Electronic Supplementary Information (ESI)

Rational design and in-situ fabrication of MnO$_2$@NiCo$_2$O$_4$ nanowire arrays on Ni foam as high-performance monolith de-NO$_x$ catalysts

Yan Liu, Jing Xu, Hongrui Li, Sixiang Cai, Hang Hu, Cheng Fang, Liyi Shi and Dengsong Zhang*

Research Center of Nano Science and Technology, School of Material Science and Engineering, Shanghai University, Shanghai 200444, China.

* Corresponding authors: Fax: +86-21-66136079; E-mail: dszhang@shu.edu.cn

Part I. Preparation of the reference samples.

i. Preparation details of NiCo$_2$O$_4$@Ni foam, MnO$_2$@Ni foam and NiO foam.

NiCo$_2$O$_4$@Ni foam: 4 mmol of Ni(NO$_3$)$_2$·6H$_2$O and 8 mmol of Co(NO$_3$)$_2$·6H$_2$O and 24 mmol of urea were dissolved in 80 mL of mixed solution with ethanol and H$_2$O (V:V=1:1) under stirring for 30 min. Subsequently, the cleaned nickel foams were immersed into the above mentioned homogeneous solution and then transferred into a 100 mL Teflon-lined stainless steel autoclave for 8 h of hydrothermal reaction under 110 °C. Then the autoclave was allowed to cool down naturally. Then the Ni foam was washed by deionized water upon ultrasonic vibration for 10 min to remove the surplus products, dried overnight and finally calcined in air at 500 °C for 4 h by a ramping rate of 2 °C·min$^{-1}$.

MnO$_2$@Ni foam: 0.5 mmol of KMnO$_4$ was dissolved in 80 mL deionized water and then transferred into a 100 mL Teflon-lined stainless steel autoclave. The cleaned nickel foams were immersed into the homogeneous solution and then transferred to a 100 mL Teflon-lined stainless steel autoclave for 12 h of hydrothermal reaction under 160 °C. Then, the as-prepared product was washed by deionized water upon ultrasonic vibration for 10 min, dried overnight and finally calcined in air at 500 °C for 4 h by a ramping rate of 2 °C·min$^{-1}$.

NiO foam: the cleaned nickel foams were calcined in air at 500 °C for 4 h with a hating rate of 2 °C·min$^{-1}$. 
ii. Preparation of the MnO$_2$/cordierite ceramic honeycomb catalyst

The commercial cordierite ceramic honeycomb (400 cells per square inch, square channels = 1 mm$^2$ and a wall thickness = 100 um) was purchased from the Yixing Weimin Ceramics Factory (China). Before use, the cordierite was pre-treated with ethanol and deionized water and dried overnight. In a typical synthesis, according to the loadings of active component MnO$_2$ on Ni foam (the mass difference before and after the reaction), 0.45 g of Mn(NO$_3$)$_2$ was dispersed in 10 mL deionized water under stirring for 20 min. Afterwards, the pre-treated cordierite ceramic honeycomb (1.8 cm×1.8 cm×1 cm) was immersed into the homogeneous solution and dried at 80 °C overnight. Finally, the products were calcined in air at 500 °C for 4 h at a ramping rate of 2 °C·min$^{-1}$.

---

Part II. Supplementary SEM images, elemental data, surface area data and catalytic experimental results.

Fig.S1 SEM image of the Ni foam.
Fig.S2 (a) SEM image and (b) corresponding Energy dispersive X-ray (EDX) spectrum result of the MnO$_2$@NiCo$_2$O$_4$ nanowires.
Fig.S3 (a) SEM image and (b) TEM image of the Ni-Co basic carbonates precursor.
**Fig. S4** SEM images of the (a-b) NiCo$_2$O$_4$@Ni foam; (c-d) MnO$_2$@Ni foam; (e-f) NiO foam.
**Fig. S5** SEM image of the MnO$_2$@NiCo$_2$O$_4$@Ni foam catalyst after the ion sputtering thinning.
The *in situ* DRIFTS of NH$_3$ adsorption at various temperatures were performed to investigate the adsorption behaviour of NH$_3$ molecules on the surface of MnO$_2$@NiCo$_2$O$_4$@Ni foam catalyst. As illustrated in Fig. S6, ESI, the band at 1468 cm$^{-1}$ is attributed to the asymmetric deformation vibrations of the ionic NH$_4^+$ ($\delta$$_a$(NH$_4^+$)) bound to the Bronsted acid sites, while those at 1691 and 1645 cm$^{-1}$ correspond to the symmetric deformation vibrations of the ionic NH$_4^+$ ($\delta$$_s$(NH$_4^+$)) bound to the Bronsted acid sites. The band at 1217 cm$^{-1}$ is a result of the symmetric deformation vibration of the NH$_3$ ($\delta$$_s$(NH$_3$)) coordinative bound to the Lewis acid sites, and the band at 1579 cm$^{-1}$ can be assigned to the asymmetric deformation of the NH$_3$ ($\delta$$_a$(NH$_3$)) coordinated to the Lewis acid sites.\(^{1,2}\) The result shows that there are both Bronsted acid sites and Lewis acid sites on the surface of the MnO$_2$@NiCo$_2$O$_4$@Ni foam catalyst.

![Fig. S6 In situ DRIFTS of NH$_3$ adsorption on MnO$_2$@NiCo$_2$O$_4$@Ni foam catalyst from 30 to 350 °C.](image-url)
The *in situ* DRIFTS of NO+O₂ adsorption at various temperatures were also conducted to investigate the adsorption behaviour of NOₓ molecules on the surface of MnO₂@NiCo₂O₄@Ni foam catalyst. As shown in Fig.S7, ESI, the bands at 1540 and 1248 cm⁻¹ are attributed to the monodentate nitrate,⁵ and the band at 1290 cm⁻¹ corresponds to nitrate species.¹ The result shows that the catalyst has a great ability of chemisorption and activation of reactant molecules on the surface.
Fig. S8 NH$_3$-SCR performance of the Ni foam and NiO foam as a function of temperature. Reaction conditions: [NO] = [NH$_3$] = 500 ppm, [O$_2$] = 3 vol. %, N$_2$ as balance gas, and GHSV = 20,000 h$^{-1}$. 
<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Element calculated by ICP-AES (wt. %)</th>
<th>Element calculated by EDX (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn</td>
<td>Ni</td>
</tr>
<tr>
<td>MnO₂@NiCo₂O₄@Ni foam</td>
<td>1.85</td>
<td>93.91</td>
</tr>
<tr>
<td>NiCo₂O₄@Ni foam</td>
<td>—</td>
<td>94.95</td>
</tr>
<tr>
<td>MnO₂@Ni foam</td>
<td>0.81</td>
<td>98.17</td>
</tr>
</tbody>
</table>

Table S1  Mn, Ni and Co contents calculated from ICP-AES and EDX of the MnO₂@NiCo₂O₄@Ni foam and the reference samples.
Table S2 Surface areas of the monolith MnO$_2$@NiCo$_2$O$_4$@Ni foam catalyst and the reference samples.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Surface area of the monolith catalyst (m$^2$/m$^3$ cat.)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO$_2$@NiCo$_2$O$_4$@Ni foam</td>
<td>1.53 × 10$^6$</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$@Ni foam</td>
<td>1.22 × 10$^6$</td>
</tr>
<tr>
<td>MnO$_2$@Ni foam</td>
<td>1.09× 10$^6$</td>
</tr>
<tr>
<td>Ni foam</td>
<td>0.98 × 10$^6$</td>
</tr>
</tbody>
</table>

$^a.$ The specific surface areas were determined using the Brunauer-Emmett-Teller (BET) equation and then converted into the surface area of the monolith catalyst according to the following equation:

$$A_{\text{monolith}} = A_{\text{BET}} \times \frac{m}{V} \times 10^6$$

Where $A_{\text{BET}}$ (m$^2$/g) is the specific surface areas of the catalysts determined by the Brunauer-Emmett-Teller (BET) equation, $A_{\text{monolith}}$ (m$^2$/m$^3$ cat) refers to the surface areas of the monolith catalysts, $m$ (g) and $V$ (cm$^3$) is on behalf of the corresponding quality and volume of the monolith catalysts, respectively.
Fig. S9 NO$_2$ concentration of MnO$_2$@NiCo$_2$O$_4$@Ni foam as a function of temperature during the SCR reaction. Reaction conditions: [NO] = [NH$_3$] = 500 ppm, [O$_2$] = 3 vol.%, N$_2$ as balance gas, and GHSV = 20,000 h$^{-1}$.

The NO$_2$ concentration of MnO$_2$@NiCo$_2$O$_4$@Ni foam during NH$_3$-SCR performance test was also tested to evaluate the change of NO$_2$ concentration. As the inlet stream does not contain NO$_2$, the NO$_2$ detected comes from the oxidation of NO. And the existence of NO$_2$ in the reactant gas can participate in fast-SCR (NO + NO$_2$ + 2NH$_3$ → 2N$_2$ + 3H$_2$O). As can be seen, the concentration of NO$_2$ is relatively low below 200 °C, which could be deduced that more NO$_2$ molecules take part in the fast-SCR reaction. After 200 °C, the NO$_2$ increases rapidly, which is attributed that NH$_3$ is oxidized into NO and NO$_2$ at higher temperature.
Fig. S10 NH$_3$-SCR performance as a function of temperature. Reaction conditions: [NO] = [NH$_3$] = 500 ppm, [O$_2$] = 3 vol. %, N$_2$ as balance gas, and GHSV = 60,000 h$^{-1}$.

References