available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on Rare Earth Catalysis)

(La_{0.8}A_{0.2})MnO₃ (A = Sr, K) perovskite catalysts for NO and C₁₀H₂₂ oxidation and selective reduction of NO by C₁₀H₂₂

Anne Giroir-Fendler*, Sonia Gil, Alexandre Baylet

Lyon University, Lyon, F-69003, Lyon 1 University, CNRS UMR 5256 IRCÉLYON, Albert Einstein Avenue, 2 Villeurbanne, F-69622, France

ARTICLE INFO

Article history:

Received 15 May 2014

Accepted 20 June 2014

Published 20 August 2014

Keywords:

LaMnO₃ substituted perovskite

Nitrogen oxide oxidation

Decane oxidation

Hydrocarbons-selective catalytic reduction

ABSTRACT

In this work, we studied the catalytic activity of LaMnO₃ and (La_{0.8}A_{0.2})MnO₃ (A = Sr, K) perovskite catalysts for oxidation of NO and C₁₀H₂₂ and selective reduction of NO by C₁₀H₂₂. The catalytic performances of these perovskites were compared with that of a 2 wt% Pt/SiO₂ catalyst. The La site substitution increased the catalytic properties for NO or C₁₀H₂₂ oxidation compared with the non-substituted LaMnO₃ sample. For the most efficient perovskite catalyst, (La_{0.8}Sr_{0.2})MnO₃, the results showed the presence of two temperature domains for NO adsorption: (1) a domain corresponding to weakly adsorbed NO, desorbing at temperatures lower than 270 °C and (2) a second domain corresponding to NO adsorbed on the surface as nitrate species, desorbing at temperatures higher than 330 °C. For the Sr-substituted perovskite, the maximum NO₂ yield of 80% was observed in the intermediate temperature domain (around 285 °C). In the reactant mixture of NO/C₁₀H₂₂/O₂/H₂O/He, (La_{0.8}Sr_{0.2})MnO₃ perovskite showed better performance than the 2 wt% Pt/SiO₂ catalyst: NO₂ yields reaching 50% and 36% at 290 and 370 °C, respectively. This activity improvement was found to be because of atomic scale interactions between the A and B active sites, Sr²⁺ cation and Mn⁴⁺/Mn³⁺ redox couple. Thus, (La_{0.8}Sr_{0.2})MnO₃ perovskite could be an alternative free noble metal catalyst for exhaust gas after treatment.

© 2014, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Since the signature of the international Kyoto protocol on 11 December 1997, most countries decided to discuss and implement regulations on gas emissions [1,2]. The main compounds emitted by vehicles are unburned hydrocarbons (HC), CO, soot particles, and nitrogen oxides (NO_x). To respect the European regulations, technical solutions were tested and implemented by automobile manufacturers [3,4]. For selective reduction of NO_x, two techniques have been developed: NH₃-selective catalytic reduction (SCR) and HC-SCR. In the first technique, NH₃ is used as a reactant to selectively reduce NO to N₂ in the presence of oxygen [5]. The second technique uses unburned hydrocarbons from the exhaust gas or hydrocarbons injected into

the exhaust gas line to reduce NO to N₂ [6]. To achieve the desired chemical reactions, noble metals like Pd, Rh, and Pt are generally used. However, such platinum group metal-based catalysts suffer from thermal and sulfur deactivation. Moreover, despite the constant efforts made by catalyst suppliers and car manufacturers to decrease the noble metal loading, more than the half of the overall price of such systems comes from noble metals. To act as a noble metal substitute for oxidation reactions, different types of mixed oxide materials have been investigated. One of these materials is perovskite catalysts [7]. Such materials have an ABO₃ general formula, where the A site is a rare-earth or alkaline cation and the B site is a transition metal. The nature of the A and B sites modify the chemical stoichiometry while maintaining the structural network [8,9].

* Corresponding author. Tel: +33-472-431586; E-mail: anne.giroir-fendler@ircelyon.univ-lyon1.fr

DOI: 10.1016/S1872-2067(14)60173-X | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 8, August 2014

Usually, high calcination temperatures are required to obtain the definite crystal structure, and thus increase the sintering phenomena. However, in spite of their low specific surface areas, these types of materials have been extensively investigated because of their synthesis simplicity [10], cost efficiency, and high thermal stability. Moreover, partial substitution of A and/or B sites by different coordination cations can modify the valence and the oxygen non-stoichiometry, which influences the bulk oxygen mobility and redox properties of perovskite. These two parameters play an important role in the catalytic properties [8,9]. The CO oxidation reaction over perovskite catalysts was first reported more than 50 years ago, and the potential of perovskite catalysts for engine exhaust gas treatment was suggested in the 1970s [11]. For this purpose, the most studied perovskite compositions are LaCoO_3 , LaFeO_3 , and LaMnO_3 [7–13].

In this study, perovskites were used as a noble-metal-free catalyst for NO reduction by $\text{C}_{10}\text{H}_{22}$ in lean burn conditions. Decane was used as a representative model molecule of the unburned HCs present in the exhaust streams or added (like NH_3) to increase their concentration in the HC-SCR process. The influence of A site substitution was investigated and compared with an unsubstituted LaMnO_3 perovskite and a Pt/SiO_2 reference catalyst.

2. Experimental

2.1. Catalyst preparation

The perovskite catalysts were prepared by a complexation route [10]. The reagents were $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar), $\text{Sr}(\text{NO}_3)_2$ (Acros Organics), $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar), KNO_3 (Aldrich), and maleic acid ($\text{C}_4\text{H}_4\text{O}_4$, Alfa Aesar). The nitrate precursors were dissolved in a 10 vol% aqueous solution of maleic acid. After salt dissolution, the pH of the mixture was kept at 9 by adding an aqueous solution of NH_3 . The mixture was dried overnight in an oven at 130 °C. The powder was heated under air at 800 °C for 4 h to remove the organic compounds and form the perovskite phase.

2.2. Characterizations

The quantitative measurement of the sample composition was performed by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Horiba Jobin Yvon Activa spectrometer. The solid sample was previously dissolved in acidic conditions. The specific surface areas (S_{BET}) were estimated from N_2 adsorption at −196 °C (BET method) using a Tristar surface area and porosity measurement apparatus from Micromeritics. The samples were characterized at room temperature by X-ray diffraction (XRD) to confirm the presence of the perovskite phase. The XRD measurements were carried out with a Siemens D5005 diffractometer using $\text{Cu } K_\alpha$ radiation at $\lambda = 0.15418 \text{ nm}$.

2.3. $\text{C}_{10}\text{H}_{22}$ oxidation test

The catalytic performances for $\text{C}_{10}\text{H}_{22}$ oxidation were evaluated in a U-shaped quartz reactor with 200 mg of catalyst. The reaction mixture was composed of 240 ppm $\text{C}_{10}\text{H}_{22}$ and 9 vol% O_2 in He (carrier gas). The total flow rate was 120 mL min^{-1} , corresponding to a space velocity of about 35,000 h^{-1} . The reaction products were analyzed by micro gas chromatography for CO_2 (Porapak Q) and gas chromatography for $\text{C}_{10}\text{H}_{22}$. The catalytic performances were investigated as follows: (1) introduction of the reactive mixture at room temperature, (2) heating from room temperature to 500 °C at 5 °C min^{-1} , (3) plateau at 500 °C for 15 min, and (4) cooling from 500 °C to room temperature at 2 °C min^{-1} . The light-off curves presented in this paper were recorded during the cooling ramp. The total $\text{C}_{10}\text{H}_{22}$ conversion was calculated by

$$X_{\text{C}_{10}\text{H}_{22}}(\%) = 100 \times \left(1 - \frac{[\text{C}_{10}\text{H}_{22}]_t}{[\text{C}_{10}\text{H}_{22}]_0} \right) \quad (1)$$

2.4. NO oxidation test

The catalytic activity tests for NO oxidation were performed in the same device and under the same conditions as the $\text{C}_{10}\text{H}_{22}$ oxidation test (Section 2.3). However, the reaction stream, selected to simulate traces of NO in air, was a mixture of 1000 ppm NO, 20 vol% O_2 , and He (vector gas). The space velocity was about 35,000 h^{-1} . The reactants and products (NO , NO_2 , and O_2) were analyzed by gas chromatography for O_2 , with on-line IR and UV analyzers (Rosemount) for NO and NO_2 , respectively.

In a previous study of the SCR of NO by propene under lean-burn conditions [13], it was shown that the catalytic properties of Pt-based catalysts were stable under reactive mixture at 500 °C. The catalytic activity values reported in this study correspond to those recorded during the decrease of temperature after the stabilization step at 500 °C for 15 min. A substantial amount of NO_2 was formed in the pipes of the apparatus, before the reactor and in the exhaust lines, as previously observed for studies of the SCR of NO by propene in the presence of oxygen [13]. Indeed, the thermodynamic equilibrium of the reaction leads to the formation of NO_2 at room temperature. The NO_2 formed in the pipes was subtracted from the total NO_2 amount before the conversion of NO into NO_2 :

$$Y_{\text{NO} \rightarrow \text{NO}_2}(\%) = 100 \times \frac{[\text{NO}_2] - [\text{NO}_2]_0}{[\text{NO}]_0 + [\text{NO}_2]_0} \quad (2)$$

2.5. NO/ $\text{C}_{10}\text{H}_{22}$ test

A simulated diesel exhaust gas composition was used to evaluate the catalytic properties of perovskites for NO reduction by $\text{C}_{10}\text{H}_{22}$. The reaction mixture was composed of 400 ppm NO, 240 ppm $\text{C}_{10}\text{H}_{22}$, and 9 vol% O_2 in He (carrier gas) in the presence of H_2O (1.5 vol%). The test was carried out under the same experimental conditions as the above oxidation tests. The $\text{C}_{10}\text{H}_{22}$ conversion was calculated by Eq. (1) and the N_2 , N_2O and NO_2 yields were determined by

$$Y_{\text{NO} \rightarrow \text{N}_2}(\%) = 100 \times \frac{2[\text{N}_2]}{[\text{NO}]_0 + [\text{NO}_2]_0} \quad (3)$$

$$Y_{\text{NO-N}_2\text{O}}(\%) = 100 \times \frac{2[\text{N}_2\text{O}]}{[\text{NO}]_0 + [\text{NO}_2]_0} \quad (4)$$

$$Y_{\text{NO-NO}_2}(\%) = 100 \times \frac{[\text{NO}_2] - [\text{NO}_2]_0}{[\text{NO}]_0 + [\text{NO}_2]_0} \quad (5)$$

2.6. Temperature-programmed desorption (TPD) of NO

TPD experiments after adsorption of NO were performed with the perovskite samples. For each experiment, 100 mg of solid was placed on a quartz wool bed in a U-shaped quartz reactor. The catalyst was pretreated at 400 °C for 15 min under He. After purging under He, NO adsorption was performed at 300 °C for 1 h under a NO/He mixture containing 2000 ppm NO. Then, the sample was cooled to 25 °C under the same atmosphere. After purging under He for 15 min, TPD was performed under He (60 mL min⁻¹) with a temperature ramp of 20 °C min⁻¹ up to 500 °C. The sample was then cooled under He at 25 °C. TPD was monitored by an INFICON IPC 400 quadrupole mass spectrometer. Signals at $m/e = 14, 28, 30, 44$, and 46 amu corresponding to N⁺, N₂⁺ or CO⁺, NO⁺, CO₂⁺ or N₂O⁺, and NO₂⁺ ions, respectively, were recorded. Owing to NO signal calibration, the amount of NO desorbed per square meter of catalyst was calculated.

3. Results and discussion

3.1. Characterizations

The specific surface area (S_{BET}) and chemical analysis of the different catalysts are summarized in Table 1. The noble metal catalyst showed very high S_{BET} value (~350 m² g⁻¹) whereas the S_{BET} values of the perovskite catalysts were very low (< 20 m² g⁻¹). A cation substitution site effect was observed. In particular, the insertion of Sr or K cations into the A sites delays the sintering phenomenon, and would thus lead to an increase of the specific surface area of the perovskite [14,15].

For all of the catalysts, the XRD patterns shown in Fig. 1 have peaks that are characteristic of the perovskite structure: the orthorhombic LaMnO₃ crystal phase (JCPDS 01-089-2471). Cation substitution in the same content (20 wt%) does not modify the peak positions.

3.2. Catalytic performance measurements for C₁₀H₂₂ oxidation

The catalytic properties of perovskite samples were evaluated for C₁₀H₂₂ oxidation reaction in lean conditions and compared with the 2% Pt/SiO₂ reference catalyst. The light-off curves are shown in Fig. 2 and the temperature at 10% (T_{10}), 50% (T_{50}), 90% (T_{90}) C₁₀H₂₂ conversion are summarized in

Fig. 1. XRD patterns for perovskite catalysts. (1) LaMnO₃; (2) (La_{0.8}Sr_{0.2})MnO₃; (3) (La_{0.8}K_{0.2})MnO₃.

Table 2. The Pt sample showed the lowest activation temperature of around 90 °C, and the lowest light-off temperature (T_{50}) at 127 °C. Among the perovskites, the best catalytic performances of the noble-metal-free catalysts for the C₁₀H₂₂ oxidation reaction was obtained over (La_{0.8}Sr_{0.2})MnO₃ with a T_{50} of 190 °C. The second group of active materials is composed of LaMnO₃ and (La_{0.8}K_{0.2})MnO₃ with a T_{50} of 227 and 237 °C, respectively. The results of the catalytic activity show that the presence of the K⁺ cation in the A site, i.e., (La_{0.8}K_{0.2})MnO₃, inhibits the reaction while Sr substitution improves the catalytic performance compared with the unsubstituted material.

Fig. 2. C₁₀H₂₂ conversion for 2% Pt/SiO₂ and perovskite catalysts.

Table 1

Sample characterizations of perovskite catalysts.

Catalyst	S_{BET} (m ² g ⁻¹)	Formula based on ICP analysis
2% Pt/SiO ₂	350	—
LaMnO ₃	5	La _{0.98} MnO _{3 ± δ}
(La _{0.8} Sr _{0.2})MnO ₃	18	(La _{0.80} Sr _{0.19})MnO _{3 ± δ}
(La _{0.8} K _{0.2})MnO ₃	16	(La _{0.88} K _{0.20})MnO _{3 ± δ}

Table 2

T_{10} , T_{50} , and T_{90} for 2% Pt/SiO₂ and perovskite catalysts.

Catalyst	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)
2% Pt/SiO ₂	110	127	134
LaMnO ₃	186	227	263
(La _{0.8} Sr _{0.2})MnO ₃	160	190	226
(La _{0.8} K _{0.2})MnO ₃	188	237	280

Fig. 3. NO₂ yield versus temperature for 2% Pt/SiO₂ and perovskite catalysts.

3.3. Catalytic performance measurements for NO oxidation

The influence of A site substitution on the catalytic properties of perovskite catalysts for NO oxidation to NO₂ are shown in Fig. 3. The activity curve calculated from the thermodynamic data under our operating conditions is also shown (1000 ppm NO, 20 vol% O₂). NO oxidation to NO₂ is thermodynamically favoured at low temperatures. The 2% Pt/SiO₂ reference catalyst showed the best catalytic activity for NO oxidation to NO₂. The maximum NO₂ yield of 100% was observed at 240 °C. Above 240 °C, the activity curve of the Pt sample corresponded to the thermodynamic equilibrium curve. High catalytic performance was also observed by Denton et al. [13] with different Pt loadings. Concerning the effect of the substitution of the cation A, above 380 °C, all of the conversion curves are superposed on the thermodynamic curve. This result indicates that whatever the nature of the A cation, NO/NO₂ equilibrium is reached above 380 °C. However, the (La_{0.8}Sr_{0.2})MnO₃ perovskite gave the best NO₂ yield with a maximum of 80% at 285 °C. The (La_{0.8}K_{0.2})MnO₃ sample showed a lower activity with a maximum NO conversion of 68% at 332 °C. The unsubstituted LaMnO₃ sample had the lowest catalytic activity (53% at 365 °C). The better performance of the Sr-substituted perovskites cannot only be explained by the higher *S*_{BET} (18 m² g⁻¹) because the second highest *S*_{BET} of 16 m² g⁻¹ for (La_{0.8}K_{0.2})MnO₃ does not improve the NO₂ yield compared with the sample with lower *S*_{BET}. The presence of the divalent ion Sr²⁺ [9] in the (La_{0.8}Sr_{0.2})MnO₃ sample increases the average oxidation state of the cation in position B. These effects have been suggested to

Fig. 4. Profiles corresponding to NO⁺ ions (at 30 amu) detection during NO TPD of (La_{0.8}Sr_{0.2})MnO₃ and (La_{0.8}K_{0.2})MnO₃ catalysts (weight normalised).

enhance the oxidation catalytic activity of this type of system by either facilitating oxygen mobility or enhancing the redox activity of the Mn cation [15].

3.4. NO-TPD experiments

Despite their similar specific surface area (18 and 16 m² g⁻¹), the (La_{0.8}Sr_{0.2})MnO₃ and (La_{0.8}K_{0.2})MnO₃ samples showed different catalytic activity for C₁₀H₂₂ and NO oxidation. To understand this difference, TPD of NO was carried out. The desorption profiles of NO⁺ ions at 30 amu normalized to the weight of catalyst are shown in Fig. 4. The NO amounts per m² of catalyst are summarized in Table 3. For both samples, two temperature domains of NO adsorption were observed: (1) a low temperature domain between 0 and 310 °C for (La_{0.8}Sr_{0.2})MnO₃ and 0 and 370 °C for (La_{0.8}K_{0.2})MnO₃, and (2) a high temperature domain between 310 and 500 °C for (La_{0.8}Sr_{0.2})MnO₃, and 370 and 500 °C for (La_{0.8}K_{0.2})MnO₃. The peak observed at high temperature is attributed to the decomposition of nitrate (NO₃⁻) adsorbed at the surface of the Mn sites. Even in the absence of oxygen in the gas feed, the Mn⁴⁺/Mn³⁺ and/or Mn³⁺/Mn²⁺ redox systems allowed the adsorption and the oxidation of NO₂ into NO₃ because of labile oxygen atoms of the network. The K-substituted perovskite showed the higher amount of nitrate species. The values obtained for this high temperature peak were 1.55 μmol_{NO} m⁻² for (La_{0.8}K_{0.2})MnO₃ and 0.78 μmol_{NO} m⁻² for (La_{0.8}Sr_{0.2})MnO₃. The total nitrate decomposition after the isotherm at 500 °C were 3.33 μmol_{NO} m⁻² for (La_{0.8}K_{0.2})MnO₃ and 2.11 μmol_{NO} m⁻² for (La_{0.8}Sr_{0.2})MnO₃. The higher nitrate decomposition observed on K-based perovskite is attributed to the ability of alkali and alkaline earths elements to trap NO_x in the form of nitrate [16].

Table 3

Amount of NO expressed in μmol_{NO} desorbed per m² for (La_{0.8}Sr_{0.2})MnO₃ and (La_{0.8}K_{0.2})MnO₃ catalysts (weight normalization) from TPD experiments.

Catalyst	1 st TPD peak		2 nd TPD peak		Isotherm at 500 °C		Overall NO desorption
	Peak (°C)	NO amount	Peak (°C)	NO amount	Time	NO amount	
(La _{0.8} Sr _{0.2})MnO ₃	0–310 °C	1.67	310–500	0.78	30	1.33	3.68
(La _{0.8} K _{0.2})MnO ₃	0–370 °C	4.10	370–500	1.55	30	1.78	7.43

The most interesting range is the low temperature range. Three peaks were observed for both samples and correspond to NO desorption. However, these three peaks are different in terms of their temperatures and areas. For the $(\text{La}_{0.8}\text{Sr}_{0.2})\text{MnO}_3$ sample, the main NO desorption peak occurred at a low temperature of around 95 °C. NO desorption continued, with a second peak observed at 135 °C and a third peak at 210 °C, until total desorption occurred at a temperature below 300 °C. The overall amount of NO desorbed at low temperature was $1.67 \mu\text{mol}_{\text{NO}} \text{ m}^{-2}$. However, an opposite trend was observed for the $(\text{La}_{0.8}\text{K}_{0.2})\text{MnO}_3$ sample. The intensity of the desorption peaks of NO are increased with increasing temperature. The maximum NO desorption occurred at 230 °C, which is 135 °C higher than the maximum desorption for $(\text{La}_{0.8}\text{Sr}_{0.2})\text{MnO}_3$ perovskite. Complete NO desorption was achieved at a much higher temperature of around 370 °C than for $(\text{La}_{0.8}\text{Sr}_{0.2})\text{MnO}_3$ perovskite. The overall amount of NO desorbed at low temperature was $4.10 \mu\text{mol}_{\text{NO}} \text{ m}^{-2}$. Thus, the $(\text{La}_{0.8}\text{Sr}_{0.2})\text{MnO}_3$ catalyst is more active for NO and $\text{C}_{10}\text{H}_{22}$ oxidation. This activity efficiency could be related to the weak bonding of NO adsorbed on the surface of Sr-substituted perovskites. Indeed, NO oxidation in the presence of O_2 is related to the NO adsorption property. The maximum NO_2 yield was observed at 280 °C for $(\text{La}_{0.8}\text{Sr}_{0.2})\text{MnO}_3$ and at 370 °C for $(\text{La}_{0.8}\text{K}_{0.2})\text{MnO}_3$. For both systems, this temperature corresponds to the transition between NO adsorption and nitrate formation observed during the TPD experiments. The weakly adsorbed NO could migrate from the A site to oxygen adsorbed on the B site, and thus favour the catalytic activity toward NO oxidation. In this transition behaviour, the adsorption of NO and nitrate formation was negligible. This suggests that the distance between A and B sites is important for the oxidation reaction. The B sites are often claimed to be the active sites in perovskite because of the presence of the redox system ($\text{Co}^{3+}/\text{Co}^{2+}$, $\text{Mn}^{4+}/\text{Mn}^{3+}$, $\text{Mn}^{3+}/\text{Mn}^{2+}$).

3.5. Catalytic performance measurements in HC-SCR

To check if similar good performance could be obtained with a mixture of both NO and $\text{C}_{10}\text{H}_{22}$ reactants,

$(\text{La}_{0.8}\text{Sr}_{0.2})\text{MnO}_3$ perovskite was tested under HC-SCR conditions and compared with the 2% Pt/ SiO_2 reference catalyst. The simulated gas mixture was composed of 240 ppm $\text{C}_{10}\text{H}_{22}$, 400 ppm NO, 9 vol% O_2 , and 1.5 vol% H_2O . The $\text{C}_{10}\text{H}_{22}$ conversion and NO_2 , N_2O , and N_2 yields are shown in Fig. 5. On the 2% Pt/ SiO_2 catalyst, 50% $\text{C}_{10}\text{H}_{22}$ conversion (180 °C) was 50 °C higher than the corresponding temperature observed during the $\text{C}_{10}\text{H}_{22}$ oxidation test (127 °C). The presence of NO did not influence $\text{C}_{10}\text{H}_{22}$ oxidation over $(\text{La}_{0.8}\text{Sr}_{0.2})\text{MnO}_3$ perovskite. The T_{50} value was similar to that during experiments without NO (190 °C). Decane conversion reached 100% at around 200 °C for both samples. The inhibition of $\text{C}_{10}\text{H}_{22}$ oxidation on the Pt-based catalyst can be explained by its catalytic activity for SCR. Indeed, reduction of NO to N_2O starts at the same temperature as $\text{C}_{10}\text{H}_{22}$ oxidation, and the maximum N_2O production of 65% was observed at 195 °C when the $\text{C}_{10}\text{H}_{22}$ conversion reached 100%. Moreover, in the same temperature range (< 200 °C), N_2 was produced in lower amount than N_2O with a maximum yield of 18% at 210 °C. N_2O and N_2 produced by the reduction of NO by $\text{C}_{10}\text{H}_{22}$ indicate that the number of Pt active sites for $\text{C}_{10}\text{H}_{22}$ adsorption decreases in favour of NO adsorption. For temperatures higher than 200 °C, the N_2 and N_2O yields decreased and NO conversion to NO_2 started and increased to reach a maximum of 37% at 370 °C. Compared with NO oxidation without $\text{C}_{10}\text{H}_{22}$, the maximum yield of NO_2 was lower and shifted to higher temperatures (100% at 240 °C). In addition, even at 500 °C, the NO_2 yield had not reached the thermodynamic equilibrium.

The catalytic behavior of the $(\text{La}_{0.8}\text{Sr}_{0.2})\text{MnO}_3$ perovskite was different to that of the Pt catalyst. For temperatures lower than 210 °C, the competition between $\text{C}_{10}\text{H}_{22}$ and NO was less important, and thus $\text{C}_{10}\text{H}_{22}$ oxidation was not inhibited by NO adsorption. The maximum N_2O and N_2 yields (~13% at 210 °C) were observed when $\text{C}_{10}\text{H}_{22}$ conversion reached 100%. NO_2 oxidation started at 200 °C and reached a maximum of 50% at 290 °C. Even though the maximum NO_2 yield was lower than that for the NO oxidation test without $\text{C}_{10}\text{H}_{22}$, it was observed at approximately the same temperature (between 285 and 290 °C). The lower maximum NO_2 yield for the NO/ $\text{C}_{10}\text{H}_{22}$ mixed reactant system compared with the NO system can be ex-

Fig. 5. $\text{C}_{10}\text{H}_{22}$ conversion and NO_2 , N_2O , and N_2 yields for 2% Pt/ SiO_2 (A) and $(\text{La}_{0.8}\text{Sr}_{0.2})\text{MnO}_3$ (B) under simulated diesel exhaust gas conditions (400 ppm NO, 240 ppm $\text{C}_{10}\text{H}_{22}$, 9 vol% O_2 , and 1.5 vol% H_2O in He).

Graphical Abstract

Chin. J. Catal., 2014, 35: 1299–1304 doi: 10.1016/S1872-2067(14)60173-X

(La_{0.8}A_{0.2})MnO₃ (A = Sr, K) perovskite catalysts for NO and C₁₀H₂₂ oxidation and selective reduction of NO by C₁₀H₂₂

Anne Giroir-Fendler*, Sonia Gil, Alexandre Baylet
Lyon University, France

Improvement of the catalytic activity of (La_{0.8}Sr_{0.2})MnO₃ compared with Pt/SiO₂ is because of atomic scale interactions between the Sr²⁺ cation and Mn⁴⁺/Mn³⁺ redox couple, making (La_{0.8}Sr_{0.2})MnO₃ perovskite an alternative noble-metal-free catalyst for exhaust gas after treatment.

plained by the competitive oxidation reactions of NO and C₁₀H₂₂ over Mn⁴⁺/Mn³⁺ and/or Mn³⁺/Mn²⁺ redox systems, and was not because of the competition between NO reduction and oxidation because the N₂O and N₂ yields remained low. These Mn⁴⁺/Mn³⁺ and/or Mn³⁺/Mn²⁺ redox systems are the active species involved in the Mars–van Krevelen mechanism, which is generally described for HC oxidation over mixed oxide samples [17,18]. Nevertheless, compared with the Pt/SiO₂ catalyst, this perovskite system allows the thermodynamic equilibrium to be reached at 500 °C with a NO₂ yield of around 25%.

The (La_{0.8}Sr_{0.2})MnO₃ sample showed better oxidation properties for NO₂ production than the 2% Pt/SiO₂ catalyst. In addition, the *S*_{BET} of the perovskite (18 m² g^{−1} was ca 19 times lower than the Pt catalyst (350 m² g^{−1}). Thus, for experiments carried out with the same catalyst weight, the perovskite structure allows atomic scale interactions between active sites, and thus balances the *S*_{BET} decrease. Such interactions are difficult to obtain by impregnation of noble metals at the surface of mixed oxides.

4. Conclusions

Among the substituted LaMnO₃ perovskites studied, the (La_{0.8}Sr_{0.2})MnO₃ sample showed the best catalytic performances for C₁₀H₂₂ oxidation (*T*₅₀ = 190 °C) and NO oxidation to NO₂ (NO₂ yield 80% at 285 °C). As a reference, the noble metal catalyst had a *T*₅₀ value at 110 °C for C₁₀H₂₂ oxidation and a maximum NO conversion of 100% at 240 °C. The good catalytic performance of the Sr-substituted perovskite was mainly because of Sr²⁺ cation and Mn⁴⁺/Mn³⁺ and/or Mn³⁺/Mn²⁺ redox couple interactions, which made up for their low specific surface areas (18 m² g^{−1}). The A site substitution by Sr was assumed to be the active site for NO and C₁₀H₂₂ adsorption, while Mn cations were involved in the oxidation mechanism through oxygen activation. The atomic scale interactions in the perovskite structure were assumed to be the main reason for the catalytic activity improvement. The test of the (La_{0.8}Sr_{0.2})MnO₃ sample with the HC-SCR gas mixture showed that the perovskite sample had better activity for NO oxidation than the Pt catalyst: 50% at 290 °C and 36% at 370 °C, respectively. Pt activity was inhibited by competition between NO reduction

and C₁₀H₂₂ oxidation at temperatures lower than 200 °C, and between NO reduction and oxidation at higher temperatures. Thus, (La_{0.8}Sr_{0.2})MnO₃ perovskite is a good candidate for HC-SCR of NO by C₁₀H₂₂.

Acknowledgments

Thanks are due to the scientific service of IRCÉLYON for ICP and XRD analyses. Financial supports by national agency for research are gratefully acknowledged.

References

- [1] Barrett S. *Oxf Rev Econ Policy*, 1998, 14: 20
- [2] Grubb M, Vrolijk C, Brack D. *The Kyoto Protocol: A Guide and assessment*. London: Earthscan in Cooperation with Royal Institute of International Affairs, 1999. 281
- [3] Lenaers G. *Sci Total Environ*, 1996, 189–190: 139
- [4] Kaspar J, Fornasiero P, Hickey N. *Catal Today*, 2003, 77: 419
- [5] Otto K, Shelef M, Kummer J T. *J Phys Chem*, 1970, 74: 2690
- [6] Burch R, Breen J P, Meunier F C. *Appl Catal B*, 2002, 39: 283
- [7] Royer S, Berube F, Kaliaguine S. *Appl Catal A*, 2005, 282: 273
- [8] Zhang C H, Wang C, Zhan W C, Guo Y L, Guo Y, Lu G Z, Baylet A, Giroir-Fendler A. *Appl Catal B*, 2013, 129: 509
- [9] Zhang C H, Hua W C, Wang C, Guo Y L, Guo Y, Lu G Z, Baylet A, Giroir-Fendler A. *Appl Catal B*, 2013, 134–135: 310
- [10] Zhang C H, Guo Y L, Guo Y, Lu G Z, Boreave A, Retailleau L, Baylet A, Giroir-Fendler A. *Appl Catal B*, 2014, 148–149: 490
- [11] Voorhoeve, R J H, Johnson, D W, Remeika, J P, Gallagher, P K. *Science*, 195: 827
- [12] Berger D, Fruth V, Jitaru I, Schoonman J. *Mater Lett*, 2004, 58: 2418
- [13] Denton P, Giroir-Fendler A, Praliard H, Primet M. *J Catal*, 2000, 189: 410
- [14] Wu X D, Xu L H, Weng D. *Catal Today*, 2004, 90: 199
- [15] Rida K, Benabbas A, Bouremmad F, Pena M A, Martinez-Arias A. *Catal Commun*, 2006, 7: 963
- [16] Takahashi N, Shinjoh H, Iijima T, Suzuki T, Yamazaki K, Yokota K, Suzuki H, Miyoshi N, Matsumoto S I, Tanizawa T, Tanaka T, Tateishi S S, Kasahara K. *Catal Today*, 1996, 27: 63
- [17] Tabata K, Hirano Y, Suzuki E. *Appl Catal A*, 1998, 170: 245
- [18] Baylet A, Royer S, Labrugère C, Valencia H, Marécot P, Tatibouët J M, Duprez D. *Phys Chem Chem Phys*, 2008, 10: 5983