scientific reports

OPEN



Dual rare earth-doped Pt–Sn/ Al₂O₃ catalysts with synergistic Ce and Sm effects on highefficiency aromatization and coke suppression in naphtha reforming

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In the present study, the effect of rare earth (RE) metals of Ce and Sm on the naphtha reforming process catalyst, i.e., Pt-Sn/y-Al₂O_{3.} is investigated. Two-, three-, and four-metal catalysts were synthesized through the successive wet impregnation of the support, employing various concentrations of cerium at 0.17 and 0.47 wt% and samarium at 0.33, 0.51, and 0.87 wt%. The corresponding catalytic activity on the naphtha reforming reactions was conducted in a reactor at 5 bar, 500 $^{\circ}$ C, and WHSV = 2 h⁻¹. FESEM, BET, NH₃-TPD, and H₃-TPR were employed to scrutinize the physicochemical and active site properties of the developed catalysts. Besides, TGA was used to determine the deactivation rate of the developed catalysts. It is shown that adding a suitable amount of RE metals can reduce the Pt particle agglomeration and promote the distribution of the metal particles. Catalytic testing demonstrated that Ce and Sm-containing catalysts, especially SPC(0.47) S(0.33), exhibited superior aromatization activity, producing high levels of C₈ and C₉ aromatics, which are valuable for gasoline blending. Such catalysts also showed reduced cracking and paraffin production, which was attributed to the optimal balance of metallic and acidic properties resulting from the REMs. In addition, such RE dopants could diminish the degree of graphitization, resulting in decreased coke content and a lower combustion temperature, facilitating the catalyst regeneration process. Moreover, incorporating RE metals could inhibit the reduction of tin oxides, enhancing platinum's role as the promoter. Besides, the catalysts containing 0.47 wt% cerium, 0.33 wt% samarium and a combination of both RE metals exhibited superior activity in producing reformate with a high-octane number.

Keywords Naphtha reforming, Multi-metallic catalysts, Rare earth metals, Pt-Sn active sites

As a key process in the petrochemical and petroleum refining industries, catalytic naphtha reforming is widely used to convert naphtha hydrocarbons with a low octane number into more valuable high-octane gasoline components without changing the boiling point range¹. As a fraction of petroleum, naphtha with a boiling point between 30 °C and 200 °C generally constitutes 15–30% of crude oil by weight. The main hydrocarbon molecules with 5–12 carbon atoms constituting the complex naphtha mixture include olefins, paraffins, aromatics, and naphthenes². Furthermore, the reformate generated in the catalytic naphtha reforming process contains invaluable aromatic components, including benzene, toluene, and xylenes (BTX), critical petrochemical materials^{3–5}. In this process, naphtha hydrocarbons are converted into isomers and cyclic hydrocarbons through the dehydrogenation of naphthenes to aromatics, paraffin dehydrocyclization, linear paraffin isomerization, and naphthene isomerization^{6,7}.

As a bifunctional catalyst, a naphtha reforming catalyst is composed of a metal function, primarily platinum, and an acid function, typically chlorided alumina. While the metal function is responsible for catalyzing the dehydrogenation and hydrogenation reactions, the acid function promotes the cyclization and isomerization reactions⁸. Striking an adequate balance between the two functions is necessary for the naphtha reforming catalyst to reach optimal performance.

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In order to enhance the yield and efficiency of the process, a critical issue is the enhancement of the stability and selectivity of the catalyst and decreasing the catalyst deactivation rate³. Since the 1960s, platinum–tin reforming catalysts have been developed to address such issues^{9,10}. At present, considerable published data on the contribution of tin to the characteristics of Pt-containing catalysts is available in the literature^{11–13}. Sn enhances the stability and selectivity of catalysts compared to nonmetallic catalysts. In addition, Sn impedes the formation of agglomerated Pt particles when burning coke. In an alumina–platinum catalyst, adding 0.3 wt% Sn could reduce the number of acid sites based on the outcomes of NH₃-temperature-programmed desorption (NH₃-TPD). While the strong acid sites at which the hydrogenolysis and hydrocracking reactions occurred are blocked partially, the medium-strength cyclization and isomerization sites remain unchanged¹⁴.

Furthermore, conventional catalytic systems of platinum on the acidic alumina are typically promoted with metallic (rhenium, iridium, tin, etc.) additives^{9,12,15,16}. Promoters should be engaged in the catalyst at the chlorine and platinum deposition or alumina support preparation stages¹⁷. The as-prepared catalyst includes promoters in the metal/oxide form, which can enhance stability and selectivity (C_5^+ reformate yields) by interactions with platinum due to decreased coke formation⁹. Currently, trimetallic catalysts are receiving increasing interest for gasoline reforming purposes. The associated literature has focused on the physicochemical characterization, synthesis, and utilization of the Pt-Re–Ge^{11,15}Pt–Ir–Sn^{18,19}Pt–Re–Sn^{11,14}etc., systems. The main characteristics of the trimetallic catalysts include higher resistance to coke formation and selectivity compared to the bimetallic catalysts. The elements of the periodic table Group IVB (Pb and Ge) and Group IVA (Zr and Ti) may also serve as potential additives to the Pt-Sn reforming catalysts^{9,20}. Once the stable oxides of these elements undergo activation under the gasoline reforming process conditions, they are partially reduced to their metallic state. As a result, only a fraction of the promoters added may interact with platinum, and the rest maintain their oxidized form on the support, which changes the acidity of the support²¹.

Another group of metals pointed out in several patents for their positive effects on the catalytic function of the reforming process are rare earth metals (REMs) such as scandium, yttrium, cerium, lanthanum, samarium, etc. REMs, especially lanthanum and cerium, show promising features, such as strong interactions between metal and rare earth oxide, establishing thermal stabilization for the alumina support. Additionally, CeO₂ possesses a high oxygen storage capacity, which helps to minimize coke formation²². Zhang et al. (2007) found that incorporating a small amount of La (around 1.4 wt%) into PtSnNa/ZSM-5 catalysts can reduce acidity, stabilize active sites, and prevent tin reduction and coke formation, leading to improved catalyst stability and performance²³. Zhang et al. (2013) showed that doping PtSnNa/Al₂O₃ catalysts with 0.3-1.0 wt% La can also decrease acidity and coke formation, with the 1.0 wt% La-doped catalyst showing the best stability and performance²⁴. Vu et al. (2011) observed that Ce forms a separate CeO₂ phase on Al₂O₃ supports compared to La and Y. Pt-Sn catalysts supported on La-Al₂O₃ and Ce-Al₂O₃ exhibited the best catalytic stability and activity for the dehydrogenation of propane²⁵. Yu et al. (2006) found that adding 1.1 wt% Ce to Pt-Sn/ γ -Al₂O₃ catalysts improved high-temperature stability and prevented coke accumulation while achieving over 38% propane conversion²². Zhou et al. (2015) showed that incorporating 0.6 wt% Ce in the γ -Al₂O₂ support modified the pore structure and promoted Pt particle features, with the coke depositing on the external support surface rather than on active sites²⁶. According to these inventions, the multicomponent catalyst showed better activity, stability, and C_5^+ selectivity. Nonetheless, the effect of the rest of REMs, e.g., Sm, on the catalytic characteristics of bimetallic Pt-Sn reforming catalysts remains unclear.

The present investigation aims to present a detailed study of the effects of Sm and Ce doping on the metallic and acidic functions in γ -Al₂O₃-supported bimetallic Pt-Sn reforming catalysts. Ce and Sm were doped onto Pt-Sn/Al₂O₃ to reform hydrotreated naphtha. The product was analyzed by gas chromatography to investigate its content, and the catalysts used were characterized by thermogravimetric analysis (TGA) to measure the amount of coke and the catalyst's performance.

Experimental methods Catalysts preparation procedure

The support used was a commercial granular γ -Al₂O₃ from Sasol Company, featuring a Brunauer–Emmett– Teller (BET) surface area of 209.81 m²/g, a total pore volume of 0.5175 cm³/g, and a mean pore diameter of 9.8670 nm. The metal precursor salts were hexachloroplatinic acid (H,PtCl, 4H,O), tin (II) chloride dehydrate (SnCl,.2H,O), cerium (III) nitrate hexahydrate (Ce (NO₄),.6H,O) and samarium (III) nitrate hexahydrate (Sm $(NO_3)_{3.6}H_{3.0}$. The metals were incorporated on γ -Al₂O₃ by successive wet impregnation of the support with an aqueous precursor. The aqueous solution of SnCl, is unstable due to a hydrolysis reaction of SnCl, leading to a different preparation method. Initially, the precursor was dissolved in deionized water and heated at 70 °C for 30 min, after which 37% hydrochloric acid (HCl) was added¹⁴. The amounts and concentrations of the precursor solutions were adjusted to achieve final compositions of 0.33 wt% Pt, 0.165 wt% Sn, 0.17 wt% and 0.47 wt% Ce, and 0.33 wt%, 0.51 wt%, and 0.87 wt% Sm. According to the previous studies, the optimum mass percentages of Pt and Sn are between 0.3 and 0.35 wt% and 0.1–2 wt%, respectively, with a Pt/Sn atomic ratio of 2^{27-29} . Before impregnation, the support was calcined at 500 °C for 3 h with a heating rate of 10 °C/min to eliminate organic impurities. For a monometallic catalyst, a specific amount of γ -Al₂O₃ was immersed in 0.2 N HCl (1.5 mL HCl per gram of γ -Al₂O3) for 1 h without mixing. A specific volume of precursor was added to the support solution and stirred for 1 h; afterward, the solvent was evaporated by heating at 70 °C while stirring slowly. Then, the catalyst was placed in the oven at 120 °C overnight to dry completely and calcined at 500 °C for 4 h in a furnace under an air atmosphere. The same procedure was followed to incorporate the next metals. The order for adding metals was Sn, Pt, Ce, and Sm simultaneously; therefore, the catalysts were named in the order of their addition. The abbreviation of the as-synthesized catalysts is mentioned in Table 1. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Vista-MPX, Varian Inc., USA) was used to analyze and characterize the Ce, Pt, Sm, and Sn loads in the catalyst samples. Table 1 demonstrates general consistency between the actual and

		Pt (wt%)		Sn (wt%)		Ce (wt%)		Sm (wt%)	
Catalyst	Symbol	Theory	Actual	Theory	Actual	Theory	Actual	Theory	Actual
Sn-Pt/y-Al ₂ O ₃	SP	0.33	0.31	0.165	0.151	-	-	-	-
Pt-Ce/γ-Al ₂ O ₃	PC(0.17)	0.33	0.30	-	-	0.17	0.17	-	-
Sn-Pt-Ce/γ-Al ₂ O ₃	SPC(0.47)	0.33	0.32	0.165	0.149	0.47	0.45	-	-
Sn-Pt-Sm/y-Al ₂ O ₃	SPS(0.33)	0.33	0.30	0.165	0.150	-	-	0.33	0.31
Sn-Pt-Sm/y-Al ₂ O ₃	SPS(0.51)	0.33	0.30	0.165	0.162	-	-	0.51	0.47
Sn-Pt-Sm/y-Al ₂ O ₃	SPS(0.87)	0.33	0.32	0.165	0.155	-	-	0.87	0.81
Sn-Pt-Ce-Sm/γ-Al ₂ O ₃	SPC(0.47)S(0.33)	0.33	0.30	0.165	0.148	0.47	0.46	0.33	0.30
Sn-Pt-Ce-Sm/y-Al ₂ O ₃	SPC(0.47)S(0.51)	0.33	0.31	0.165	0.156	0.47	0.44	0.51	0.47
Sn-Pt-Ce-Sm/y-Al2O3	SPC(0.47)S(0.87)	0.33	0.30	0.165	0.152	0.47	0.46	0.87	0.82

 Table 1. Summary of abbreviated names and quantitative loading of promoters for various as-synthesized catalysts.

theoretical loadings of the elements in these samples. As can be seen, the actual values are slightly lower than the theoretical values, which can be attributed to partial losses during the catalyst and support preparation³⁰.

Catalyst characterizations

The distribution of metals and the morphological characteristics of the nanomaterial surface were determined using the field emission scanning electron microscopy (FESEM) technique by employing a MIRA3 TESCAN device. Also, the energy-dispersive spectrometry (EDS) system of solid-state was used to determine the elemental composition. Using an Autosorb Quantachrome 1MP device, the textural specifications of the prepared catalysts, such as the specific surface area, average pore diameter, and pore volume, were determined using the Nitrogen adsorption/desorption isotherms and BET technique. The specimens were treated for five hours at 300 °C before conducting the measurements.

A Nanosord NS91 (manufactured by Sensiran Co., Iran) apparatus was used to conduct the NH₂-Temperature Programmed Desorption (NH₃-TPD) and H₂-Temperature Programmed Reduction (H₂-TPR) tests. After placing 50 mg of each as-synthesized catalyst in a U-shaped quartz reactor, the NH₂-TPD tests were carried out. Before conducting each TPD run, the desired catalyst was degassed in a flow of 10 ml/min helium for 1 h at a temperature of 300°C and then was cooled down until reaching a temperature of 110 °C. Then, the process was followed by the adsorption of 5% NH₂/He for 30 min at a temperature of 110 °C. Then, to remove the loosely bound ammonia, the samples were purged in a He stream at a temperature of 110 °C for 30 min. The catalyst was then heated again in a flow of He at a heating rate of 10 °C /min within the 110 to 900 °C temperature range. The H_{2} -TPR tests were carried out in a U-shaped quartz reactor on 40 (and 28) mg of each catalyst. The degassing process of the catalyst was carried out in a flow of 10 ml/min argon for one hour at a temperature of 300°C before conducting each H₂-TPR run. Then, it was cooled down to room temperature under the same atmosphere. Subsequently, the temperature was raised to 900 °C at a heating rate of 10 °C/min, and the sample was reduced using 10 ml/min of the 5.0% H₂/Ar mixture. Finally, the catalysts were subjected to the thermogravimetric analysis (TG-DTG) (Perkin Elmer-Pyris Diamond) in the air atmosphere; the temperature was maintained between 25 °C and 700 °C with a heating rate of 10 °C/min. During the analysis, the differential and actual thermal analyses were recorded.

The catalytic activity test

The naphtha reforming reaction was conducted in a tubular fixed-bed reactor with weight hourly space velocity (WHSV)=2, $H_2/fed=4$ (molar ratio), feed flow rate=0.12 ml/min, temperature (T)=500 °C, and pressure (P)=5 bar. Before the reaction, as-synthesized catalysts were reduced in H_2 flow (65 cc/min, 4 h, 500 °C, and 5 bar). Figure 1 demonstrates the naphtha reforming experimental laboratory setup. Mass flow controllers adjust a specific mass flow rate for H_2 and N_2 streams while injecting the feedstock into the reactor using a high-performance liquid chromatography (HPLC) pump. Gas and feedstock are combined using a mixing valve and introduced to the fixed-bed reactor simultaneously. The fixed-bed reactor is placed in the middle of a cylindrical furnace, divided into upper, middle, and lower zones. Each zone includes a temperature control system that contains a proportional-integral-derivative (PID) controller and a thermocouple for temperature measurement. Catalysts are placed in the middle zone, where rock wool prevents them from moving downward. A spiral duct heat exchanger and a gas-liquid separator separate hydrocarbons from the gas in the product stream. Pressure transmitters measure the pressure of the catalyst bed and the outlet stream. Calibration is needed to obtain accurate results prior to each test.

The naphtha sample analyzed in this study was characterized using a Shimadzu GC-2014 C gas chromatograph. Table 2 provides an overview of its composition, including the types and structures of hydrocarbons based on carbon number.

Results and discussion

Morphology of the catalysts

FESEM micrographs examine the morphology and metal dispersion of the catalysts. The microimage of the SPC(0.47) catalyst is shown in Fig. 2, while the FESEM images of SP, PC, and SPC(0.47)S(0.33) catalysts are



Fig. 1. Schematic representation of the experimental laboratory setup employed for catalytic naphtha reforming.

Sample	Paraffin (wt%)	Olefin (wt%)	Naphthene (wt%)	Aromatic (wt%)	Others (wt%)	Total (wt%)
C ₃₋	0	0	0	0	1.77	1.77
C ₄	0	0	0	0	0.34	0.34
C ₅	0	0	0	0	2.89	2.89
C ₆	6.96	0	4.56	1.79		13.30
C ₇	15.68	0	10.09	5.50		31.27
C ₈	13.82	0	9.43	7.13		30.38
C ₉	9.98	0	4.28	2.66		16.93
C ₁₀₊					3.12	3.12
Total	46.44	0	28.36	17.08	8.12	100

Table 2. Chemical composition of naphtha.

provided in Figures S1, S3, and S5, respectively. The synthesized SPC(0.47) catalyst shows a more uniform dispersion without any major agglomeration on the catalyst surface. Also, no trace of cracks originating during the drying and calcination processes on the SPC(0.47) catalyst surface is observed. This can confirm a reliable synthesis method.

Figure 2b is an elemental mapping image of the SPC(0.47) sample representing the signals of Al, Cl, O, Pt, Sn, and Ce. In comparison, Figure S2b displays an elemental mapping image of the SP catalyst that displays the signals of Al, Cl, O, Pt, and Sn. Furthermore, Figs. 2c-h, S2, S4, and S6 represent the EDS elemental mapping images for SPC(0.47), SP, PC, and SPC(0.47)S(0.33) catalysts, respectively, to enhance understanding of dispersion degree. According to these figures, the SPC(0.47) catalyst demonstrates higher dispersion.



Fig. 2. (a) FESEM images of the SPC(0.47) catalyst; (b) Energy Dispersive Spectroscopy (EDS) spectra for SPC(0.47); EDS elemental mapping for (c) aluminum (Al); (d) chlorine (Cl); (e) oxygen (O); (f) platinum (Pt); (g) tin (Sn); and (h) cerium (Ce).



Fig. 3. Nitrogen adsorption-desorption isotherms and BJH pore size distribution curves for fresh catalysts.

Catalyst	BET surface area (m ² .g ⁻¹)	Total pore volume (cm ³ .g ⁻¹)	Average pore diameter (nm)
SP	196.4	0.474	7.30
PC(0.17)	194.7	0.461	7.41
SPC(0.47)	183.1	0.447	7.20
SPS(0.87)	181.7	0.441	7.19
SPC(0.47)S(0.33)	179.5	0.438	7.20
SPC(0.47)S(0.51)	177.2	0.431	7.22
SPC(0.47)S(0.87)	175.3	0.422	7.21

Table 3. Textural characterization of as-synthesized catalysts.

Textural analysis

The textural characteristics of the as-prepared catalysts were characterized using the N₂ adsorption-desorption isotherms conducted at a temperature of -196 °C. Figure 3; Table 3 depict the physicochemical physiochemical characteristics of the fresh catalysts. The characteristics of the PC(0.17) catalyst include a pore volume of 0.46 cm³/g and a BET surface area (S_{BET}) of 194.7 m²/g. As the CO chemisorption results presented in Lin et al.'s research confirmed, the Ce doping led to the promotion of the dispersion of the metallic platinum. Also, a further increase in Ce loading (> 0.5 wt%) resulted in decreased Pt dispersion. They hypothesized that one could isolate the platinum particles by overloading Ce species, which further reduced the surface area of the catalyst and the platinum dispersion. This issue may justify the decreasing trend observed in the catalytic activity once the Ce loadings are increased. The Sn loading decreased the pore volume and S_{BET} of the SPC(0.47) catalyst to 0.447 cm³/g and 183.1 m²/g, respectively. Introducing Sm into the SPC(0.47), the catalyst decreased the pore volume and S_{BET} indicate the dependence on the Sm loadings. At higher loadings, the pore channel of the alumina support may have been blocked by the Sm species, leading to a decrease in the pore volume and S_{BET}^{31,32}.

According to Fig. 3, all the catalysts feature a typical type IV adsorption isotherm characterized by an H1 hysteresis loop, indicating a mesoporous structure characterized by cylindrical pores^{33,34}. In addition, the associated pore size distribution clearly showed that mesopores dominated the catalysts, characterized by an unimodal pore structure centered below 10 nm.

Acidic properties of the fresh catalysts

The catalytic performance, particularly the dehydrogenation reaction, is directly linked to the surface acidity of the catalyst. Unwanted acidic sites may provoke side effects such as polymerization and isomerization reactions of the formed olefins, which lead to carbon deposition. According to NH₃ desorption temperature, the acid sites can be divided into three categories: weak acidic sites (TD < 250 °C), medium acidic sites (250 °C < TD < 450 °C), and strong acidic sites (TD > 450 °C)³⁵.

The NH_3 -TPD profiles of four catalysts - SP, SPC(0.47), SPS(0.87), and SPC(0.47)S(0.33) - are presented in Figs. 4a-d, respectively. All samples display similar peak patterns, indicating three types of acidic sites: weak (I), medium (II), and strong (III). The maximum temperatures corresponding to these three types of peaks are summarized in Table 4. Figure S7 also presents semi-quantitative results of acidic strength distribution obtained through deconvolution analysis using Origin software.



Fig. 4. NH₃-TPD profiles for (**a**) SP, (**b**) SPC(0.47), (**c**) SPS(0.87), and (**d**) SPC(0.47)S(0.33) catalysts. Adsorption Duration: 30 min; Heating Rate: 10 °C per minute; Flow Rate: 10 mL per minute; Gas Mixture: 5% NH₃ in He.

	T _M (℃)				NH. desorption	Peak fraction (%)		
Catalyst	Ι	ΙI	III	Total area (a.u.)	$(\mu \text{ mol NH}_3/\text{gr catalyst})$	I	II	III
SP	206	438	703	43.41	1300	11.97	34.8	53.23
SPC(0.47)	218	459	844	32.20	1067	8.70	46.85	44.45
SPS(0.87)	215	450	808	40.90	1301.2	8.53	34.18	57.30
SPC(0.47)S(0.33)	227	454	712	37.45	1376	9.64	30.27	60.09

Table 4. Summary of acidity measurements from NH₃-TPD analysis for catalysts: (a) SP, (b) SPC(0.47), (c) SPS(0.87), SPC(0.47)S(0.33).

Table 4 represents the amount of acidic sites on the catalysts, indicating the addition of 0.47 wt% Ce decreased the total amount of acidic sites from 1300 to 1067 μ mol/gr compared to the SP catalyst. However, adding Ce reduced the proportion of strong acid sites while increasing the fraction of medium acid sites. In all regions, the ammonia desorption temperatures were higher for the SPC(0.47) catalyst than for SP, indicating that adding Ce increased the strength of the acid sites. High-strength acid sites are especially good for promoting side reactions across the catalyst surface and lead to the least desirable processes such as cracking, coking, and hydrogenolysis^{36,37}. Accordingly, adding Ce may contribute to eliminating strong acid sites and prevent these unfavorable side reactions during the catalytic reforming process. The lower total acid sites for SPC(0.47) can be ascribed to the increased quantity of basic sites in CeO₂. The Ce cation can occupy empty sites on the alumina surface, creating a positive charge and forming Lewis acid sites³⁸. It explains the increased strength of the acidic sites in SPC(0.47).

Furthermore, the addition of Sm did not affect the total acidity of the Pt-Sn catalyst; however, it did increase the fraction of strong acid sites while simultaneously reducing the number of medium acid sites. It is found that the required ionization energy (the minimal energy required to remove an electron from an atom) is 9.04×10^{-19} J for Sm. The acceptor sites of Al₂O₃ can ionize hydrocarbon molecules characterized by the ionization energy of 14.8×10^{-19} J. As a result, one may expect electronic injection from Sm to the support^{39,40}. Considering the SPC(0.47)S(0.33) sample, the desorption of NH₃ increased from 1300 to 1376 µmol/g. This finding also aligns with the higher percentage of ammonia desorption on weak acid sites, which increased from

53.23 to 60.09%. The decrease in strong and medium acid site fractions for the SPC(0.47)S(0.33) sample can be most likely explained by the electron transfers between the metal and the support.

Reduction behavior of the catalysts

In the H_2 -TPR analysis, the catalysts provide important data on metal-support interaction and the reducibility of active metals. Figure 5 shows the H_2 -TPR profile of the as-synthesized samples. The profile of the SP catalyst shows at least two unresolved peaks at 267 °C and 506 °C, reflecting the difference in interaction between Al_2O_3 support and the platinum species. The peaks observed were accounted for by a series of oxychlorinated platinum species formed when impregnating the chloroplatinic acid onto the Al_2O_3 substrate, followed by thermal treatments such as calcination and drying²⁵. Two major categories of platinum oxides may be identified from the available literature: one that strongly interacts with the support and another for which the interaction with the support is much weaker. The latter can be reduced at relatively low temperatures, whereas the former requires high temperatures to be reduced. The hydrogen uptake at 267 °C and 506 °C may thus be assigned to the reduction processes of these two Pt species^{22,41,42}.

Furthermore, the third peak at 684 °C may be attributed to a reduction step of tin oxides. Previous literature indicated that Sn (IV) can be reduced to Sn (II); however, because of its strong interaction with the support, it does not fully reduce to Sn $(0)^{14,43}$. In addition, all the profiles showed well-defined peaks between 690 °C and 750 °C, which are likely ascribed to the reduction of other ions in the alumina support⁴⁴.

Previous studies²² indicate that the platinum deposition on the CeO₂ surface can facilitate CeO₂ reduction. This enhancement is explained by the presence of noble metals, which can increase the oxygen storage capacity of CeO₂ through interactions between CeO₂- and noble metals^{45,46}. In addition, the presence of CeO₂ leads to the shift of the second reduction peak of platinum oxides to lower temperatures, specifically from 506 °C to 485 °C. This finding shows that Pt may preferentially interact with CeO₂ rather than Al₂O₃⁴⁷. Additionally, other researchers have indicated that CeO₂ deposited on Al₂O₃ facilitates the reduction of platinum oxide species⁴⁸. In contrast, the SnO₂ reduction temperature peak observed in the H₂-TPR plot increased from 667 °C to 684 °C, which suggests that CeO₂ may inhibit the reduction of SnO₂. This finding aligns with the previous analyses suggesting that CeO₂ may prevent the reduction of SnO₂ to metallic Sn, leading to the formation



Fig. 5. H_2 -TPR profiles for (**a**) SP, (**b**) SPC(0.47), (**c**) SPS(0.87), and (**d**) SPC(0.47)S(0.33) catalysts. The samples were subjected to reduction using a flow rate of 10 mL/min with a 5.0% H_2 /Ar mixture, and the temperature was increased to 900 °C.

of a PtSn alloy^{12,22}. Accordingly, the hindrance of SnO_2 reduction on the Pt-Sn-Ce catalyst may contribute to maintaining the Pt activity.

Figure 5c indicates that, in comparison with the SP catalyst, the SPS catalyst with constituents including Sn, Sm, and Pt exhibits significant differences in configuration. The peak at 191 °C is attributed to the reduction steps of samarium oxide species, while the next two peaks at higher temperatures correspond to the reduction of platinum oxide species⁴⁹. This finding suggests that Sm weakens the metal-support interaction. A slight shift to lower temperatures for the Pt reduction peaks indicates that Sm also acts as a promoter for reducing Pt species. It implies that the incorporation of REMs into Al_2O_3 results in decreased reduction temperatures for the Pt species. This finding aligns with the previous report indicating that La enhances the reduction of the Pt species through an electron-pushing effect²³. Furthermore, a similar shift in the Pt reduction peaks toward lower temperatures was observed with SiO₂ support when the rare earth metal oxides were added⁵⁰.

Many attempts have been reported to enhance the reducibility of CeO_2 , mainly because its reduction is relatively slower than its oxidation⁵¹⁻⁵³. One of the successful techniques for increasing reducibility is the introduction of dopants. Transition metals, REMs, and precious metals could change the Ce coordination and finally form longer Ce–O bonds. Their presence causes the structural distortions of the CeO₂ lattice, as the expanded bonds between cations and oxygen change the geometry of the entire structure⁵⁴. The substitution of smaller cations than the host cations may result in a combination of elongated and shortened metal-oxygen bonds, therefore facilitating the expulsion of oxygen. This is because oxygen atoms bonded to metals via long bonds are less stable and easier to detach⁵⁵.

Regarding the precious metal-based catalysts, the higher reactivity of metal-oxide surfaces is associated with stronger reducibility. This can be potentially attributed to hydrogen and oxygen spill-over processes at the metal-oxide interface. Such a phenomenon results in a rapid redox cycle and improved reducibility, improving performance for various catalytic reactions, e.g., deoxygenation and reforming⁴⁶. In CeO₂-based oxygen storage substances, active metal ions (Cu²⁺, Pd²⁺, Ni²⁺, Pt²⁺, Sm⁺³, Rh³⁺, and La³⁺) can be substituted for Ce⁴⁺ to create a Ce(1-x)MxO₂- δ solid solution⁵⁶⁻⁵⁸. The generation of solid solution significantly enhances the reforming reaction due to the formation of the vacancies. It also enhances the dispersion of active metals due to the strong metal-support interaction (SMSI) effect. Such a mutual synergistic interaction between CeO, and the active metal promotes the CeO₂ redox, while CeO₂ results in stabilized active metal dispersion^{59,60}. A higher reducibility enhances lattice oxygen mobility, forming abundant oxygen vacancies. These vacancies not only facilitate oxidant activation but also promote SMSI. This interaction anchors active metal nanoparticles such as Pt more effectively, suppressing agglomeration and enhancing uniform dispersion across the catalyst surface. This improved dispersion increases the number of accessible active sites, which directly contributes to the selective conversion of reactants while reducing side reactions such as coke deposition⁶¹. Similarly, adding a rare earth element such as Sm as a promoter causes a stronger interaction between the CeO, supports and the active metals, leading to improved dispersion of the active metals⁶². Such an improved dispersion results in higher catalytic efficiency in oxidation catalysis and catalytic reforming.

The performance of the catalysts

The catalytic activity of the synthesized catalysts was analyzed at a WHSV of 2 h⁻¹, a pressure of 5 bars, and a temperature of 500 °C. The technique employed for the analysis was gas chromatography, the results of which are shown in Fig. 6. The systematic study provides insights into the selectivity and efficacy of the desired catalysts under the specified operating parameters, facilitating a comparative evaluation of their activities during the catalytic processes. According to Fig. 6, the maximum aromatic content in the resulting product is attributed to the catalyst SPC(0.47)S(0.33), which suggests its highest activity in aromatization reactions. The minimum amount of paraffin obtained with such a catalyst can be explained by a higher dehydrocyclization reaction rate.

Likewise, the behavior of the SPC(0.47) and SPS(0.87) catalysts is almost the same as that of the SPC(0.47) S(0.33), indicating better aromatic yield compared to the SP catalyst. In contrast, the SP catalyst shows the minimum amount of naphthenes because of its higher isomerization/dehydrogenation activities. On the other hand, the SPS(0.51) catalyst presents the minimum aromatic yield coupled with the maximum contents of paraffins and naphthenes. This effect suggests a reduction in the isomerization activity on the acidic sites of the catalyst or a decrease in dehydrogenation activity on its metallic sites. It seems that the addition of 0.51 wt% Sm is insufficient to improve the metallic and acidic sites of the catalysts. By contrast, 0.33 wt% Sm for the four metallic catalysts and 0.87 wt% Sm for the three metallic catalysts show superior performance. This indicates that metal loading optimization improves product selectivity and catalytic activity in naphtha reforming.

Table 5 shows the composition of olefins, paraffins, aromatics, and naphthenes in the hydrotreated naphtha feed. It is noteworthy to mention that the feed lacks light paraffins. However, as shown in Table 6, these species are found in the reformate, indicating that cracking occurred during reforming. The SPC(0.47) S(0.33), and SPS(0.51) catalysts show a reduced cracking activity, whereas the PC(0.17) catalysts exhibit a relatively higher level of cracking activity. The reduction in cracking reactions after using REMs can be due to their specific electronic characteristics. The empty *f* orbitals found in REMs lead to Lewis acidity formation. This may extensively contribute to selectivity and catalytic behavior during the cracking reactions. As a result, incorporating REMs optimizes the reforming process by minimizing undesirable cracking while promoting the desired aromatization reactions.

Figure 7 presents the conversion rates of paraffins (C_6 , C_7 , C_8 , and C_9) for all the studied catalysts. The conversion rate tends to increase with the carbon number for the PC(0.17), SPS(0.87), and SP catalysts. Therefore, the conversion becomes more effective for the heavier paraffins, especially for C_8 and C_9 . The SPS(0.51) catalyst reduces conversion efficiency for heavier paraffins. This indicates that the catalyst is more effective for lighter paraffins, particularly C_6 and C_7 . Notably, the SPC(0.47)S(0.33) catalyst reaches its maximum conversion rate





	Paraffin	Olefin	Naphthene	Aromatic
C_3^{-}	0	0	0	0
C_4	0	0	0	0
C ₅	0	0	0.003	0
C ₆	6.96	0	40.56	1.79
C ₇	15.68	0	10.09	5.5
C ₈	13.82	0	9.43	7.13
C ₉	9.98	0	4.28	2.66

 Table 5.
 Weight% (wt%) of paraffins, olefins, naphthenes, and aromatics in hydrotreated naphtha feedstock.

catalyst	C_3 ⁻	C ₄	C ₅
SP	0.01	0.18	0.88
PC(0.17)	0.47	2.09	3.72
SPC(0.47)	0.02	0.08	0.24
SPS(0.51)	0	0.01	0.09
SPS(0.87)	0.01	0.18	0.88
SPC(0.47)S(0.33)	0	0.01	0.17
SPC(0.47)S(0.51)	0.1	0.41	1.03
SPC(0.47)S(0.87)	0	0.07	0.54

Table 6. Weight% (wt%) of light paraffins in reformate for various catalysts.

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Fig. 7. Conversion of paraffin components (C₆, C₇, C₈, and C₉) across different catalysts.

with C_8 paraffin, revealing its exceptional efficiency in processing such materials. This trend shows the different catalytic behaviors of various formulations and their implications for optimizing naphtha reforming processes.

Figure 8 shows the amounts of different aromatic products, such as toluene, benzene, xylenes, ethylbenzene, and C_9 aromatics. It indicates that the SPS(0.51) catalyst is associated with the maximum concentrations of both toluene and benzene, as well as the minimum amount of C_9 aromatics and xylenes. The trend might be explained by dealkylation reactions in which the more significant aromatic compounds lose their alkyl groups preferentially. In contrast, the SPC (0.47), SPS(0.87), and SPC(0.47)S(0.33) catalysts present the maximum amounts of C_9 aromatics and xylenes, even higher than the SP catalyst. This finding shows that the reformates from these catalysts can obtain a higher octane number, which increases their applicability for gasoline. In addition, it can be observed that all synthesized catalysts, except SPS(0.51), generate lower amounts of toluene and benzene compared to the SP catalyst. The decrease is noteworthy, especially in light of the carcinogenic characteristics of benzene, and is considered an environmental advantage. Reducing benzene content in gasoline formulations is essential in mitigating health risks linked to benzene exposure and improving air quality.

Thermal characteristics of the spent catalysts

A thermogravimetric (TG) analysis was conducted from room temperature up to 700 °C in an air atmosphere to conduct a more detailed analysis of the coke content in the spent catalysts. As illustrated in Fig. 9, the TG profiles for all the spent catalysts can be divided into two distinct regimes: the range from room temperature to 200 °C and then to 550 °C. The first peak observed between 25 °C and 100 °C is linked to the release of reactive materials and surface water, while the second stage, occurring from 350 °C to 500 °C, corresponds to the combustion of the coke deposited on the catalyst surface³⁴. According to Wang et al., three different types of carbon can be generated on the spent PtSn/ γ -Al₂O₃ catalyst, including graphite-like coke, aromatic coke, and aliphatic coke aliphatic carbon⁶³. Coke combustion at lower temperatures is primarily due to deposits covering active metals, whereas at higher temperatures, it is associated with deposits on the external support surface^{64,65}. This indicates that coke was mainly located on the support surface of the spent catalysts for all the samples analyzed. The first stage reflected a weight loss of 4.08%, which can be explained by the presence of a large amount of coke deposited on the external surface of the support (see Fig. 9a). The addition of Ce shows a decrease in the degree of graphitization and the burning temperature of coke, thus facilitating the regeneration processes. This can be explained by the fact that CeO₂ benefits from a better storage capacity.

Additionally, the main decoking of the synthesized SPS(0.87) catalyst shifts to a lower temperature than the SP catalyst. More specifically, the estimated coke content for the SPS(0.87) catalyst is 3.17%, increasing to about



Fig. 8. The weight% of aromatic components in the product for various catalysts.

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4.08% for the SP catalyst. Notably, the coke content of the SPC (0.47)S(0.33) catalyst is considerably lower than that observed for both Ce-containing and Ce-free catalysts. This reflects its better resistance to coke formation during the recycling tests. In the SPC (0.47)S(0.33) catalyst, an increased ratio and promotion of weak acidic surface sites can provide better anchoring and dispersion of active components, resulting in the stability of the catalyst (Table 2; Fig. 3). Similarly, the least carbon deposition observed in the SPC (0.47)S(0.33) catalyst can be attributed to the strengthened weak acid sites, better dispersion of platinum-based active components, and its large surface area, which hinder carbon deposition.

Morphology of the spent catalysts

Figures 10 (a-d) illustrate the morphology of the spent catalysts at different magnifications analyzed by FESEM. The reforming reaction leads to coke accumulation on the surface of the catalyst and metal particles either by full or partial encapsulation. Carbon species, including coke, tend to deposit preferentially on the catalyst surface, particularly within voids or porous regions, where the absence of neighboring atoms gives rise to highly reactive surface sites⁶⁶. Consequently, strong carbon filaments may dig into the pores and thus break the support material, leading to catalyst particle agglomeration due to structural collapse⁶⁷.

The structural changes are clarified by the FESEM images after adding Sm to the Pt-Sn/ γ -Al₂O₃ and Pt-Sn-Ce/ γ -Al₂O₃ (Figs. 10 (c-d)). Both SPS(0.87) and SPC(0.47)S(0.33) catalysts have a uniform aggregate structure with reduced particle size, which can be clearly seen in comparing Fig. 10a and b. It is widely acknowledged that coke deposition (coking) requires a large group of neighboring sites for carbon growth. Besides, there is a relationship between metal particle size and coke formation. Small particle sizes (less than 20 nm) promote carbon gasification and the formation of small-diameter filaments^{68,69} As mentioned in the H₂-TPR analysis, it can be concluded that adding REMs can improve particle dispersion on the catalyst support. This improvement leads to a reduction in the metal particle size on the catalyst, which subsequently decreases coke formation, reduces the size of the deposited coke particles, and ultimately minimizes catalyst deactivation.

Conclusions

The effect of different doping contents of Ce and Sm on the naphtha reforming catalyst (Pt-Sn/ γ -Al₂O₃) was investigated and compared with a commercial catalyst. The FESEM results showed that the addition of Ce could reduce the amount of agglomeration while improving the distribution of Pt nanoparticles. Also, TGA/DTG results indicated that due to the higher oxygen storage capacity of ceria, the degree of graphitization and coke



Fig. 9. TGA/DTG profiles for (a) SP, (b) SPC(0.47), (c) SPS(0.87), and (d) SPC(0.47)S(0.33) catalysts.

burning temperature decreased, which could facilitate regeneration. Furthermore, based on NH_3 -TPD results, adding Ce and Sm diminished the total amount of acidic sites, especially Ce, which could reduce the strong acid sites. According to the H_2 -TPR results, adding Ce reduced the H_2 consumption due to the presence of CeO₂ while preventing the reduction of SnO₂. This could inhibit the formation of PtSn alloy to suppress a decline in Pt activity. In addition, the results of the catalytic reaction of SPC(0.47)S(0.33), SPS(0.87), and SPC(0.47) showed superior performance in aromatization reactions, mainly producing C_8 and C_9 aromatics because of more dehydrocyclization reaction for such catalysts. Moreover, adding Ce and Sm showed a decrease in the cracking reaction during the reforming process.



Fig. 10. FE-SEM images of spent (a) SP, (b) SPC(0.47), (c) SPS(0.87), and (d) SPC(0.47)S(0.33) catalysts.

Data availability

Data is provided within the manuscript or supplementary information files.

Received: 7 February 2025; Accepted: 27 May 2025 Published online: 06 June 2025

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Author contributions

Farhad Keivanimehr wrote the main manuscript and was responsible for formal analysis, investigation, resource management, and software implementation. He also participated in the review and editing process. Roshanak Kabiri was responsible for synthesizing materials, conducting formal analysis, and providing resources. Sajjad Habibzadeh was responsible for conceptualization and methodology development, overseeing project administration and supervision, and editing the manuscript. Maryam Mokhtarian contributed to data curation, formal analysis, investigations and preparing figures.

Declarations

Competing interests

The authors declare no competing interests.

Additional information

Supplementary Information The online version contains supplementary material available at https://doi.org/1 0.1038/s41598-025-04371-z.

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