. The weight loss for La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ and La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃ is 1.95 % and 6.87 % for 0.1 % TCE and 11.56 % and 18.6 % for 1% TCE, respectively. By combining this result with XPS results as in Fig. S5, it can be concluded that the poisoning effect of Cl⁻ species is suppressing the reaction between steam and carbon during SRT reaction. Similar kinds of carbon species were also deposited over La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ tested in the presence of H₂S at 800 °C. Overall, it is observed that the amount of carbon deposited over La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ is significantly lower than La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃ at all SRT conditions.

3.7. Poisonous effect of H₂S and TCE compounds

Ni and Co-based catalysts are the most commonly explored nonnoble metal-based catalysts for various hydrocarbon reforming reactions by virtue of their ability to activate C-C and C-H bonds of hydrocarbons [64]. Among them, mono-metallic Co and its combination with other oxides (Mo, Fe, and etc.) are much applied for reforming of hydrocarbons in the presence of sulfur-like poisonous compounds, due to its redox nature and ability to form reactive metal sulfide species. In this study, the role of introducing base metal oxide on the toluene reforming reaction is studied, and it was observed that an optimum perovskite catalyst composition of La_{0.8}Sr_{0.2} Co_{0.5}Ti_{0.5}O₃ achieved the best steam reforming performance compared to other catalysts. Generally, the catalyst's performance was expressed with respect to the toluene conversion and long term catalytic stability. The initial toluene conversion is mainly influenced by the number of surface-active metal species and the rate of reaction between the reactants on metal sites. The catalytic deactivation is caused by metal sintering, metal species conversion to oxides, or other inactive states and carbon encapsulation during reforming reaction. In this study, steam reforming of toluene activity as in Fig. 5 shows stable toluene conversion over perovskite materials, however different catalysts have different toluene conversions throughout the testing period. It is also observed that replacement of about 0.2La with Sr in La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ enhanced the surface Co species availability (it is confirmed by H₂ chemisorption analysis) and basicity (CO₂-TPD, Fig. 3). The basic sites the material helps to enhance the activation of steam and reaction with toluene and also neutralize the acidic sites of the material, which are responsible for hydrocarbon cracking reaction. As a result, a reduction in the carbon deposition rate is observed. It is confirmed from the carbon analysis of spent La_{1-x}Sr_x--Co_{0.5}Ti_{0.5}O₃ materials (Fig. S7).

According to a well-accepted toluene reforming mechanism, toluene is first decomposed on the active metal species to generate hydrogen and carbon. The deposited carbon reacts with the reforming agent, i.e., steam to generate CO, CO₂, and more H₂. The competition between these two reactions causes either encapsulation or suppression of carbon formation around the active centers during reforming reaction [6]. Compared to the activities in Fig. 5, it is clearly observed that there is a lower catalytic performance in the presence of various concentrations of Cl- compounds (TCE) (Fig. 6). For La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ material, the initial toluene conversion was decreased with an increase in TCE concentration in the reactant mixture. This decrease in the activity is possibly caused by the accumulation of carbon during the reforming reaction, which is confirmed by DT/TGA analysis (Fig. 12A). The deposition of carbon for La_{0.6}Sr_{0.4}-Co_{0.5}Ti_{0.5}O₃ is much higher than other catalysts, which could be a possible reason for continuous deactivation behavior, although the reaction period. Furthermore, upon exposure to 50 ppm of H₂S at 800 °C, both perovskite catalysts showed a sudden decrease in the catalytic performance (Fig. 7). It could be due to the conversion of metallic Co to considerable stable cobalt sulfide compounds [65]. At the same reaction temperature, the catalytic performance is recovered back to nearly 95 % of initial performance in the absence of H₂S. The decomposition of cobalt sulfide to generate metallic



Fig. 12. DT/TGA profiles (A) after SRT at 700 °C in the presence of TCE compound over (a) $La_{0.6}Sr_{0.4}$ - $Co_{0.5}Ti_{0.5}O_3$ (1%), (b) $La_{0.8}Sr_{0.2}$ - $Co_{0.5}Ti_{0.5}O_3$ (1%), (c) $La_{0.6}Sr_{0.4}$ - $Co_{0.5}Ti_{0.5}O_3$ (0.1%) and (d) $La_{0.8}Sr_{0.2}$ - $Co_{0.5}Ti_{0.5}O_3$ (0.1%), and (B) at 800 °C in the presence of 50 ppm of H₂S over (a) $La_{0.8}Sr_{0.8}$ - $Co_{0.5}Ti_{0.5}O_3$ and (b) $La_{0.6}Sr_{0.4}$ - $Co_{0.5}Ti_{0.5}O_3$ catalysts.

cobalt species results in catalytic recovery at the same reaction temperature. The slight decrease in the activity compared to initial performance in the post H_2S exposure region is possible because of the accumulation of carbon during reforming reaction, confirmed by DT/TG analysis (Fig. 12B).

In essence, the promotional effect of introducing Sr in La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ perovskite materials is primarily credited to its ability to enrich the surface metal sites and suppress the coking rate by promoting the reaction between steam and carbon precursors deposited on cobalt surface during SRT process.

4. Conclusions

Overall, an optimum La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ perovskite material composition of showed superior steam reforming of toluene performance of all La_{1-x}Sr_x-Co_{0.5}Ti_{0.5}O₃ perovskite materials. The tests for H₂S and chloride compounds tolerance shown that La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ catalyst possesses resistance towards 0.1–1% of the TCE compound. Moreover, upon introducing 50 ppm of H₂S at 800 °C, the toluene conversion on La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ material is dropped to 20 %, and

that was maintained for 5 h of H₂S exposure. Subsequently, after stopping H₂S in feed, this catalyst was able to regenerate about 95 % of initial activity at the same reaction temperature. This result indicates that the poisoning effect of sulfur compounds for La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ material is temporary during the SRT reaction at 800 °C. Furthermore, O₂-TPD and XPS results revealed that the oxygen mobility of La₁. $_{x}Sr_{x}Co_{0.5}Ti_{0.5}O_{3}$ material could be significantly enhanced by replacing a small amount of La with Sr species. From XRD analysis, the stability of cubic perovskite structures during the reductive and reaction environment, and insignificant Co agglomeration was perceived. From CO2-TPD studies, lower strength basic sites are higher for the best catalyst, i.e., La_{0.8}Sr_{0.2}-Co_{0.5}Ti_{0.5}O₃ is observed. TGA has shown the negligible coke formation during SRT reaction at 700 °C, and that the addition of TCE and H₂S in feed led to enhanced carbon formation during SRT reaction at 700 °C and 800 °C, respectively. Finally, these kinds of perovskite structured La_{1-x}Sr_xCo_{0.5}Ti_{0.5}O₃ materials have good potential for application in high-temperature biomass/MSW derived tar reforming processes, where tolerance towards inorganic sulfur and chloride compounds is a necessity.

CRediT authorship contribution statement

Ashok Jangam: Conceptualization, Methodology, Investigation, Writing - original draft. Sonali Das: Methodology, Writing - review & editing. Subhasis Pati: Methodology, Writing - review & editing. Sibudjing Kawi: Resources, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2021.118013.

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