Non-thermal plasma-assisted low temperature NSR process on a LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> perovskite catalyst

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Introduction
Pt/BaO/Al<sub>2</sub>O<sub>3</sub> (PBA) catalyst is the most commonly studied model composition for NO<sub>x</sub> storage-reduction catalysis, it 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<sub>x</sub> trap (LNT) catalysts is especially important for light duty diesel applications [2]. Due to their high NO<sub>x</sub> 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
Pt/30BaO/Al<sub>2</sub>O<sub>3</sub> and LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> perovskite samples were prepared by incipient wetness impregnation and the combustion synthesis method, respectively. The NO<sub>x</sub> storage-reduction behavior of LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> perovskite was investigated in this study (lean phase: 500 ppm NO, 8% O<sub>2</sub>, balance Ar, duration: 10 min; rich phase: 1% H<sub>2</sub>; balance Ar, discharge power: 20 w, duration: 2 min). In addition, the microstructure of the LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> catalyst was characterized by XRD, XPS and H<sub>2</sub>-TPR techniques.

Results and Discussion
The NSC measurements were performed for LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> at 30 - 400°C, and the results compared with a traditional LNT catalyst of the Pt/BaO/Al<sub>2</sub>O<sub>3</sub> type. As shown in Table 1, it is clear that LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> has much higher NO<sub>x</sub> storage capacity at low temperatures (< 300°C) compared with those of the PBA catalyst.

Table 1. NO<sub>x</sub> storage capacities (NSCs) measured under lean conditions (500 ppm NO, 8% O<sub>2</sub>, N<sub>2</sub> balance, 50 min storage time, GHSV= 30,000 h<sup>-1</sup>.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NO&lt;sub&gt;x&lt;/sub&gt; storage capacity (μmol/g)</th>
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<tbody>
<tr>
<td></td>
<td>30 °C</td>
</tr>
<tr>
<td>Pt/30BaO/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>86.9</td>
</tr>
<tr>
<td>LaMn&lt;sub&gt;0.9&lt;/sub&gt;Fe&lt;sub&gt;0.1&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>380.5</td>
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NO<sub>x</sub> storage and reduction were investigated under cycling conditions over LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub>, as well as over Pt/30BaO/Al<sub>2</sub>O<sub>3</sub> for comparison, results are shown in Fig. 1a. Compared with PBA, LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> sample displays much lower NO<sub>x</sub> removal efficiency at all temperatures. The highest NO<sub>x</sub> 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<sub>x</sub> removal efficiency of LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> over the temperature range 30-400°C was greatly enhanced compared with the performance obtained in the absence of the H<sub>2</sub>-plasma in the rich phase (Fig. 1a). Indeed, cycle-averaged NO<sub>x</sub> conversions were higher than 80% in the temperature range 30°C - 300°C. This indicates that the stored NO<sub>x</sub> on LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> could be reduced by the H<sub>2</sub>-plasma, and that the catalyst was effectively regenerated during rich phase operation.

Figure 1. NO<sub>x</sub> conversion during lean/rich cycling at different temperatures (catalysis only) (a); NO<sub>x</sub> 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<sub>2</sub>-TPR techniques indicated that doping Fe into LaMnO<sub>3</sub> causes weakening of the Mn-O bond, which results in the generation of relatively more active surface oxygen species in LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> compared to LaMnO<sub>3</sub>. This, leads to better NO<sub>x</sub> storage capacity compared with LaMnO<sub>3</sub>. 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 Pt/BaO/Al<sub>2</sub>O<sub>3</sub> type. By employing an H<sub>2</sub>-plasma in the rich phase to regenerate the NO<sub>x</sub> saturated LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub>, NO<sub>x</sub> conversion was greatly improved, especially in the low temperature region. Indeed, NO<sub>x</sub> conversions were greater than 80% in the temperature range 30 - 300°C. These results indicate that the use of an H<sub>2</sub>-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<sub>x</sub> storage capacity of the perovskite with non-thermal plasma assisted activation of H<sub>2</sub>, high NO<sub>x</sub> conversions were achieved over the LaMn<sub>0.9</sub>Fe<sub>0.1</sub>O<sub>3</sub> catalyst over a broad temperature range.

References