



## Simultaneous Catalytic Removal of NO<sub>x</sub> and Diesel Soot Particulates Over LaSrBO<sub>4</sub> (B = Mn, Cu, Co, Fe) Oxides

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A series of LaSrBO<sub>4</sub> complex oxides were prepared by the citric acid complexation and characterized by XRD, XPS, H<sub>2</sub>-TPR, NO-TPD and catalytic activity experiments. According to the investigations, LaSrMnO<sub>4</sub> shows the best performance, the maximum conversion rate from NO to N<sub>2</sub> is up to 69 %. The existence of oxygen is very important for the simultaneous removal of NO<sub>x</sub> and diesel soot particulates. The low temperature desorbed NO species would mainly influence the N<sub>2</sub> yield. The mobility of adsorbed oxygen species would mainly influence the selectivity of the reaction.

**Key Words:** Diesel soot, Nitrogen oxide, Simultaneous removal, K<sub>2</sub>NiF<sub>4</sub>-type oxides.

### INTRODUCTION

Soot particulates and nitrogen oxides emitted from diesel exhaust have been causing severe health and environmental problems. Fine soot particulates contain lots of mutagenic hydrocarbons, it could easily reach far down into the lung tissue when inhaled and have a detrimental impact on human health. Nitrogen oxides not only contribute to the production of acid rain, but also cause the photochemical smog under the influence of sun light. The content of carbon monoxide and unburnt hydrocarbons is low, so nitrogen oxides and soot particulates are main substances to be removed from diesel engines exhaust<sup>1</sup>. Yoshida first proposed to the simultaneously conversion of soot and NO<sub>x</sub> into CO<sub>2</sub> and N<sub>2</sub>, respectively in an oxidizing atmosphere by using catalyzed soot traps<sup>2</sup>. Most of the studies have been focused on this technology and there were various reported catalyst systems used in this reaction, such as metals and metal oxide catalysts<sup>3-9</sup>, perovskite catalysts<sup>10-15</sup>, spinel type catalysts<sup>9,16-18</sup>, K<sub>2</sub>NiF<sub>4</sub>-type catalysts<sup>20,21</sup>, etc. According to investigations<sup>11-15,19-22</sup>, A-site partial substitution could improve the catalytic performance. Teraoka *et al.*<sup>15</sup> found that K-doped La-Mn-O perovskite-type oxides were good candidate catalysts for the removal of diesel soot and nitrogen oxides. Liu *et al.*<sup>20,22</sup> found that K-doped La<sub>2-x</sub>K<sub>x</sub>CuO<sub>4</sub> and Na-doped Ln<sub>2-x</sub>Na<sub>x</sub>CuO<sub>4</sub> catalyst at A-site show better catalytic activities than the unsubstituted catalysts. For La<sub>2-x</sub>K<sub>x</sub>CuO<sub>4</sub> catalyst<sup>20</sup>, the optimal substitution amount of potassium x is equal to 0.5, the highest

conversion rate from NO<sub>x</sub> to N<sub>2</sub> is 22 %. For La<sub>2-x</sub>Na<sub>x</sub>CuO<sub>4</sub> catalyst<sup>22</sup>, the optimal substitution amount of Na (x) is equal to 0.3 for the reduction of NO<sub>x</sub>, the conversion rate of NO<sub>x</sub> is 21.4 %. In general, the conversion rate of NO<sub>x</sub> into N<sub>2</sub> is not high and they are not very suitable for the exhaust conditions. Further efforts should focus on the activity of the catalysts. Our previous work find that La<sub>2</sub>NiO<sub>4</sub> is an effective catalyst for the target reaction, partially substitution of Sr for La at A-site could improve the catalytic performance. It is still not clear how the catalytic performances will change when Ni is completely substituted by other elements.

In this paper, LaSrBO<sub>4</sub> (B = Mn, Cu, Co and Fe) complex oxides were prepared, characterized and tested. The potential of these catalysts used for simultaneous removal of nitrogen oxides and diesel soot have been investigated.

### EXPERIMENTAL

**Catalyst preparation:** A series of LaSrBO<sub>4</sub> (B = Mn, Cu, Co, Fe) complex oxides with K<sub>2</sub>NiF<sub>4</sub>-type structure were prepared by the citric acid complexation<sup>21</sup>. All chemical reagents were from Tianjin Guangfu Fine Chemical research Institute, China. The corresponding metal nitrates were utilized as starting materials for obtaining an aqueous solution with appropriate stoichiometry. The citric acid was added into the mixed aqueous solution of metal nitrates in a desired proportion under ultrasonic vibration. The mixed aqueous solution was heated and stirred to evaporate water. The residual

solid composition was dried at 70 °C for 8 h, followed by decomposition at about 450 °C for 2 h in air and then calcined in air at 1100-1200 °C for 4 h.

The crystal structures of the fresh catalysts were determined by a powder X-ray diffractometer (D/MAX-2038), using  $\text{CuK}\alpha$  ( $\lambda = 0.1542$  nm) radiation combined with Nickel filter operating at 30 kV and 30 mA. The diffractometer data were recorded for  $2\theta$  values between 20 and 90° at a scanning rate of 4° ( $2\theta$ )/min<sup>-1</sup>. The patterns were compared with JCPDS reference data for phase identification.

H<sub>2</sub>-TPR measurements were measured in a home-made apparatus. 200 mg sample was pretreated at 400 °C for 1 h under nitrogen atmosphere and subsequently cooled to 100 °C. Afterwards, the TPR experiment was carried out by using 10 % hydrogen in nitrogen at a constant flow rate of 50 mL/min, from 100-800 °C at a heating rate of 10 °C/min. The hydrogen consumption signal was monitored by a thermal conductivity detector (TCD).

The NO-TPD measurements were carried out by using 200 mg sample in the same instruments as H<sub>2</sub>-TPR. Before the experiment, the catalyst was pretreated in helium atmosphere by heating up to 900 °C at the rate of 10 °C/min. Chemisorption of NO was performed by passing a flow of 30 % NO/He through the sample bed at room temperature for 0.5 h. The sample was purged on helium, until no NO was detected, the NO-TPD test was carried out up to 900 °C at a heating rate of 10 °C/min under helium atmosphere. The gas flow rate was fixed at 20 mL/min.

The X-ray photoelectron spectra (XPS) were obtained at room temperature with a PHI-1600 ESCA spectrometer by using Mg K $\alpha$  as X-ray source (1253.6 eV) under a residual pressure of  $1 \times 10^{-7}$  Pa. The binding energies were calibrated with respect to the C1s peak of a contaminant carbon (BE = 284.6 eV).

**Catalytic activity measurement:** The catalytic activities of the prepared samples were evaluated with a temperature programmed reaction. The reaction temperature varied from 100 °C to 800 °C at a heating rate of 5 °C/min. Printex-U from Degussa was used as model soot, which was more difficult to burn than diesel soot<sup>14</sup>. The model soot was mixed with the catalyst in a weight ratio of 1:10 in an agate mortar for 0.5 h to obtain a tight contact and then 500 mg mixture was placed in the tubular stainless steel reactor ( $F = 8$  mm, i.d.)<sup>14,21</sup>.

Reactant gases containing 1.0 vol. % NO and 5.0 vol. % O<sub>2</sub> balanced with He were passed through a mixture of the catalyst and Printex-U at a flow rate of 50 mL/min.

The outlet gas was analyzed *via* two on-line gas chromatographs (Agilent 6820), equipped with thermal conductivity detector and two stainless steel columns in series, respectively. The first column was packed with porapak Q for separating N<sub>2</sub>O and CO<sub>2</sub>. Another was packed with 5A molecular sieves for N<sub>2</sub>, O<sub>2</sub> and CO. There was not detectable N<sub>2</sub>O and CO during the test, which was similar to the reports of Peng and Zhao<sup>13,14</sup>.

From the activity measurements, the following parameters were derived in order to evaluate the catalytic performance; total amounts of CO<sub>2</sub> and N<sub>2</sub> ( $V[\text{CO}_2]$ ,  $V[\text{N}_2]$ ), ignition temperature ( $T_{\text{ig}}$ ), the maximum conversion of NO ( $P_{\text{N}_2}$ ) and its

temperature ( $T_{\text{max-N}_2}$ ), the selectivity to N<sub>2</sub> formation ( $S[\text{N}_2]$ ).  $P_{\text{N}_2}$  could be calculated by  $2[\text{N}_2]_{\text{out}}/[\text{NO}]_{\text{in}}$ , where  $[\text{N}_2]_{\text{out}}$  and  $[\text{NO}]_{\text{in}}$  were concentrations of N<sub>2</sub> in the outlet gas and NO in the inlet gas, respectively<sup>14</sup>.  $T_{\text{ig}}$  could be estimated by extrapolating the steeply ascending portion of the carbon dioxide formation curve to zero carbon dioxide concentration<sup>13</sup>. Selectivity to N<sub>2</sub> formation: ( $S[\text{N}_2] = V[\text{N}_2]/V[\text{CO}_2]$ )<sup>15</sup>.

## RESULTS AND DISCUSSION

**XRD results:** The X-ray diffraction patterns of LaSrBO<sub>4</sub> (B = Cu, Fe, Mn, Co) samples are showed in Fig. 1. According to the JCPDS reference data, the mainly sharp peaks of K<sub>2</sub>NiF<sub>4</sub> structure should be at  $2\theta = 24, 31.3, 32.9, 43.6$  and 47°. Comparing with these samples in Fig. 1, all samples show the K<sub>2</sub>NiF<sub>4</sub>-type structure. No other phases can be found within the XRD allowable error.

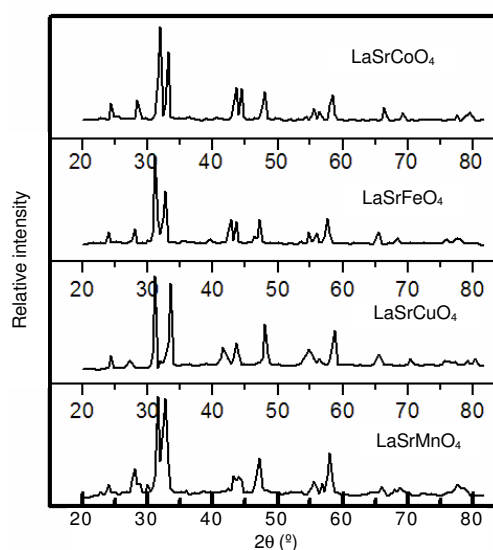


Fig. 1. X-Ray diffraction patterns of LaSrBO<sub>4</sub> (B = Cu, Fe, Mn, Co) catalysts

**Catalytic activity measurements:** Fig. 2 is the results of catalytic conversion of soot and NO<sub>x</sub> into CO<sub>2</sub> and N<sub>2</sub> over LaSrBO<sub>4</sub> samples. Lin *et al.*<sup>13</sup> considered that soot oxidation is a key precursor for the redox process between soot and NO<sub>x</sub>, it is necessary to pay attention to the ignition temperature. Fig. 2 showed that the non-catalytic combustion of soot occurs mainly between 500 and 700 °C, the ignition temperature ( $T_{\text{ig}}$ ) is 450 °C (Table-1). Comparing the LaSrBO<sub>4</sub> (B = Cu, Fe, Mn, Co) samples with the non-catalytic combustion of soot under the same reaction conditions, all of the ignition temperatures decrease and remove to the low temperature range (Table-1). For LaSrFeO<sub>4</sub> and LaSrCuO<sub>4</sub>, they have lower ignition temperature, 205 and 210 °C, respectively. Their optimum temperature for N<sub>2</sub> formation ( $T_{\text{max-N}_2}$ ) is 350 and 400 °C, which is lower than the other two samples. It seems that the optimum N<sub>2</sub> formation temperature is associated with the ignition temperature. The lower ignition temperature could promote the formation of N<sub>2</sub> at low temperature range. For LaSrMnO<sub>4</sub> and LaSrCoO<sub>4</sub>, their  $T_{\text{max-N}_2}$  values are both 450 °C, significantly higher than the other two samples, their higher ignition temperature maybe the possible reason.

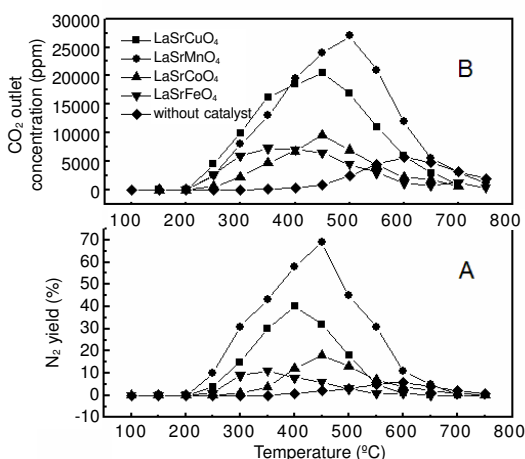


Fig. 2. N<sub>2</sub> yield and CO<sub>2</sub> concentration profiles during temperature programmed reaction over LaSrBO<sub>4</sub> catalysts. (A) N<sub>2</sub> yield (B) outlet CO<sub>2</sub> concentration profile

Samples	T <sub>ig</sub> (°C)	T <sub>max-N<sub>2</sub></sub> (°C)	T <sub>max-CO<sub>2</sub></sub> (°C)	P <sub>N<sub>2</sub></sub> (%)	S[N <sub>2</sub> ] (%)
Soot	450	600	600	6	5.3
LaSrMnO <sub>4</sub>	230	450	500	69	14
LaSrCuO <sub>4</sub>	210	400	450	40	10.6
LaSrCoO <sub>4</sub>	260	450	450	18	9.3
LaSrFeO <sub>4</sub>	205	350	350	11	7.5

Another criterion of the catalytic performance is the maximum productivity of N<sub>2</sub> (P<sub>N<sub>2</sub></sub>) and its temperature (T<sub>max-N<sub>2</sub></sub>). It can be seen from Fig. 2 and Table-1 that LaSrMnO<sub>4</sub> shows excellent catalytic performance. It has the highest P<sub>N<sub>2</sub></sub> value (69 %), which is quite similar to the last result (P<sub>N<sub>2</sub></sub> = 72 %) reported by Wang *et al.*<sup>23</sup> on La<sub>0.7</sub>Ag<sub>0.3</sub>MnO<sub>3</sub> catalyst. Besides, LaSrMnO<sub>4</sub> shows good catalytic performance within a more widely temperature range, there is about 10 % NO can be converted to N<sub>2</sub> at 250 °C; for other samples, the conversion rate is far less than 10 % at this temperature. LaSrMnO<sub>4</sub> also shows better catalytic performance at higher temperature range. In fact, the yield of CO<sub>2</sub> is consisted of two parts: the complete oxidation of soot and the reduction of NO<sub>x</sub>. The latter part could be described by the selectivity to N<sub>2</sub> formation S[N<sub>2</sub>]<sup>15</sup>. When the latter reaction play the dominate role in whole reaction, the S[N<sub>2</sub>] value is high. For LaSrMnO<sub>4</sub>, the S[N<sub>2</sub>] value is 14 %, which is higher than other samples, these results indicate that LaSrMnO<sub>4</sub> is an effective catalyst for NO<sub>x</sub> reduction.

LaSrCuO<sub>4</sub> also shows good catalytic performance, its P<sub>N<sub>2</sub></sub> value is 40 %, lower than that of LaSrMnO<sub>4</sub>, but this catalyst have lower T<sub>max-N<sub>2</sub></sub> value and lower ignition temperature. It also shows better performance than the reported K<sub>x</sub>Na doped La<sub>2-x</sub>A<sub>x</sub>CuO<sub>4</sub> type oxides<sup>20,22</sup>. For LaSrCoO<sub>4</sub>, the N<sub>2</sub> yield is low, its P<sub>N<sub>2</sub></sub> value is 18 % and T<sub>max-N<sub>2</sub></sub> is 450 °C. For LaSrFeO<sub>4</sub>, its N<sub>2</sub> yield is also very low, the P<sub>N<sub>2</sub></sub> value is only 11 %, its S[N<sub>2</sub>] value is 7.5 %, lower than the other three samples, the lower S[N<sub>2</sub>] value indicates that LaSrFeO<sub>4</sub> is inappropriate for NO<sub>x</sub> reduction. Thus, it is suggested that LaSrMnO<sub>4</sub> and LaSrCuO<sub>4</sub> would be the recommended catalysts for the target reaction.

Another noticeable occurrence on LaSrMnO<sub>4</sub> and LaSrCuO<sub>4</sub> samples, which is different from LaSrCoO<sub>4</sub> and LaSrFeO<sub>4</sub>, is that the peak temperature for N<sub>2</sub> formation does not coincide with CO<sub>2</sub>. For LaSrMnO<sub>4</sub>, the N<sub>2</sub> yield peak is at 450 °C, which indicates that this catalyst has the best catalytic activities for NO<sub>x</sub> reduction at this temperature, but this catalyst may has more excellent performance for the soot combustion at 500 °C. The quantity of CO<sub>2</sub> from NO<sub>x</sub> reduction at 500 °C is less than that of 450 °C, but the total amount of CO<sub>2</sub> at 500 °C is larger than that of 450 °C. This may be the possible reason for the two peaks do not coincide with each other.

Fig. 3 shows the catalytic performance of LaSrCoO<sub>4</sub> along with temperature when the reactant gases composition changed. When the reactant gases contains NO and O<sub>2</sub>, the DeNO<sub>x</sub> reaction will happen within a lower temperature range (250-600 °C) and have a higher NO conversion rate (18 %). When the reactant gases contain NO only, the optimum temperature for DeNO<sub>x</sub> reaction move up to a higher temperature range (350-700 °C) and the N<sub>2</sub> conversion rate is very low, only 8 %. Therefore, it is important for the reactant gas containing O<sub>2</sub>. In the oxygen atmosphere, NO is easily to react with O<sub>2</sub> to produce a stronger oxidant species NO<sub>2</sub>. Liu *et al.*<sup>22</sup> indicate that NO<sub>2</sub> is a key species for the simultaneous removal of NO<sub>x</sub> and diesel soot particulates. We infer that NO<sub>2</sub> could activate soot and produce a reducing species to reduce the nitrogen oxide.

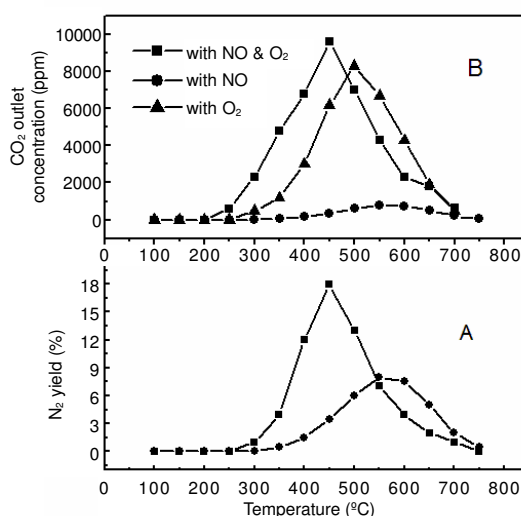


Fig. 3. N<sub>2</sub> yield and CO<sub>2</sub> concentration profiles during temperature programmed reaction over LaSrCoO<sub>4</sub> catalyst when the reactant gases changed. (A) N<sub>2</sub> yield (B) outlet CO<sub>2</sub> concentration profile

**H<sub>2</sub>-TPR:** The H<sub>2</sub>-TPR analysis results for LaSrBO<sub>4</sub> (B = Cu, Fe, Mn, Co) catalysts are shown in Fig. 4. There are two desorption peaks on the H<sub>2</sub>-TPR curves for all samples, namely, α (150 °C ≤ T ≤ 600 °C) peak and β peak (600 °C ≤ T ≤ 900 °C). Table-2 shows the reduction peak temperatures as well as the results of the selectivity to N<sub>2</sub> formation (S[N<sub>2</sub>]). In general, the reducibility of metallic ion and the mobility of oxygen species can be reflected by H<sub>2</sub>-TPR measurement. The higher the reduction peak temperature, the weaker the oxygen mobility. Contrarily, the lower the reduction peak temperature, the stronger the oxygen mobility. According to the Spinicci and Tofanari<sup>24</sup>, the α peak usually referred as the negatively

TABLE-2  
REDUCTION PEAK AREAS OF  
ANALYSIS ON H<sub>2</sub>-TPR SPECTRUM

Samples	T <sub>α</sub> (°C)	T <sub>β</sub> (°C)	S[N <sub>2</sub> ] (%)
LaSrMnO <sub>4</sub>	520	879	14
LaSrFeO <sub>4</sub>	410	740	7.5
LaSrCuO <sub>4</sub>	492	760	10.6
LaSrCoO <sub>4</sub>	476	827	9.3

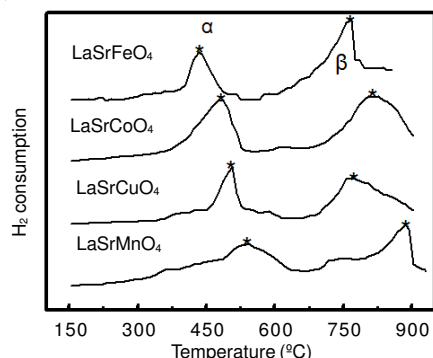


Fig. 4. H<sub>2</sub> temperature programmed reduction curves of LaSrBO<sub>4</sub> (B = Mn, Cu, Fe, Co) catalysts

charged O<sup>2-</sup> and O<sup>-</sup> and the β peak could be referred to as the lattice oxygen of catalyst. By comparing α peak temperature and S[N<sub>2</sub>] value, an obvious correlative variation trends can be observed. The α peak temperatures of H<sub>2</sub>-TPR is associated with the variation trend of S[N<sub>2</sub>] value. The higher the α peak temperature, the higher the selectivity to N<sub>2</sub> formation (S[N<sub>2</sub>]). For LaSrFeO<sub>4</sub>, its T<sub>α</sub> value is 410 °C, which is lower than other three samples, its S[N<sub>2</sub>] value is 7.5 %, which is the lowest of the four catalysts. For LaSrMnO<sub>4</sub>, its T<sub>α</sub> value is 520 °C, which is higher than other three samples, its S[N<sub>2</sub>] value is 14 %, which is the largest of the four catalysts. The other two samples also have the same corresponding relationship. It seems that the inactive adsorbed oxygen could increase the selectivity to N<sub>2</sub> formation (S[N<sub>2</sub>]). In conclusion, the B-site ions of La<sub>2</sub>BO<sub>4</sub>-type catalysts would be a key factor for the simultaneous removal of NO<sub>x</sub> and diesel soot particulates, when B-site changed, it would influence the status of oxygen species on the catalyst and then affect the catalytic ability.

**NO-TPD results:** The NO-TPD results for LaSrBO<sub>4</sub> (B = Cu, Fe, Mn, Co) catalysts are shown in Fig. 5. They all have two desorption peaks at high temperature range (400-650 °C). Meanwhile, LaSrMnO<sub>4</sub> and LaSrCuO<sub>4</sub> have a low temperature desorption peak (220-350 °C), comparing to the catalytic activity data, these two catalysts have higher N<sub>2</sub> yield than the other two samples. It seems that their higher activity may be associated with this low temperature desorption species. The research results indicate that there may be exist a negatively adsorbed NO<sup>-</sup> species on the catalyst corresponding to the electron configuration of NO<sup>-</sup> <sup>25,26</sup>, NO<sup>-</sup> is an active species for NO decomposition, it is easier to produce N<sub>2</sub> than other adsorbed species. In case of forming a negative species (NO<sup>-</sup>), only one bond should be broken for the desorption of nitrogen oxide, the desorption temperature is often lower. It is inferred that the low temperature desorption peak is associated with the NO<sup>-</sup> species, the adsorption state of NO is a key for the simultaneous removal of NO<sub>x</sub> and diesel soot particulates.

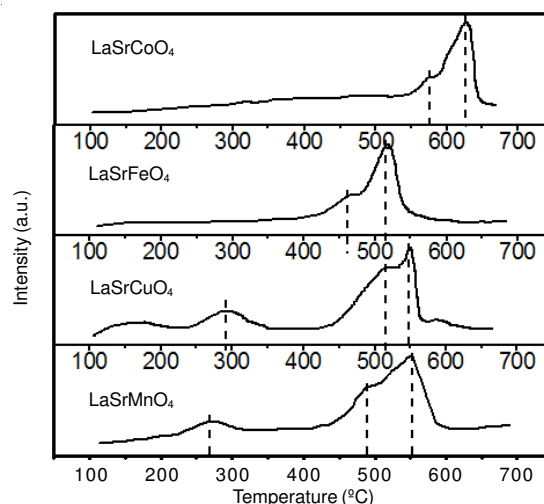


Fig. 5. NO<sup>-</sup> TPD curves of LaSrBO<sub>4</sub> (B = Mn, Co, Fe, Cu) catalysts

**XPS results:** The O1s profiles of all samples are shown in Fig. 6, the bonding energies are summarized in Table-3. There are three components observed from the fitting. These peaks are located at: (a) 528-529 eV; (b) 530-532 eV; (c) 532-534 eV. The peak at lower BE (a) can be attributed to lattice oxygen (O<sup>2-</sup>), type (b) and (c) components are attributed to adsorbed oxygen specially. Table-3 showed that the mobility of lattice oxygen species: LaSrFeO<sub>4</sub> (528.7) > LaSrCuO<sub>4</sub> (528.65) > LaSrCoO<sub>4</sub> (528.6) > LaSrMnO<sub>4</sub> (528.35), which supports the results of H<sub>2</sub>-TPR. For LaSrCoO<sub>4</sub> and LaSrFeO<sub>4</sub> samples, they have an obvious peak at 533 eV, which is attributed to adsorbed oxygen species, this species have higher mobility than other adsorbed oxygen species. According to the investigations of Shangguan *et al.* <sup>17</sup>, NO<sub>2</sub> could activate the soot and then produce a high active intermediate CO\*. This intermediate could not only react with the adsorbed oxygen species to produce CO<sub>2</sub>, but also reduce the NO to produce N<sub>2</sub>. Since there exists more active adsorbed oxygen species on the surface of LaSrCoO<sub>4</sub> and LaSrFeO<sub>4</sub>, it will be easier for the intermediate CO\* to react with the active adsorbed oxygen species and then decrease the chance of reducing NO. Comparing to the catalytic activity data, LaSrCoO<sub>4</sub> and LaSrFeO<sub>4</sub> have lower selectivity to N<sub>2</sub> formation than the other two samples, the high active adsorbed oxygen species would be the possible reason.

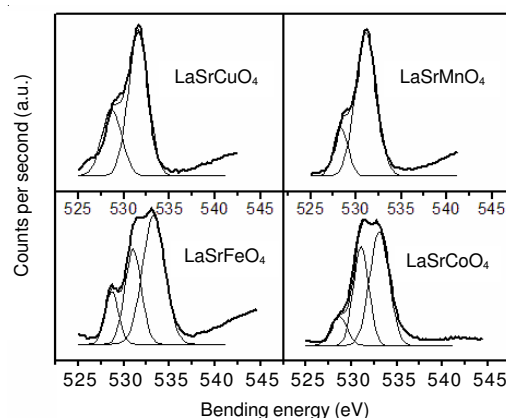


Fig. 6. O1s XPS spectra of LaSrBO<sub>4</sub> (B = Mn, Co, Fe, Cu) catalysts

TABLE-3  
BENDING ENERGIES (eV) OF CORE LEVELS OF LaSrBO<sub>4</sub>  
CATALYSTS (FIGURES IN PARENTHESIS INDICATE  
INTENSITY PERCENTAGE OF O1s COMPONENTS)

Samples	O1s	
	Lattice oxygen	Adsorbed oxygen
LaSrMnO <sub>4</sub>	528.35(18.5)	531.1(81.5)
LaSrCuO <sub>4</sub>	528.65(31.6)	531.6(68.4)
LaSrCoO <sub>4</sub>	528.6(11.6)	531.07(36.2), 533.1(52.2)
LaSrFeO <sub>4</sub>	528.7(13.8)	531.03(30.1), 533.3(56.1)

The target reaction is supposed to take place at the three-phase boundary among a solid catalyst, a solid reactant (soot particulates) and gaseous reactant (NO). Since the soot is solid particulates, it is difficult to react with NO directly. The catalytic activity curve shown in Fig. 3, also indicates that the LaSrCoO<sub>4</sub> catalyst shows poor catalytic performance ( $P_{N_2} = 8\%$ ) when the reactant gas contains NO only, however, when the reactant gases contain NO and O<sub>2</sub>, the DeNO<sub>x</sub> reaction will happen within a lower temperature range (250-600 °C) and higher catalytic efficiency ( $P_{N_2} = 18\%$ ). It is very important for the reactant gases containing O<sub>2</sub>. NO could easily react with O<sub>2</sub> and produce a strong oxidizing species NO<sub>2</sub>. It is available for NO<sub>2</sub> to activate soot and then produce a high active intermediate CO\*, which could reduce the NO to N<sub>2</sub> effectively. The results of catalytic activity measurements also indicate that the optimum temperature for the DeNO<sub>x</sub> reaction is associated with the ignition temperature, the lower the ignition temperature, the lower the optimum N<sub>2</sub> formation temperature.

The low temperature range desorbed NO species would mainly influence the N<sub>2</sub> yield, for the high active LaSrCuO<sub>4</sub> and LaSrMnO<sub>4</sub> samples, they all have a lower temperature desorption peak. In case of forming a negative species (NO<sup>-</sup>), only one bond should be broken for the desorption of nitrogen oxide, the desorption temperature is often lower. It is inferred that this desorption peak is possibly associated with the high active NO<sup>-</sup> species, it is easier for NO<sup>-</sup> species to decompose and produce N<sub>2</sub>. Therefore, these two samples have higher N<sub>2</sub> yield than the other two samples.

The total amount of CO<sub>2</sub> is mainly consisted of two parts: the complete oxidation of soot and the reduction of NO. The selectivity of simultaneous removal of NO<sub>x</sub> and diesel soot particulates could be represented by the selectivity to N<sub>2</sub> formation (S[N<sub>2</sub>]). In the oxygen atmosphere, it is easier for NO to react with O<sub>2</sub> to produce NO<sub>2</sub>, NO<sub>2</sub> is available for the soot activation and then produces an activate species CO\*. This species could not only reduce the nitrogen oxides, but also react with adsorbed oxygen species to produce CO<sub>2</sub>. From the H<sub>2</sub>-TPR spectra and XPS data, LaSrMnO<sub>4</sub> has the most inactive adsorbed oxygen species, it is unfavorable for the intermediate species CO\* to react with this inactive adsorbed oxygen species, in contrast, increasing the chance to reduce the nitrogen oxide. Therefore, this catalyst has the highest selectivity.

## Conclusion

The LaSrBO<sub>4</sub>-type oxides are proved to be effective catalysts for simultaneous removal of diesel soot and nitrogen oxides. For LaSrMnO<sub>4</sub>, the maximum conversion rate from NO to N<sub>2</sub> is up to 69 % at 450 °C. The results indicate that the optimum N<sub>2</sub> formation temperature is associated with the ignition temperature. The adsorption state of NO is a key for the title reaction, owing to the low temperature adsorbed NO species, LaSrMnO<sub>4</sub> and LaSrCuO<sub>4</sub> have higher N<sub>2</sub> yield than the other two samples. The existence of oxygen is very important, which could promote the reaction goes smoothly. The mobility of adsorbed oxygen would mainly influence the selectivity of the reaction, the inactive adsorbed oxygen could increase the selectivity of the reaction and LaSrMnO<sub>4</sub> shows the maximum selectivity among all samples.

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