

Non-thermal plasma-assisted low temperature NSR process on a $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ perovskite catalyst

Zhao-shun Zhang, Li Xu, Chuan Shi*

Laboratory of Plasma Physical Chemistry, Dalian University of Technology, Dalian, China,

*corresponding author: chuanshi@dlut.edu.cn

Introduction

$\text{Pt}/\text{BaO}/\text{Al}_2\text{O}_3$ (PBA) catalyst is the most commonly studied model composition for NO_x storage-reduction catalysis, its exhibits good catalytic performance at temperatures higher than 300 °C due to the strong surface basicity of BaO, which imparts relatively high thermal stability to the nitrate [1]. However, the low temperature activity of lean NO_x trap (LNT) catalysts is especially important for light duty diesel applications [2]. Due to their high NO_x storage capacity at low temperatures, perovskites have attracted considerable attention, however, they are limited by their regeneration activities during rich phase. As enlightened by the properties of non-thermal plasma (NTP) [3], we try to employ NTP in rich phase to regenerate the catalyst. Due to the activation of reductants by NTP, the regeneration of the LNT catalyst at lower temperatures (< 300 °C) was expected to occur with combination of plasma and catalysis.

Experimental

$\text{Pt}/30\text{BaO}/\text{Al}_2\text{O}_3$ and $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ perovskite samples were prepared by incipient wetness impregnation and the combustion synthesis method, respectively. The NO_x storage-reduction behavior of $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ perovskite was investigated in this study (lean phase: 500 ppm NO , 8% O_2 , balance Ar, duration: 10 min; rich phase: 1% H_2 balance Ar, discharge power: 20 w, duration: 2 min). In addition, the microstructure of the $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ catalyst was characterized by XRD, XPS and H_2 -TPR techniques.

Results and Discussion

The NSC measurements were performed for $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ at 30 - 400°C, and the results compared with a traditional LNT catalyst of the $\text{Pt}/\text{BaO}/\text{Al}_2\text{O}_3$ type. As shown in Table 1, it is clear that $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ has much higher NO_x storage capacity at low temperatures (< 300°C) compared with those of the PBA catalyst.

Table 1. NO_x storage capacities (NSCs) measured under lean conditions (500 ppm NO , 8% O_2 , N_2 balance, 50 min storage time, GHSV= 30,000 h^{-1}).

Catalyst	NO_x storage capacity ($\mu\text{mol/g}$)				
	30 °C	100 °C	200 °C	300 °C	400 °C
$\text{Pt}/30\text{BaO}/\text{Al}_2\text{O}_3$	86.9	152.1	219.6	398.9	508.1
$\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$	380.5	371.6	385.4	392.3	306.3

NO_x storage and reduction were investigated under cycling conditions over $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$, as well as over $\text{Pt}/30\text{BaO}/\text{Al}_2\text{O}_3$ for comparison, results are shown in Fig. 1a.

Compared with PBA, $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ sample displays much lower NO_x removal efficiency at all temperatures. The highest NO_x removal efficiency was observed at 300°C, but was only half that obtained over PBA at the same temperature.

As indicated in Fig. 1b, the NO_x removal efficiency of $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ over the temperature range 30-400°C was greatly enhanced compared with the performance obtained in the absence of the H_2 -plasma in the rich phase (Fig. 1a). Indeed, cycle-averaged NO_x conversions were higher than 80% in the temperature range 30°C - 300°C. This indicates that the stored NO_x on $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ could be reduced by the H_2 -plasma, and that the catalyst was effectively regenerated during rich phase operation.

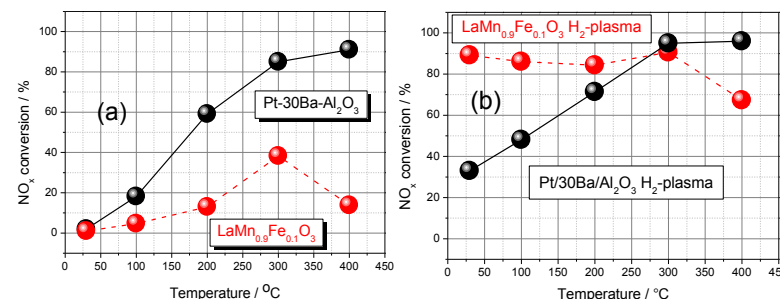


Figure 1. NO_x conversion during lean/rich cycling at different temperatures (catalysis only) (a); NO_x conversion during lean/rich cycling at different temperatures (rich phase discharge power: 20 w, duration: 2 min) (plasma enhanced catalysis) (b).

Conclusions

Characterization by XRD, XPS and H_2 -TPR techniques indicated that doping Fe into LaMnO_3 causes weakening of the Mn-O bond, which results in the generation of relatively more active surface oxygen species in $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ compared to LaMnO_3 . This, leads to better NO_x storage capacity compared with LaMnO_3 . However, due to the difficulty in regeneration during the rich phase, the perovskite showed much lower activity during lean-rich cycling compared with a traditional LNT catalyst of the $\text{Pt}/\text{BaO}/\text{Al}_2\text{O}_3$ type. By employing an H_2 -plasma in the rich phase to regenerate the NO_x saturated $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$, NO_x conversion was greatly improved, especially in the low temperature region. Indeed, NO_x conversions were greater than 80% in the temperature range 30 - 300°C. These results indicate that the use of an H_2 -plasma in the rich phase is an effective way to regenerate the perovskite catalyst, this being the rate limiting step [4]. Hence, by combining the high NO_x storage capacity of the perovskite with non-thermal plasma assisted activation of H_2 , high NO_x conversions were achieved over the $\text{LaMn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ catalyst over a broad temperature range.

References

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