Acid leaching on the denitrification efficiency of MnCe@FA catalyst derived from fly ash: Structure, crystal phase and active component interaction

Liguo Chen[a]†, Mutao Xu[a,b]†, Yongzhong Wang[c], Qijie Jin[a]*, Jing Song[d], Changcheng Zhou[d], Jisai Chen[e], Jian Yang[b], Haitao Xu[a,d]*

a School of Environmental Science and Engineering, Nanjing Tech University, Nanjing 210009, PR China

b College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, PR China

c Kelin Environmental Protection Technology Co., Suzhou 215200, PR China

d Nanjing Gekof Institute of Environmental Protection Technology & Equipment Co., Nanjing 210031, PR China

e CSSC Luzhou Environment Protection (Nanjing) Co., Nanjing 211100, PR China

†These authors contributed equally to this work.

*Corresponding authors: Haitao Xu, Qijie Jin

E-mail address: htxu@njtech.edu.cn, qijiejin@njtech.edu.cn

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Text 1. Experimental section

1. Chemicals and Materials

All chemicals are purchased from the market and used directly without treatment. Copper nitrate trihydrate ($Ce(NO_3)_3 \cdot 6H_2O$), manganese acetate tetrahydrate (CH_3COO) $2Mn \cdot 4H_2O$ and hydroxyethyl cellulose were purchased from Shanghai McLean Biochemical Technology Co., Ltd. The water used is deionized water prepared in the laboratory. The fly ash used in the experiment was taken from Taizhou Power Plant.

2. Material characterization methods

The X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (Smartlab TM 3 kW, Rigaku). The scanning speed was 10 °·min^{-1}, and the 2θ scanning range was 10 ° - 85 °. The microstructure and element mapping of the catalyst were studied by scanning electron microscopy (JEOL, JSM-5900). X-ray photoelectron spectroscopy (XPS) images were obtained by AXIS ULTRA DLD instrument (Al-Kα radiation, 1486.6 eV), and the vacuum was maintained at 10-7 Pa. The samples were dried at 100 °C. for 24 h to remove water and then tested. The obtained curves were fitted using XPSPEAK 4.1 software. The NH_3 temperature-programmed desorption (NH_3-TPD) test was performed on CHEMBET-3000 (Quantachrome) to obtain the surface acidity of the catalyst. All catalysts were preheated at 400 °C. for 1 h under helium flow and then cooled to 50 °C. for NH_3 adsorption. NH_3 was then desorbed from 50 °C to 900 °C. at a heating rate of 10 °C·min^{-1}. H_2 temperature programmed reduction (H_2-TPR) was performed using a

semi-automatic Micromeritics TPD/TPR 2900 instrument. All catalysts were preheated at 400 °C for 1 h under argon flow and cooled to 50 °C. Then it was switched to 5 % H_2/Ar and the temperature was increased from 50 °C to 800 °C at a heating rate of 10 °C·min^{-1}. Data are collected over the entire temperature range. TG and DSC data were obtained using a thermogravimetric analyzer (TGA550, America). The heating rate was 10 °C·min^{-1}, the protective atmosphere was air, and the airflow rate was 40 mL·min^{-1}.

In situ diffuse reflectance infrared spectroscopy (in situ DRIFTS) was collected by Nicolet is 50 spectrometer. All catalysts were preheated at 400 °C for 2 h under nitrogen flow, and then cooled to the desired temperature. For NH_3 adsorption and NO + O_2 adsorption, when the temperature is cooled to 200 °C, 1000 ppm NH_3 or 1000 ppm NO + 10 vol. % O_2 is pumped into the system for 30 min. Then the in situ DRIFT spectra were collected with increasing temperature. For the reaction of NH_3 and pre-adsorbed NO + O_2, 1000 ppm NO + 10 vol. % O_2 was pumped into the system for 30 min. After the temperature rises to 400 °C., the flow of NO + O_2 is stopped and N_2 is pumped into the system for 30 min. Then, 1000 ppm NH_3 was pumped into the system and in situ DRIFT spectra were collected with increasing temperature. For the reaction between NO + O_2 and pre-adsorbed NH_3, the gas order is opposite, but the steps are similar to the reaction between NH_3 and pre-adsorbed NO + O_2.

3 Catalyst activity test

The catalyst (1 ml) was added to a fixed-bed quartz reactor (inner diameter 8 mm,

as shown in Fig. S1) to study the NH_3-SCR catalytic activity. The gas flow rate of 500 ml·min^{-1} corresponds to the volume space velocity (GHSV) of 30000 h^{-1}. The reaction gas is composed of 500 ppm NO, 500 ppm NH_3 (when used), 6 vol. % O_2, and the remaining gas is N_2. The NO concentration at the inlet and outlet of the reactor was obtained by a flue gas analyzer (MRU VarioPlus, Germany). The catalytic activity was calculated by Eq. (1).

$$NO\ conversion = \frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}} \times 100\% \quad \text{Eq. (1)}$$

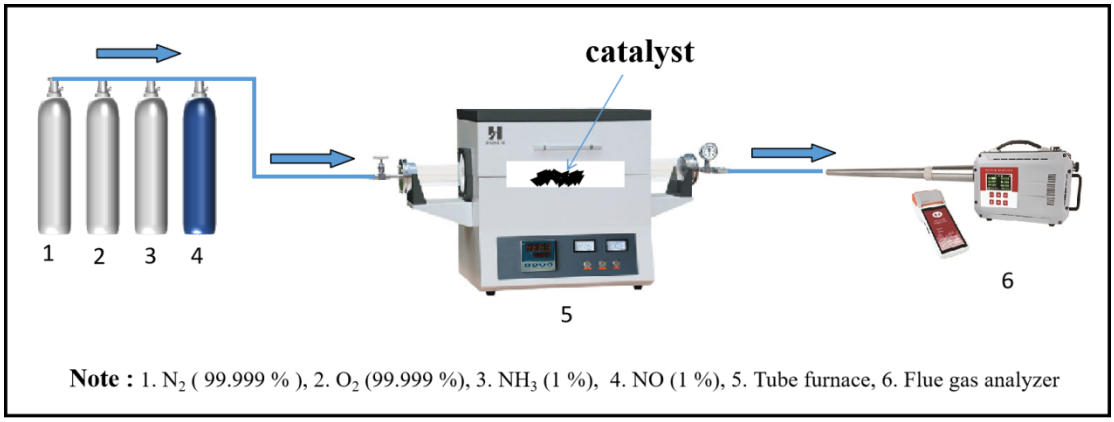


Fig.S1 Catalyst activity evaluation device diagram

Tab. S1 Comparison of the efficiency of transition metal and rare earth metal composite denitrification catalysts

Catalyst	NO_x cnoversion	Temperature	Ref.
$4FeMn_7Ce_3$	98%	150 °C	[1]
Mn-Ce/FA	89.4%	250 °C	[2]
$MnMoVO_x$	100%	250 °C	[3]
$NbFeMnCeO_x$	91%	200 °C	[4]
$Nb_{0.05}Ce_{0.05}MnO_x$	>91%	125-250 °C	[5]
0.1MnCe@FA	87%	250 °C	This work

Tab. S2 Relative element content on the surface of 0.1MC@FA (1)catalyst

Element	wt.%	σ
Ce	42.3	0.6
Mn	28.6	0.5
O	27.9	0.6
Si	0.8	0.1
Al	0.5	0.1
Ti	0.0	0.0

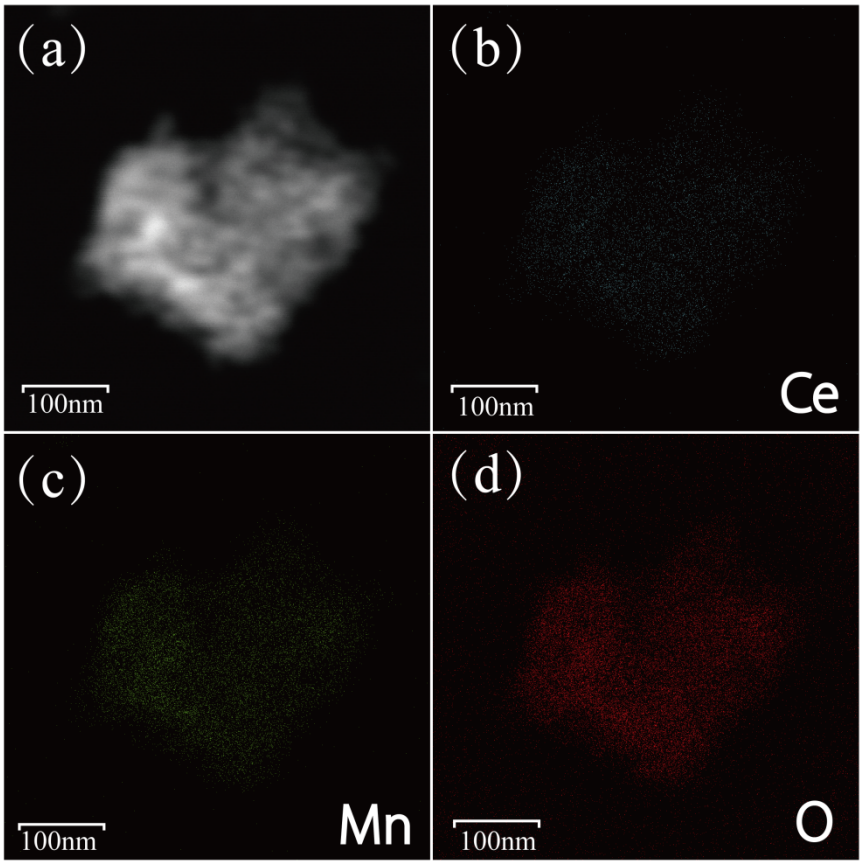
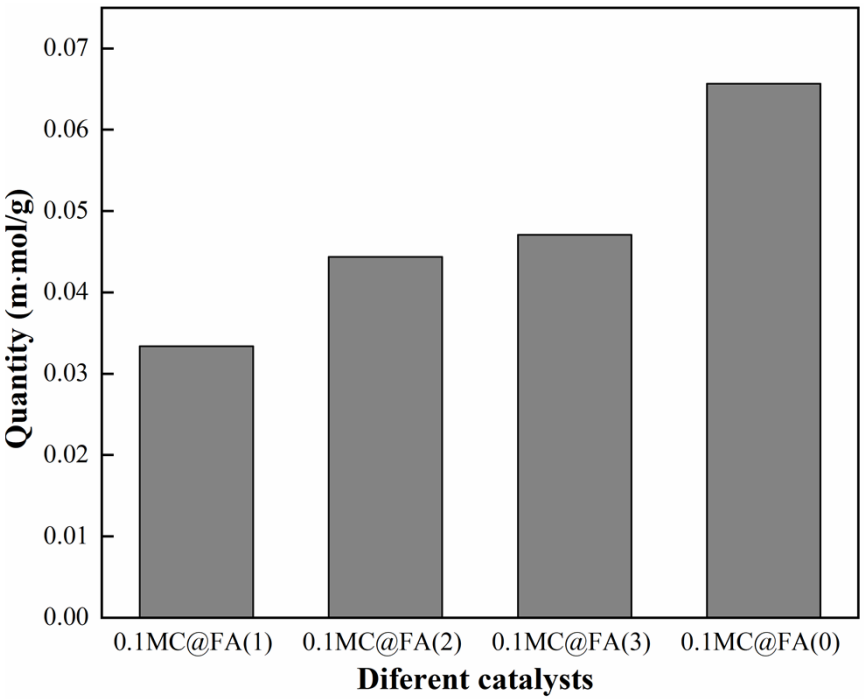


Fig. S2 The elemental mappings of 0.1MC@FA(0) catalysts



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92 Fig.S3 O_2 adsorption capacity of 0.1MC@FA catalyst

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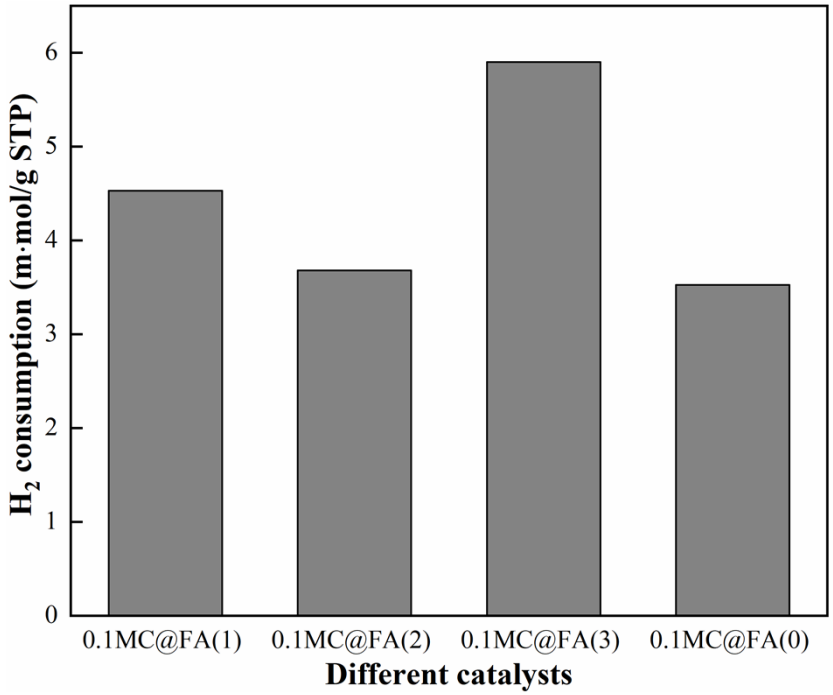

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95 Fig. S4 H_2 consumption of 0.1MC@FA catalyst

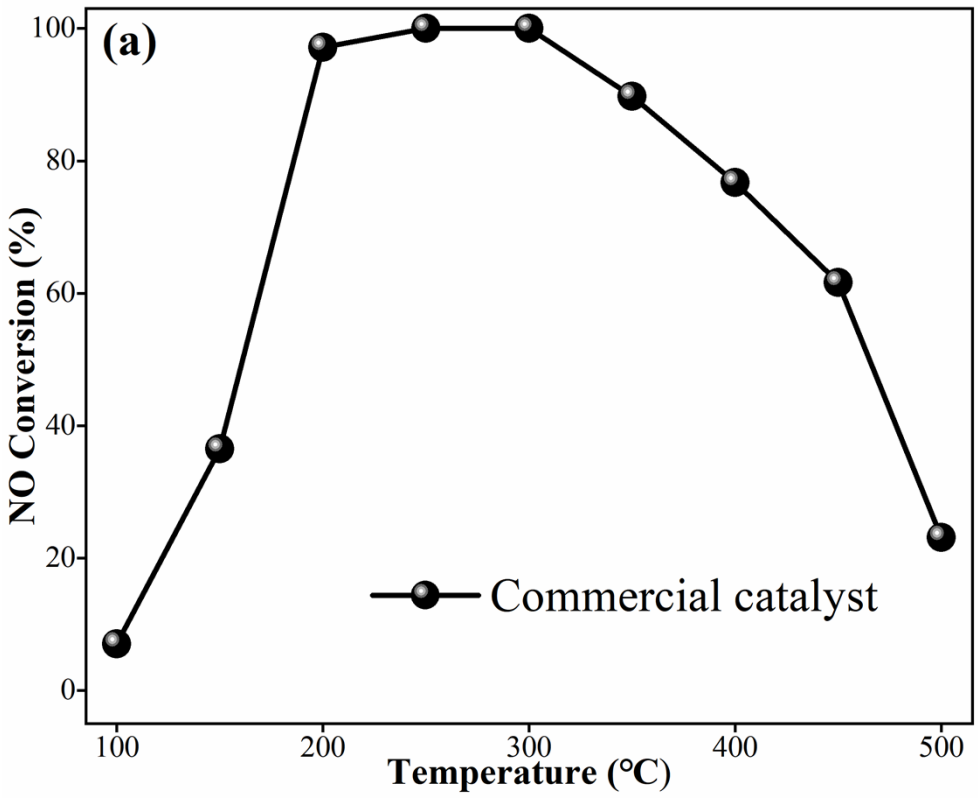

Fig. S5 Denitration efficiency diagram of commercial low temperature denitration catalyst

Reference

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