Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2015

Electronic Supplementary Information (ESI)

Rational design and *in-situ* fabrication of MnO_2@$NiCo_2O_4$ 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 $NiCo_2O_4$@Ni foam, MnO_2@Ni foam and NiO foam.

$NiCo_2O_4$@Ni foam: 4 mmol of $Ni(NO_3)_2\cdot 6H_2O$ and 8 mmol of $Co(NO_3)_2\cdot 6H_2O$ and 24 mmol of urea were dissolved in 80 mL of mixed solution with ethanol and H_2O (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 ^oC. 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 ^oC for 4 h by a ramping rate of 2 $^oC\cdot min^{-1}$.

MnO_2@Ni foam: 0.5mmol 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 ^oC. 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 ^oC for 4 h by a ramping rate of 2 $^oC\cdot min^{-1}$.

NiO foam: the cleaned nickel foams were calcined in air at 500 ^oC for 4 h with a hating rate of 2 $^oC\cdot min^{-1}$.

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 ^{o}C overnight. Finally, the products were calcined in air at 500 ^{o}C for 4 h at a ramping rate of 2 $^{o}C\cdot min^{-1}$.

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

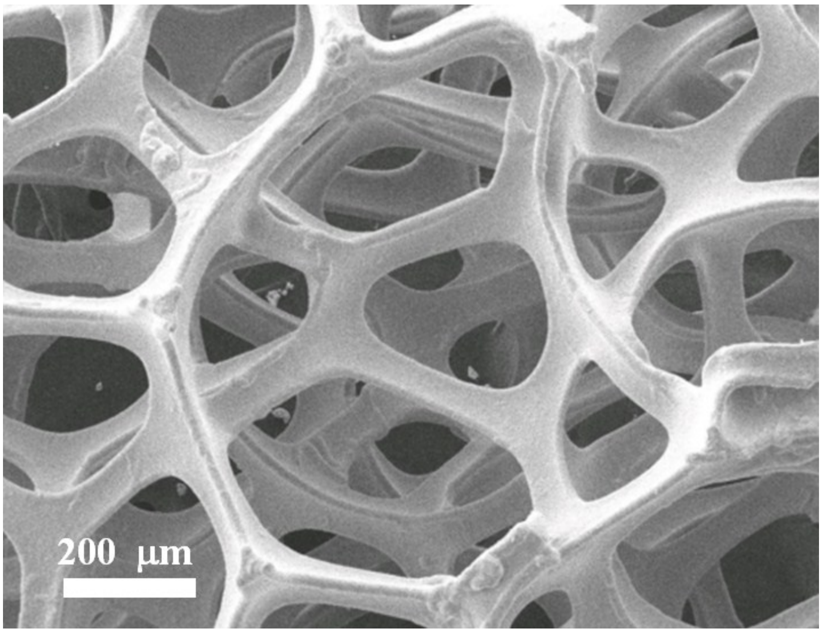

Fig.S1 SEM image of the Ni foam.

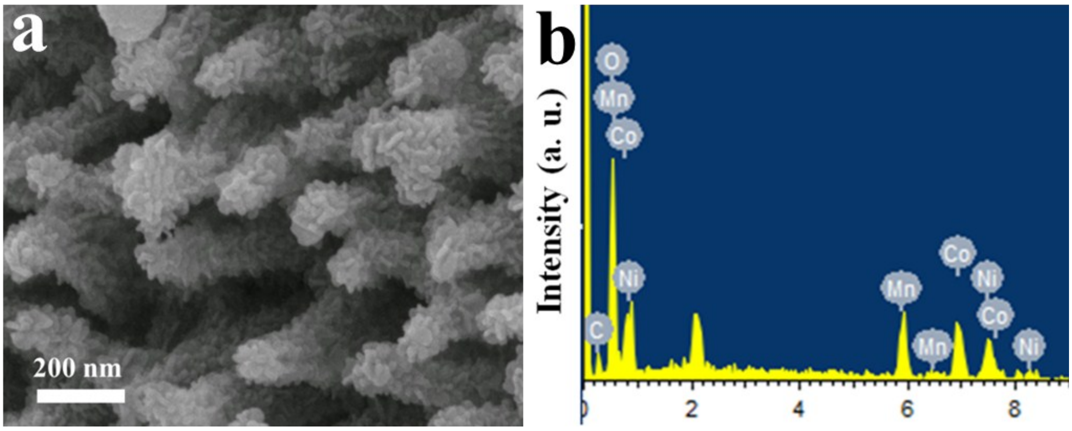

Fig.S2 (a) SEM image and (b) corresponding Energy dispersive X-ray (EDX) spectrum result of the MnO_2@$NiCo_2O_4$ nanowires.

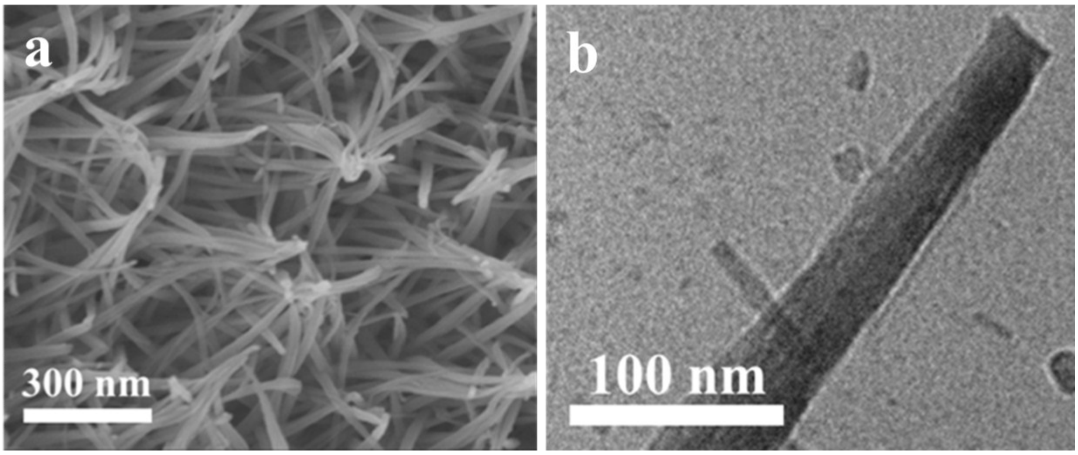

Fig.S3 (a) SEM image and (b) TEM image of the Ni-Co basic carbonates precursor.

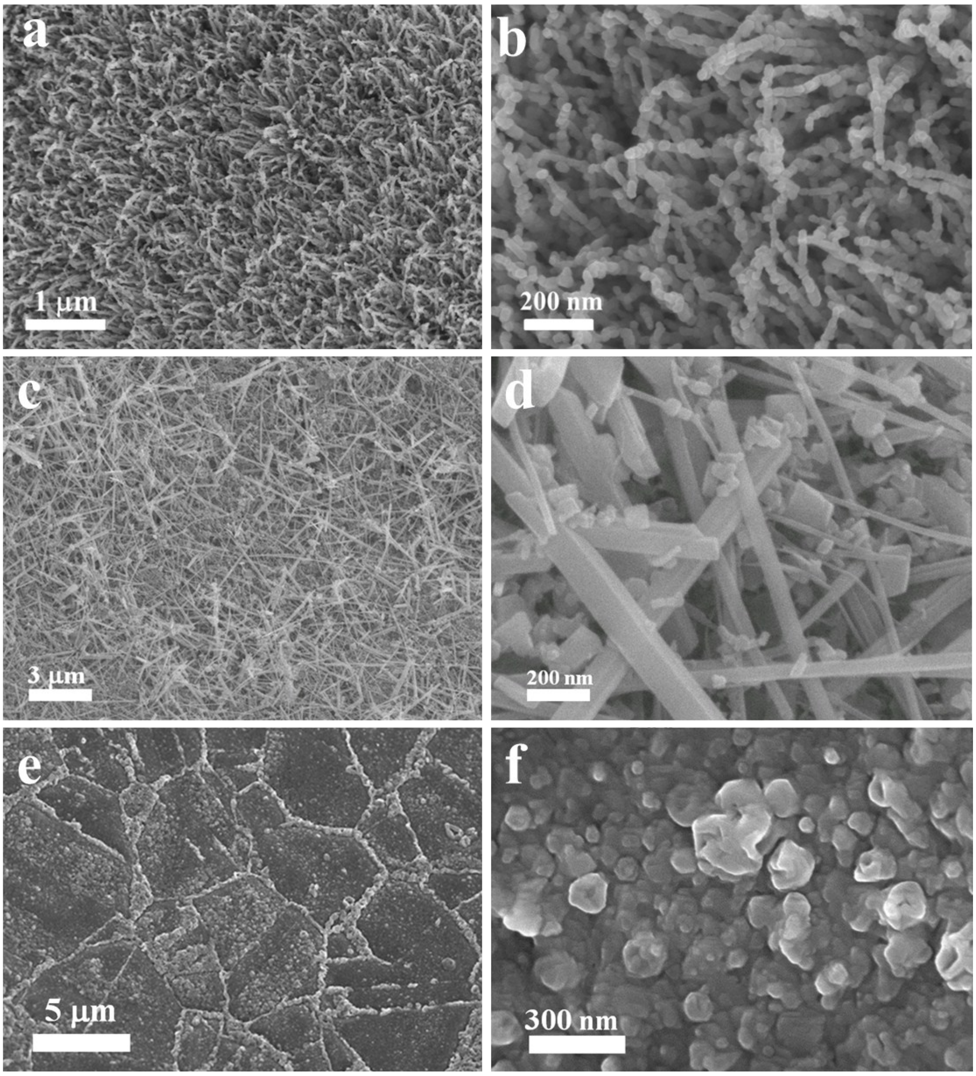

Fig.S4 SEM images of the (a-b) $NiCo_2O_4$@Ni foam; (c-d) MnO_2@Ni foam; (e-f) NiO foam.

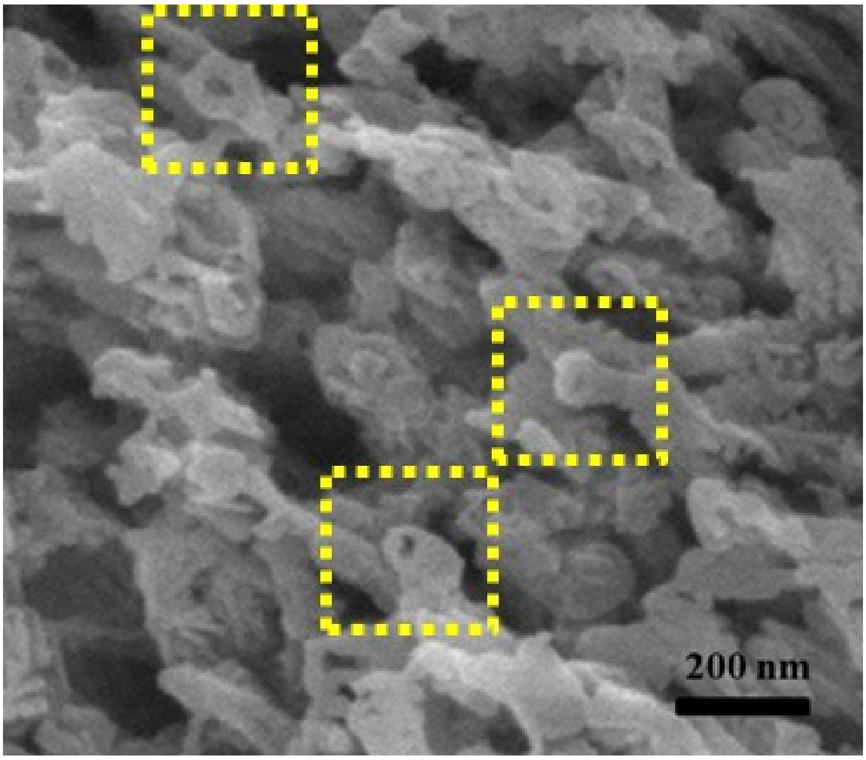

Fig.S5 SEM image of the $MnO_2@NiCo_2O_4@Ni$ foam catalyst after the ion sputtering thinning.

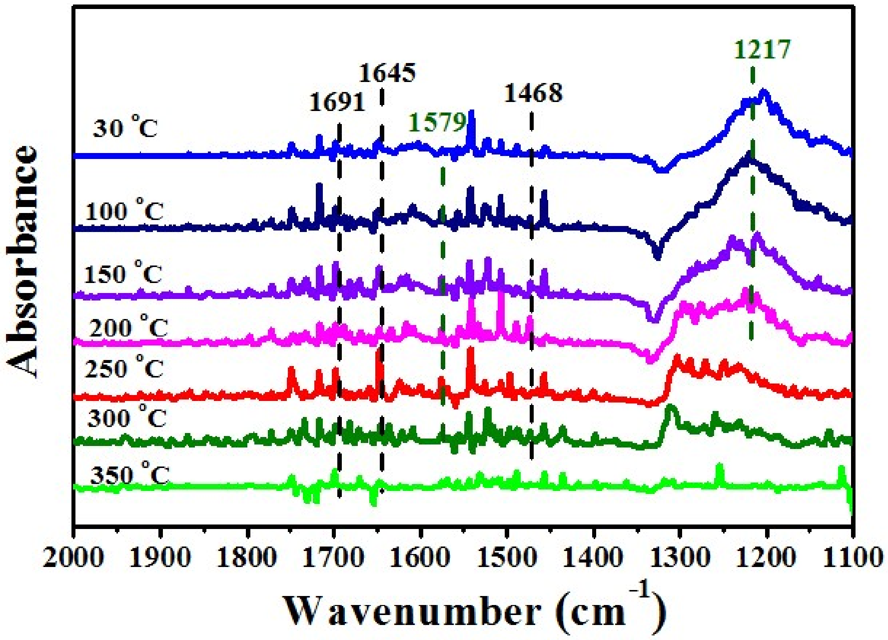

Fig.S6 *In situ* DRIFTS of NH_3 adsorption on MnO_2@$NiCo_2O_4$@Ni foam catalyst from 30 to 350 °C.

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@$NiCo_2O_4$@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^+ (δ_{as} (NH_4^+)) bound to the Brønsted acid sites, while those at 1691 and 1645 cm^{-1} correspond to the symmetric deformation vibrations of the ionic NH_4^+ (δ_s (NH_4^+)) bound to the Brønsted acid sites. The band at 1217 cm^{-1} is a result of the symmetric deformation vibration of the NH_3(δ_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 (δ_{as} (NH_3)) coordinated to the Lewis acid sites.[1, 2] The result shows that there are both Brønsted acid sites and Lewis acid sites on the surface of the MnO_2@$NiCo_2O_4$@Ni foam catalyst.

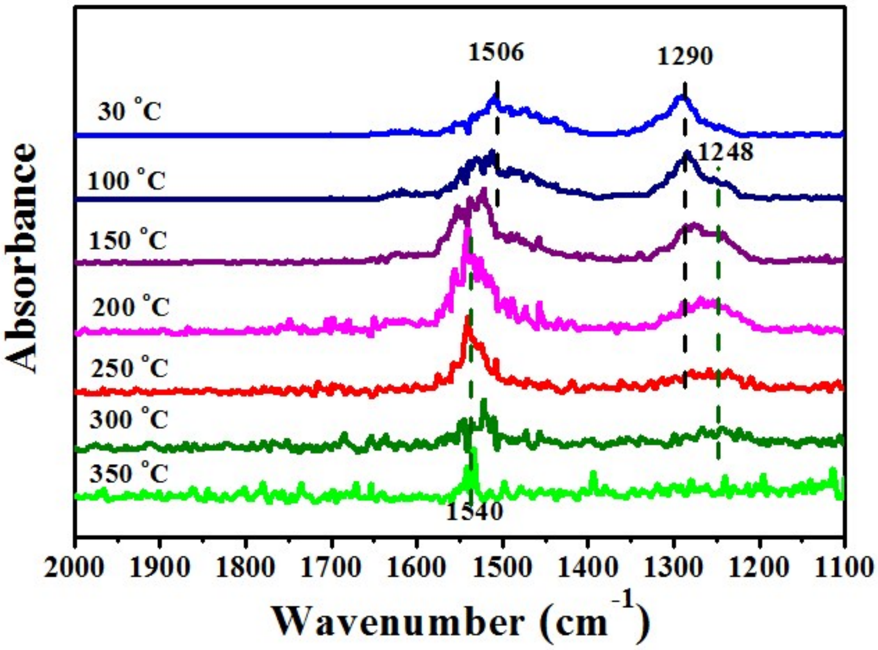

Fig.S7 *In situ* DRIFTS of NO+O_2 adsorption on MnO_2@$NiCo_2O_4$@Ni foam catalyst from 30 to 350 °C.

The *in situ* DRIFTS of NO+O_2 adsorption at various temperatures were also conducted to investigate the adsorption behaviour of NO_x molecules on the surface of MnO_2@$NiCo_2O_4$@Ni foam catalyst. As shown in Fig.S7, ESI, the bands at 1540 and 1248 cm^{-1} are attributed to the monodentate nitrate,[3] 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.

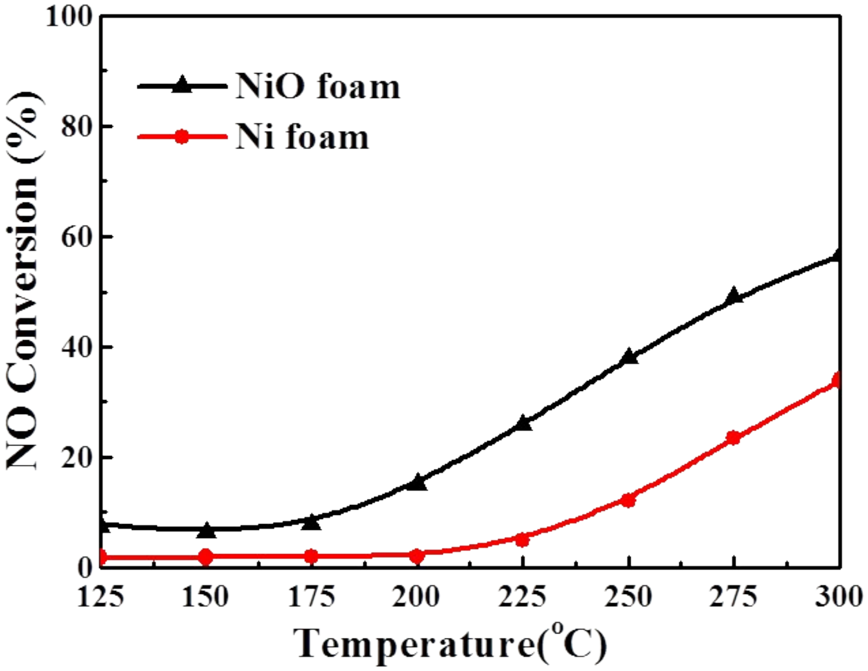

Fig.S8 NH_3-SCR performance of the Ni foam and NiO foam as a function of temperature. Reaction conditions: [NO] = [NH_3] = 500 ppm, [O_2] = 3 vol. %, N_2 as balance gas, and GHSV = 20,000 h^{-1}.

Table S1 Mn, Ni and Co contents calculated from ICP-AES and EDX of the MnO_2@$NiCo_2O_4$@Ni foam and the reference samples.

Catalysts	Element calculated by ICP-AES (wt. %)			Element calculated by EDX (at. %)		
	Mn	Ni	Co	Mn	Ni	Co
MnO_2 @$NiCo_2O_4$ @Ni foam	1.85	93.91	4.05	12.43	18.46	19.77
$NiCo_2O_4$@Ni foam	—	94.95	4.03	—	18.77	15.31
MnO_2@Ni foam	0.81	98.17	—	6.95	29.66	—

Table S2 Surface areas of the monolith MnO_2@$NiCo_2O_4$@Ni foam catalyst and the reference samples.

Catalysts	Surface area of the monolith catalyst (m^2 / m^3 cat.) [a]
MnO_2 @$NiCo_2O_4$ @Ni foam	1.53×10^6
$NiCo_2O_4$@Ni foam	1.22×10^6
MnO_2@Ni foam	1.09×10^6
Ni foam	0.98×10^6

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

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

Where A_{BET} (m^2/g) is the specific surface areas of the catalysts determined by the Brunauer-Emmett-Teller (BET) equation, $A_{monolith}$ (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.

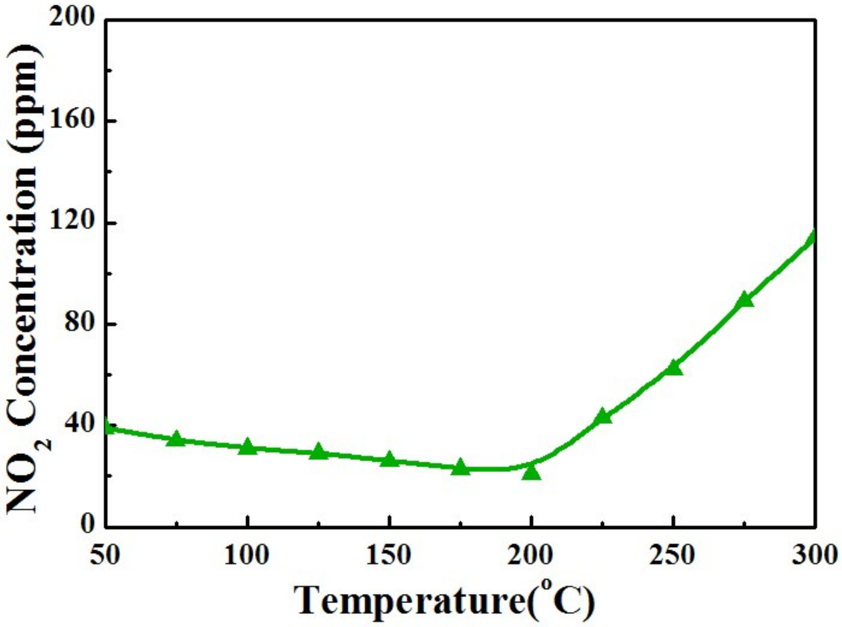

Fig.S9 NO_2 concentration of $MnO_2@NiCo_2O_4@Ni$ foam as a function of temperature during the SCR reaction. Reaction conditions: [NO] = [NH_3] = 500 ppm, [O_2] = 3 vol. %, N_2 as balance gas, and GHSV = 20,000 h^{-1}.

The NO_2 concentration of $MnO_2@NiCo_2O_4@Ni$ 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 ($NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$).[4] 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.[5]

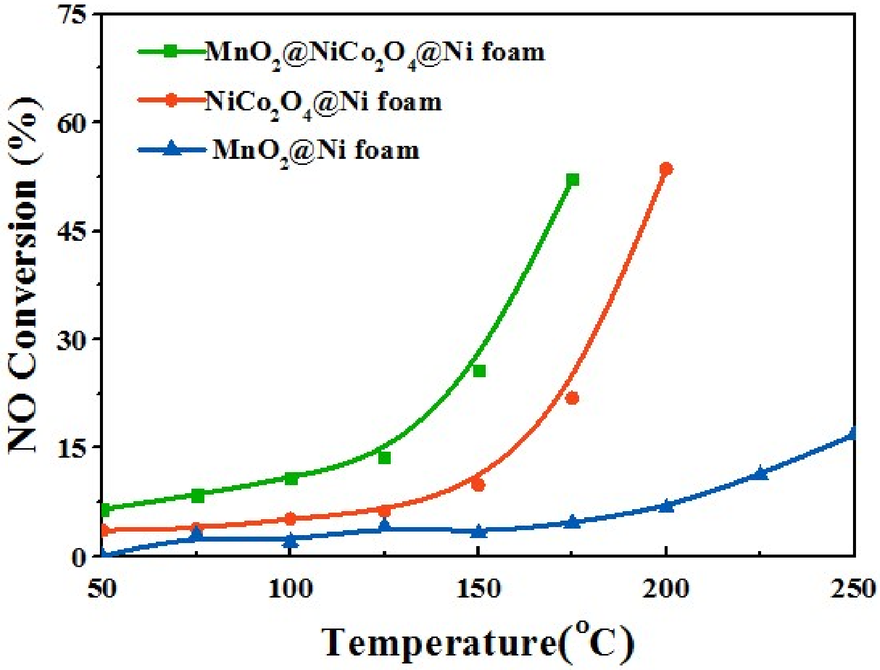

Fig.S10 NH_3-SCR performance as a function of temperature. Reaction conditions: [NO] = [NH_3] = 500 ppm, [O_2] = 3 vol. %, N_2 as balance gas, and GHSV = 60,000 h^{-1}.

References

1. B. Guan, H. Lin, L. Zhu, B. Tian and Z. Huang, *Chem. Eng. J.*, 2012, **181-182**, 307-322.
2. C. H. Lin and H. Bai, *Appl. Catal., B*, 2003, **42**, 279-287.
3. L. Chen, J. H. Li and M. F. Ge, *Environ. Sci. Technol.*, 2010, **44**, 9590–9596.
4. A. Grossale, I. Nova, E. Tronconi, D. Chatterjee and M. Weibel, *J. Catal.*, 2008, **256**, 312-322.
5. T. Yu, T. Hao, D. Q. Fan, J. Wang, M. Q. Shen and W. Li, *J. Phys. Chem. C*, 2014, **118**, 6565-6575.