

Electronic Supplementary Information (ESI)

A general strategy for *in-situ* decorating porous Mn-Co bi-metal oxides on metal mesh/foam as high performance de-NO_x monolith catalysts

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Part I. Experimental details

1. Preparation of the Mn-Co@ceramics

The commercial cordierite support (400 cells per square inch, square channels=1 mm² and a wall thickness =100 um) was purchased from the Yixing Weimin Ceramics Factory (China). The cordierite was immersed in the 3 mol/L oxalic acid aqueous solution and heated at 90 °C for 2 h before use. Afterwards, the pre-treated cordierite support were washed by deionized water and dried overnight in the constant temperature oven at 80 °C. Finally, the Mn-Co@ ceramics catalyst was synthesized by the typical synthesis route of Mn-Co@ metal support catalysts.

2. Poisoning and Regeneration of Mn-Co@Fe mesh catalysts

In this work, 0.3 wt% of K metals was induced to Mn-Co@Fe mesh catalysts by impregnation from the potassium nitrate solutions. After that, the deactivated catalysts were calcined at 500 °C for 2 h (ramping rate = 2 °C/min) and then cooled down naturally (denoted as Mn-Co@Fe mesh- 0.3% K). The regeneration of the poisoned catalysts was performed by the washing method: the deactivated catalysts (0.5 g) were washed in DI water at 30 °C for 24 h and dried in an oven at 60 °C (denoted as Mn-Co@Fe mesh-regenerated).

Part II. Supplementary results of the catalysts

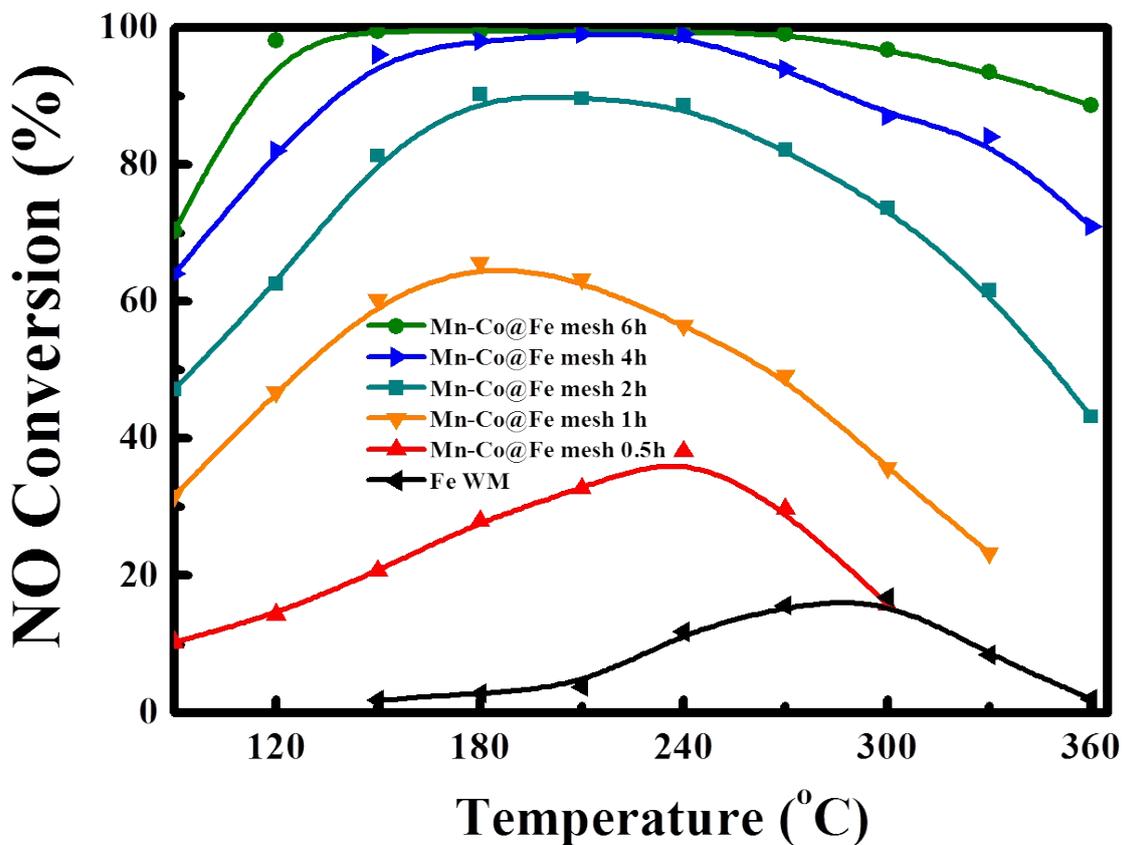


Fig.S1 Plots of NO conversion *versus* temperature for the Mn-Co@Fe mesh catalysts with different reaction time.

Reaction conditions: $[\text{NH}_3] = [\text{NO}] = 550 \text{ ppm}$, $[\text{O}_2] = 5 \text{ vol. \%}$, N_2 as balance gas, $\text{GHSV} = 10000 \text{ h}^{-1}$.

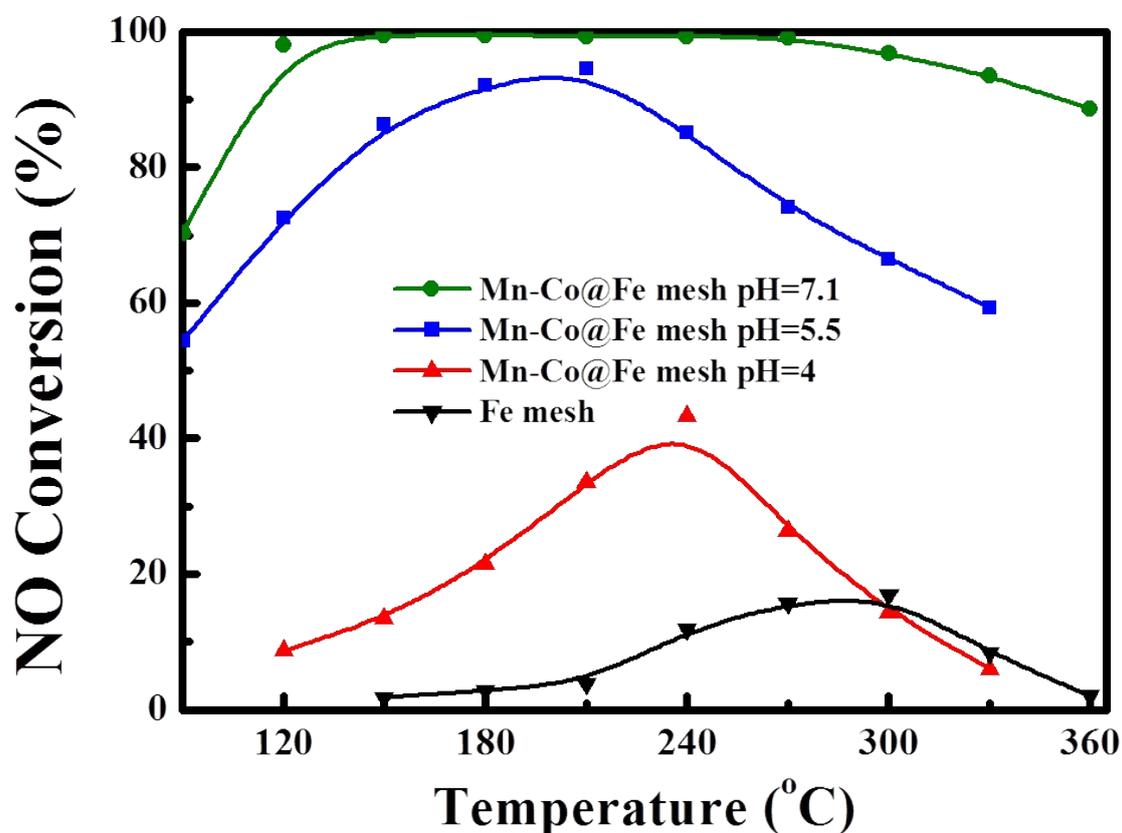


Fig.S2 Plots of NO conversion *versus* temperature for the Mn-Co@Fe mesh catalysts fabricated with different pH value. Reaction conditions: $[\text{NH}_3] = [\text{NO}] = 550$ ppm, $[\text{O}_2] = 5$ vol. %, N_2 as balance gas, GHSV= 10000 h^{-1} .

The catalytic activities of the catalysts fabricated with different pH values and the same calcination routes have been evaluated to determine the influence of the surface structure and composition to the de- NO_x properties (Fig.S2). It have been demonstrated that the Mn-Co oxides are active components and Fe-Co oxides are not quite active in the NH_3 -SCR reaction. Thus, the replacement from block-like Mn-Co oxides to flower-like Fe-Co oxides could result in the loss of surface active sites, thereafter leading to the decrease of de- NO_x activity. Although the Fe mesh coated with flower-like Fe-Co oxides have limited NH_3 -SCR activity, it might have application value in other applications such as photo catalyst or lithium batteries.

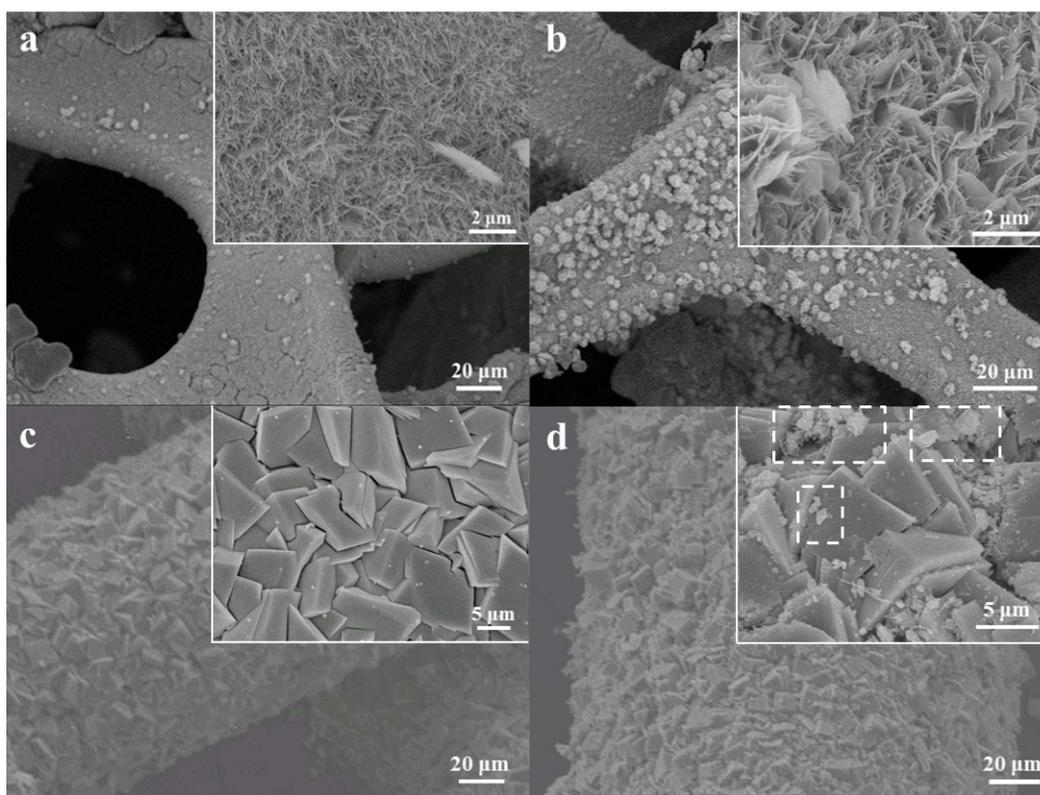


Fig.S3 SEM images of hierarchical Mn-Co hydroxide precursor *in-situ* formed on different metal supports under typical condition (pH=7.1, reaction time=6 h). (a) Ni foam, (b) Cu foam, (c) Fe mesh and (d) Ti mesh.

To confirm the versatility of this method, the fabrication strategy was extended to the Ni foam, Cu foam and Ti mesh. As shown clearly in Fig.S3, after 6h hydrothermal reaction, all of the metal supports were over-coated by Mn-Co precursors. Interestingly, under similar reaction conditions, the morphologies of Mn-Co hydroxides deposited on different metal foams were distinctive (Fig.S3, insets). The Mn-Co precursors located on the Ni foam and Cu foam presented needle-like and flake-like structure. On the other hand, for Ti mesh and Fe mesh, the cube-like Mn-Co hydroxides could be observed. Those differences could be originated from the diverse surface properties of the metal support and disparate growth speed of the Mn-Co precursors. Apparently, the growth rate of Mn-Co hydroxide precursors on the Ti mesh support is higher than that on the Fe mesh, which leads to the excess growth and formation of irregular structure on the cube-like structure (signed with dotted line, Fig.3d, inset). The observation is well consistent with the deduction we made in the growth process on Fe mesh.

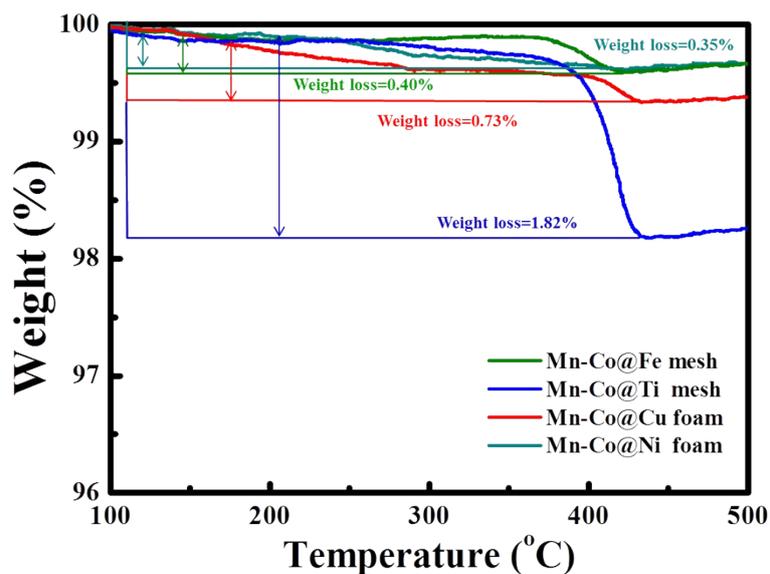


Fig.S4 TGA curves of the monolith samples before the calcination.

Thermogravimetric analyses (TGA, NETZSCH STA 449 F1) was performed to realize the thermal decomposition characteristics of the monolith samples before the calcination. The temperature was increased from 100 °C to 500 °C with a ramping rate of 10 °C/min in N₂ atmosphere. The weight loss during the test period was mainly related to the decomposition of the hydroxides species ($\text{Mn}(\text{OH})_2 \rightarrow \text{MnO} + \text{H}_2\text{O}$, $\text{Co}(\text{OH})_2 \rightarrow \text{CoO} + \text{H}_2\text{O}$), which could reflect the loading amounts of Mn-Co precursors on different monolith supports. Obviously, the highest weight loss can be found in the case of Mn-Co@Ti mesh (1.82%), followed by Mn-Co@Cu foam (0.73%), Mn-Co@Fe mesh (0.40%) and Mn-Co@Ni foam (0.35%). Combined with the XRD and XPS results, the amount of Mn-Co hydroxides loaded on 1 g of different monolith supports should be 0.091 g (Ti mesh), 0.037g (Cu foam), 0.02 g (Fe mesh) and 0.018 g (Ni foam), which implies the precipitation ratio of the Mn-Co precursors during the hydrothermal reaction is about 43.4% (Ti mesh), 17.2% (Cu foam), 9.4% (Fe mesh) and 8.2% (Ni foam). The result indicates that more Mn-Co hydroxides were generated on the Ti wire mesh under the similar reaction conditions. Combined with SEM observation, the disparate growth speed could possibly be a result to the diverse structure formed on different monolith substrate. Meanwhile, the excess growth of the Mn-Co precursor should be responsible for the irregular structures which occurred on Ti mesh supports.

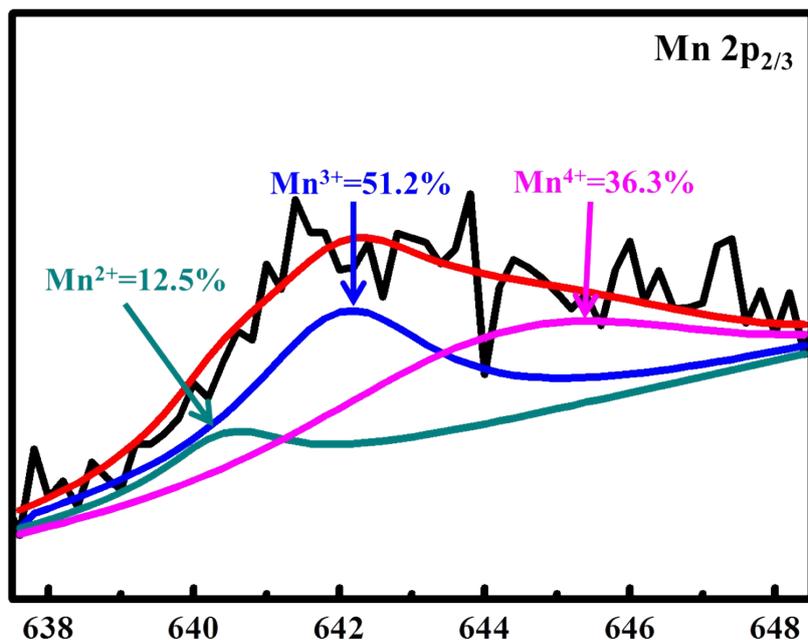


Fig.S5 XPS spectra for Mn 2p_{3/2} of the Mn-Co@Fe mesh catalysts.

The Mn 2p_{3/2} spectra of Mn-Co@Fe mesh was divided into three peaks by peak fitting deconvolutions, while the peak located at 640.5 eV, 642.2 eV and 644.3 eV can be assigned to Mn²⁺, Mn³⁺ and Mn⁴⁺, respectively. The result indicated that the Mn species located on the catalysts surface were composed of Mn⁴⁺ (36.3%), Mn³⁺ (51.2%) and Mn²⁺ (12.5%). Among them, the Mn⁴⁺ species could act as main active components in the de-NO_x process, while the Mn³⁺ species could contribute to the Mn³⁺ ↔ Mn⁴⁺ + e cycle during the catalytic process.

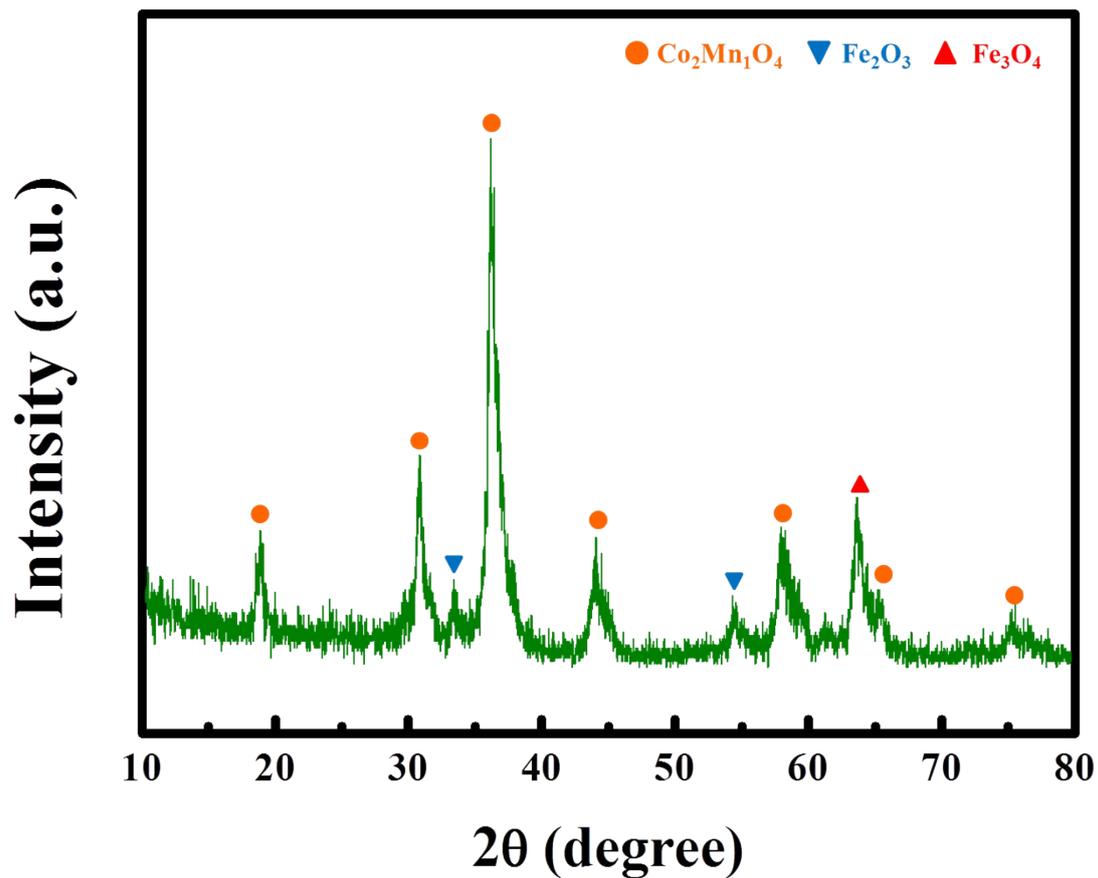


Fig.S6 XRD patterns of the powders scraped from the spent Mn-Co@Fe mesh catalysts.

The spent catalysts were scratched and the obtained powder was used for XRD analysis. The result suggested that the crystal structure of the main active components (Co_2MnO_4) was well retained after the catalytic process. Additionally, no peaks assigned to Mn or Co oxides species could be observed in the XRD patterns. Those results could reflect the stable structure of the Co_2MnO_4 spinel located on the catalysts surface.

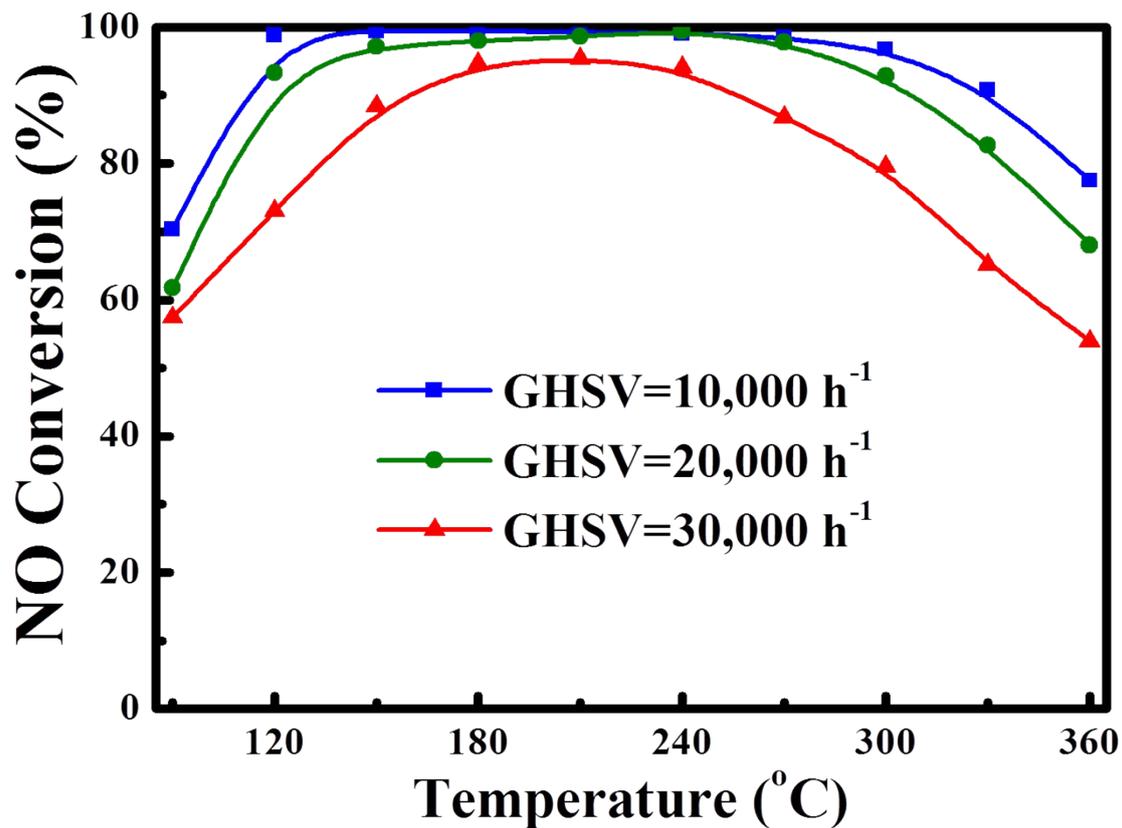


Fig.S7 Plots of NO conversion *versus* temperature for the Mn-Co@Fe mesh catalysts with the different gas hourly space velocity. Reaction conditions: [NH₃] = [NO] = 550 ppm, [O₂] = 5 vol. %, N₂ as balance gas.

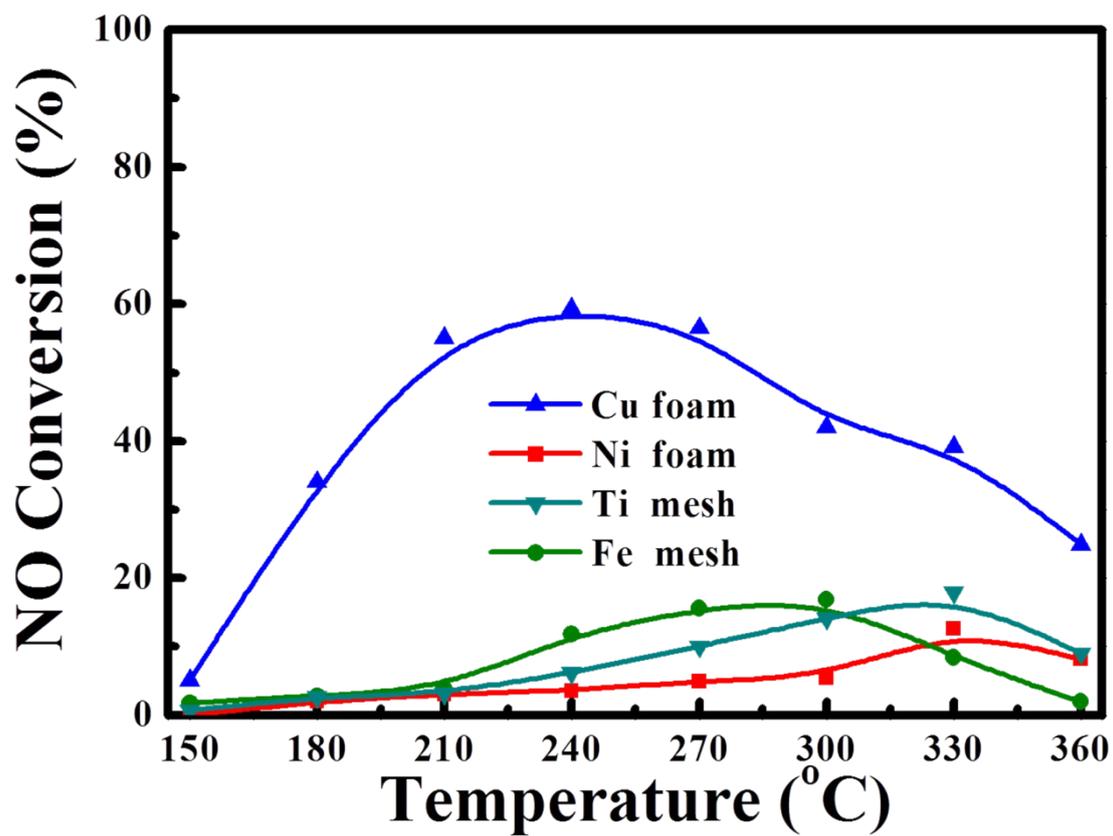


Fig.S8 Plots of NO conversion *versus* temperature for the calcined metal supports. Reaction conditions: $[\text{NH}_3] =$
 $[\text{NO}] = 550 \text{ ppm}$, $[\text{O}_2] = 5 \text{ vol. \%}$, N_2 as balance gas, GHSV= 10000 h^{-1} .

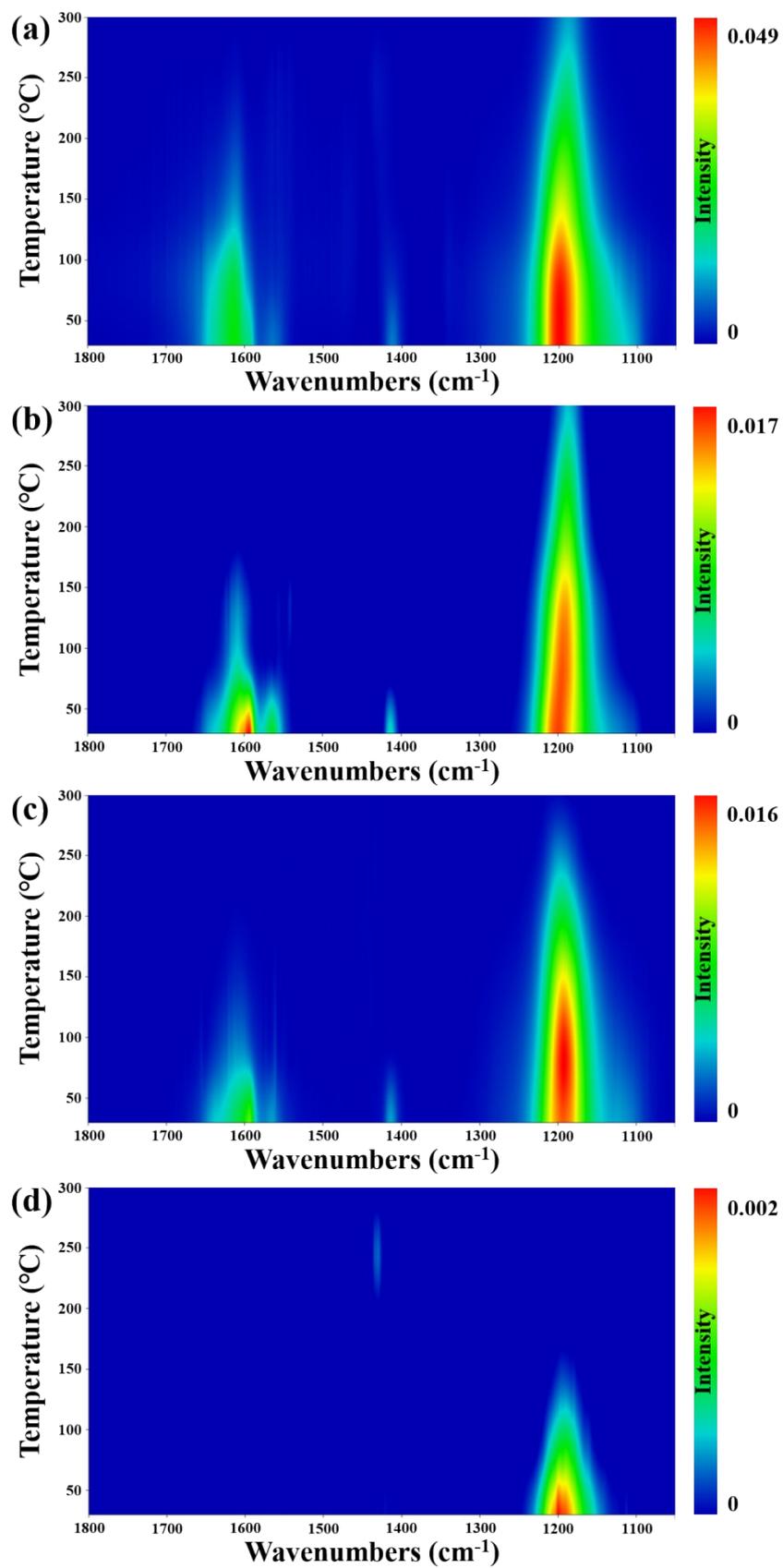


Fig.S9 *In-situ* DRIFT spectra of NH₃ desorption on (a) Mn-Co@Fe mesh, (b) Mn-Co@Ti mesh, (c) Mn-Co@Cu foam and (d) Mn-Co@Ni foam.

To further identify the surface adsorption behaviors, the *in-situ* DRIFTS of NH₃ desorption at different temperatures over all catalysts was implemented and the results are shown in Fig.S10. Obviously, the bands around 1600 cm⁻¹ and 1200 cm⁻¹ were assigned to the asymmetric and symmetric bending vibrations of N-H bond in coordinated NH₃ adsorbed on Lewis acid sites. The bands around 1415 cm⁻¹ were attributed to the symmetric bending vibration of N-H bond in NH₄⁺ species on Brønsted acid sites. It could be seen that almost all the catalysts were covered by Lewis and Brønsted acid sites except for Mn-Co@Ni foam. Besides, the ratio of Lewis acid sites was higher than Brønsted acid sites, indicating that the Lewis acid sites were dominated in all catalysts. Furthermore, with the temperature increased, the intensity of acid sites in Mn-Co@Fe mesh and Mn-Co@Ti mesh decreased more slowly. There were still a small quantity of Lewis acid sites even at 300 °C in Mn-Co@Fe mesh and Mn-Co@Ti mesh while those in Mn-Co@Cu foam and Mn-Co@Ni foam disappeared before 250 °C and 150 °C, respectively. It was well known that the acid sites for NH₃ adsorption played a key role in catalytic reactions and the Lewis acid sites of Mn-Co@Fe mesh and Mn-Co@Ti mesh exhibited great stability in relative high temperature range. Thus, the favorable adsorption performance of the block-like Mn-Co mixed oxides formed on Mn-Co@Fe mesh and Mn-Co@Ti mesh could be one of the reasons for the better catalytic activity.

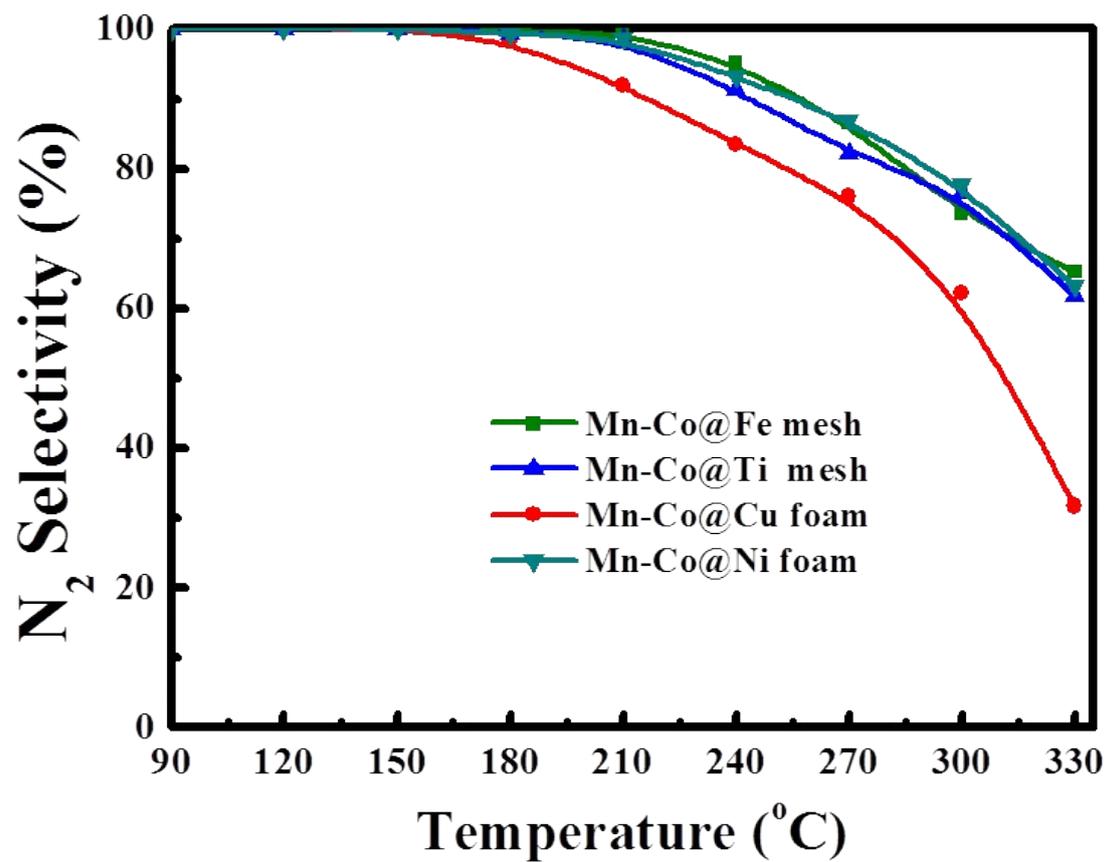


Fig.S10 N₂ selectivity of the catalysts. Reaction conditions: [NH₃] = [NO] = 550 ppm, [O₂] = 5 vol. %, N₂ as balance gas, GHSV= 10000 h⁻¹.

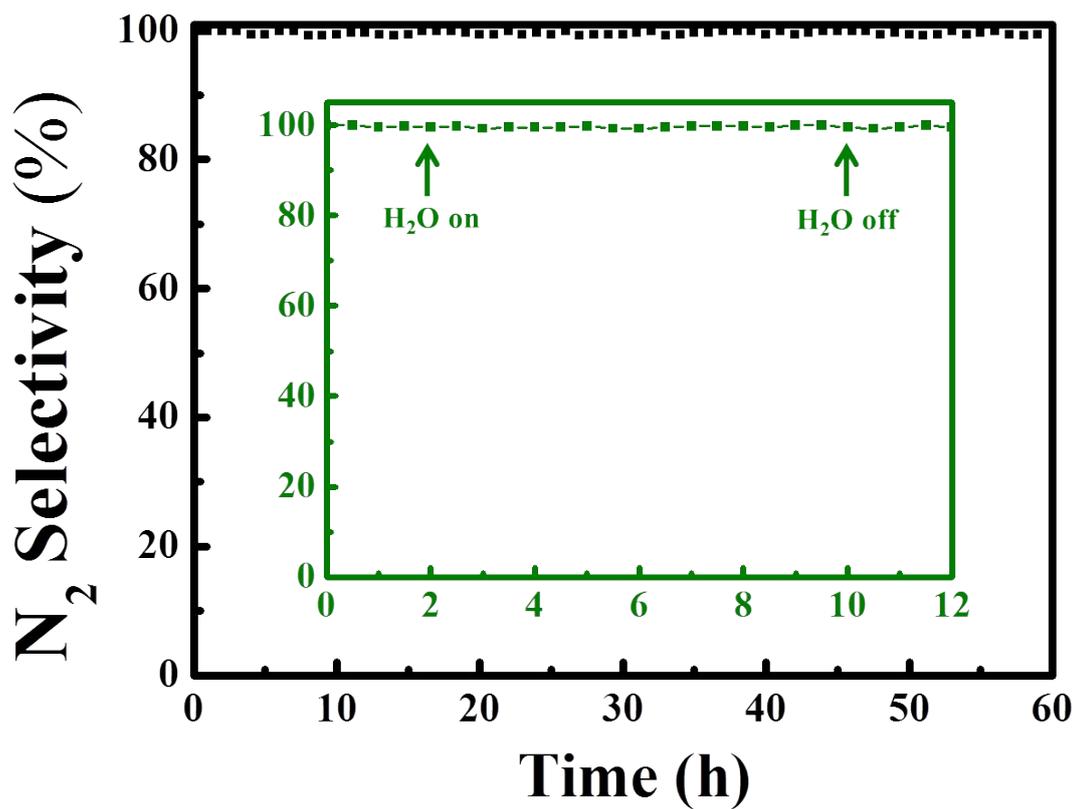


Fig.S11 N₂ selectivity of Mn-Co@Fe catalysts during the stability test and H₂O tolerance test (inset). Reaction conditions: reaction temperature = 210 °C. [NH₃] = [NO] = 550 ppm, [O₂] = 5 vol. %, [H₂O] = 10% (when used), N₂ as balance gas, GHSV= 10000 h⁻¹.

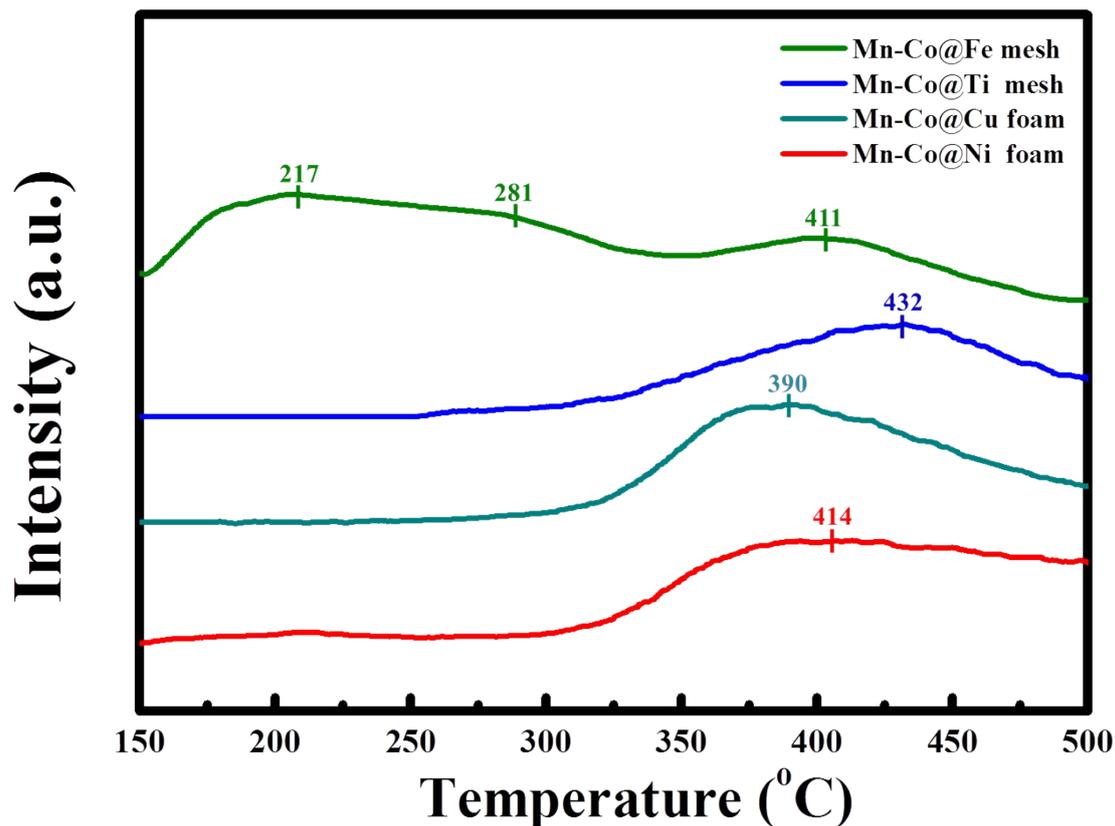


Fig.S12 TPD profiles of the monolith catalysts.

In order to understand the surface acid amount and strength of the monolith catalysts, NH_3 -TPD test were conducted. For Mn-Co@Ti mesh, Mn-Co@Cu foam and Mn-Co@Ni foam catalysts, only one single peak was observed at 432 °C, 390 °C and 414 °C, which could be assigned to the strong acid sites located on catalysts surface. Particularly, three desorption peaks located at 217 °C, 281 °C and 411°C occurred in the TPD profile of Mn-Co@Fe mesh catalysts. The results not only reflect the diverse surface properties of the monolith catalysts, but also indicate the weak and medium acid sites were greatly intensified by the interaction between Mn-Co species and Fe mesh support, which could be beneficial for the catalytic process.

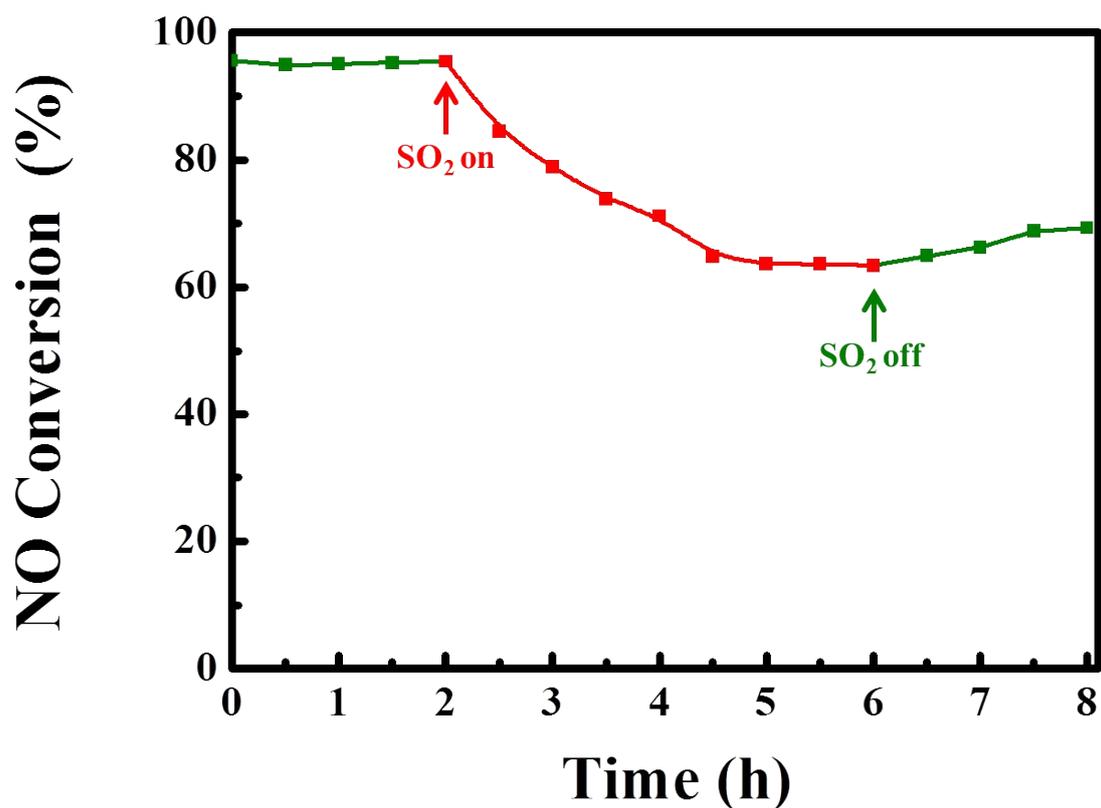


Fig.S13 SO₂ tolerance of Mn-Co@Fe mesh catalysts. Reaction conditions: reaction temperature = 210 °C. [NH₃] = [NO] = 550 ppm, [O₂] = 5 vol. %, [SO₂] = 100 ppm (when used), N₂ as balance gas, GHSV= 10000 h⁻¹.

Fig.S13 depicts the SO₂ tolerance of Mn-Co@Fe mesh catalysts. When 100 ppm of SO₂ was added into the reactant gases, the NO conversion over the catalysts decreased to 63% within 4 hours and then kept stable, indicating the dynamic balance of the generation and decomposition of surface sulfates species. After switching SO₂ off, the catalytic activities started to restore, which could be related to the continuous decomposition of the ammonium sulfate species. However, due to the irreversible sulfating of the surface metal oxides, the NO conversion could not restore to the initial level. Thus, the SO₂-resistant behavior needs to be further improved in the future.

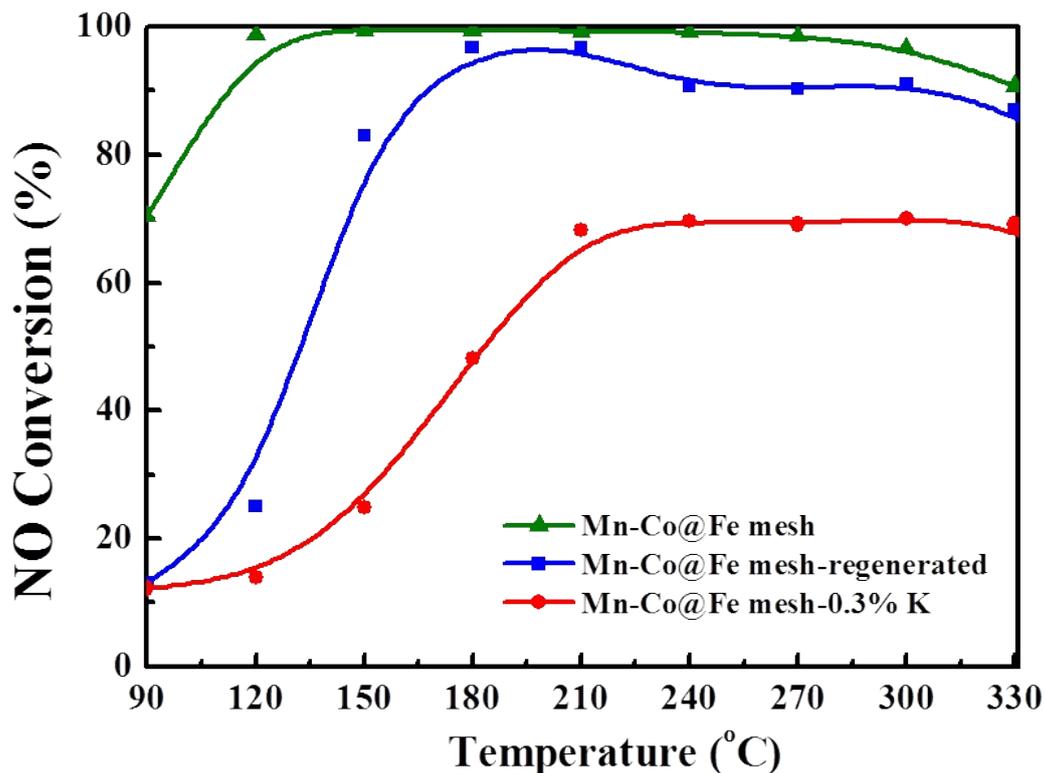


Fig.S14 Alkaline tolerance & Regeneration properties of Mn-Co@Fe mesh catalysts. Reaction conditions: $[\text{NH}_3] = [\text{NO}] = 550 \text{ ppm}$, $[\text{O}_2] = 5 \text{ vol. } \%$, N_2 as balance gas, $\text{GHSV} = 10000 \text{ h}^{-1}$.

The alkaline tolerance of the Mn-Co@Fe mesh catalysts are provided in Fig.S14. As shown clearly, though poisoned by 0.3 wt. % of K, the catalysts can still obtain 69% NO conversion below 210 °C, which is much higher than traditional $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts. It is well documented that the doping of alkali metal could decrease the NH_3 adsorption capacity of the catalysts, thereafter cause the deterioration of SCR performance. From the NH_3 -TPD results (Fig.5b and Fig.S12), the decoration of Mn-Co oxides species could greatly intensify the amount and strength of surface acid sites, which could explain the satisfactory alkali resistance of Mn-Co@Fe mesh catalysts. Moreover, due to the stable spinel structure and strong synergistic effect between the support and active species, the catalysts can be easily regenerated by a water washing method.