Supplementary Information

The Highly Efficient Removal of HCN over Cu₆Mn₂/CeO₂ Catalytic Material

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1. Experimental

1.1 Experimental setup

The catalytic materials evaluation device system was shown in Fig. S1. The air purified by four-stage scrubber and HCN with different flow rates were obtained by setting the parameters of the mass flow controller. The water content was adjusted by changing the fraction of air being diverted into the water bubbler placed in a water bath. The HCN flow and air flow was mixed in the mixing chamber, and then the reaction gas consisted of 400 mg/m³ and 5vol.% H₂O was introduced into the catalytic material bed.

![Fig. S1. HCN catalytic reaction flow diagram. 1. Air; 2. Four-stage Scrubber; 3. Mass Flow Controller; 4. Water Vapor Generator; 5. HCN; 6. Mixing Chamber; 7. 3-Way Valve; 8. Asbestos; 9. Quartz Sand; 10. Catalytic Materials; 11. Oil Bath Equipment; 12. Flue Gas Analyzer; 13. Exhaust Absorber.](image)

1.2 Detection and analysis of reacted products

The HCN removal rate and reaction products selectivity were calculated by following equations.

\[ X_{HCN} = \left(1 - \frac{C}{C_0}\right) \times 100\% \]  

S(1)

\[ S_{NH₃} = \frac{C_{NH₃}}{C_0 - C} \times 100\% \]  

S(2)

\[ S_{NO} = \frac{C_{NO}}{C_0 - C} \times 100\% \]  

S(3)
\[ S_{\text{NO}_2} = \frac{C_{\text{NO}_2}}{C_0 - C} \times 100\% \]  

\[ S_{\text{CO}} = \frac{C_{\text{CO}}}{C_0 - C} \times 100\% \]  

\[ S_{\text{CO}_2} = \frac{C_{\text{CO}_2}}{C_0 - C} \times 100\% \]  

\[ S_{\text{CN}} = \frac{C_0 - C - C_{\text{CO}_2} - C_{\text{CO}}}{C_0 - C} \times 100\% \]  

\[ S_{\text{CO}} = \frac{1}{2} \frac{C_0 - C - C_{\text{CN}} - C_{\text{NO}} - C_{\text{NO}_2} - C_{\text{NH}_3}}{C_0 - C} \times 100\% \]

where \( C_0 \) and \( C \) referred to the inlet and outlet concentration of HCN (mg/m³) respectively.

### 1.3 Characterization

The morphology and microstructure of prepared samples were examined by the scanning electron microscope (SEM, XL30s-FEG) and transmission electron microscope (TEM, JEM-2001EM).

The XRD patterns of all samples were collected using Rigaku D/max2000 PCX diffractometer using Cu Kα radiation, in the 20~80° range and with 2°/min scanning speed (\( \lambda = 0.15406 \text{ nm} \), operated at 40 kV and 100 mA).

The X-ray photoelectron spectroscopy (XPS) of the samples were performed using EACALAB 250Xi system with monochromatic Al Kα radiation (hv=1486.6 eV) to analyze the surface properties of obtained sample. The sample charging effect was compensated by calibrating the binding energy with adventitious C1s peak at 284.8 eV.

N\(_2\) physisorption measurements were conducted on a Quantachrome Autosorb-iQ instrument, and the specific surface area, pore volumes and average pore diameters were obtained according to the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) method respectively.

H\(_2\) temperature-programmed reduction (H\(_2\)-TPR) experiments were performed using a multifunction chemisorption analyzer (PX200) in a H\(_2\)-Ar mixture (10 vol% H\(_2\), 40 vol% Ar, 40 mL/min). Before the reduction, 50 mg catalyst was pretreated with N\(_2\) at 300 °C for 1 h, and then cooled to ambient temperature. After that the H\(_2\)-Ar mixture gas was introduced, and the H\(_2\)-TPR profile collected from 100~600 °C at a rate of 10 °C/min.

Fourier-transform infrared spectra (FT-IR) of the samples were recorded on a NEXUS670-FT-IR apparatus over the 4000~400 cm\(^{-1}\) wave-number range. Self-supported wafers of 1.3 cm diameter were prepared by pressing 15 mg sample. The wafers were first treated at 250 °C in a flow of high purity He for 0.5 h and then cooled to room temperature.

NH\(_3\) temperature-programmed desorption (NH\(_3\)-TPD) was performed on the same Tianjin XQ TP5080 auto-
adsorption apparatus. Prior to the experiments, 150 mg samples were pre-treated at 400 °C with He gas for 0.5 h and cooled to room temperature. Then the samples were saturated by 50 mL/min 10 vol.% NH₃ flow at 100 °C for 1 h, followed by N₂ purging for 1 h to remove the absorbed ammonium. Finally, the NH₃-TPD was measured from 100 to 800 °C.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on a DSC 214 Polyma system under flowing air at 100 mL/min and a heating rate of 10 °C/min from 50 to 700 °C.

Inductive coupled plasma optical emission spectroscopy (ICP-OES) were performed on a Pe Avio200 system. Before test, the sample was dissolved in 1 mL HNO₃ and 3 mL HCl solution and then dried at 80 °C. After sieving, the final sample was prepared into 5% acid solution.

2 Results and discussion

2.1 Catalytic activity of CeO₂ loaded with different Cu/Mn ratio

The HCN removal rate over CuₓMnᵧ/CeO₂ samples including Cu₈Mn₂/CeO₂, Cu₆Mn₄/CeO₂, Cu₄Mn₆/CeO₂ and Cu₂Mn₈/CeO₂ were displayed in Fig. S2. Besides, the catalytic activity of CuO/CeO₂ and MnOₓ/CeO₂ were also studied. As presented in Fig. S2, the catalytic activity of the prepared samples at the whole reaction temperature followed this order: Cu₈Mn₂/CeO₂ > Cu₆Mn₄/CeO₂ > Cu₄Mn₆/CeO₂ > CuO/CeO₂ > Cu₂Mn₈/CeO₂ > MnOₓ/CeO₂. It could be concluded the CuO phase played an important role in the HCN catalytic removal. When MnOₓ species were introduced into the CuO/CeO₂, all samples except Cu₂Mn₈/CeO₂ exhibited enhanced catalytic removal ability toward HCN. The lower catalytic activity of Cu₂Mn₈/CeO₂ was attributed to the low CuO loading. According to the experimental results, the optimal Cu/Mn mass ratio was 8/2.

![Fig. S2 The HCN removal rate over CeO₂ loaded with different Cu/Mn mass ratio. Reaction condition: 120000 h⁻¹, 5 vol.% H₂O.](image)

2.2 Catalytic activity of CeO₂ loaded with different bimetal oxides

| Catalysts              | HCN concentration | GHSV/h⁻¹ | T₁₀₀%, °C | References |
|------------------------|-------------------|----------|-----------|------------|
| TiO₂                   | 50 ppm            | 52 000   | 350       | 1          |
| AC–Cu–CoSPc–Ce         | 100 ppm           | 32 000   | 200       | 2          |
| Cu-Mn-O                | 160 ppm           | 25 000   | 120       | 3          |
| La₂Cuₓ/TiO₂            | 200 ppm           | 32 000   | 150       | 4          |
2.2 Thermal stability of Cu₈Mn₂/CeO₂

To investigate the thermal stability of Cu₈Mn₂/CeO₂ for HCN removal, the Cu₈Mn₂/CeO₂ samples were firstly pretreated at corresponding temperature (200 °C, 400 °C and 600 °C) for 2 h in the muffle furnace, and then tested for the HCN removal in the fixed-bed reactor. As shown in Fig. S3, it could be observed the catalytic activity of Cu₈Mn₂/CeO₂ was not influenced when pretreated temperature varied. The TG-DCS analysis were shown in Fig. S4. It could be observed the Cu₈Mn₂/CeO₂ had negligible weight loss between 50~700 °C in the TGA curve, indicating the samples exhibited excellent thermal stability. The peak at around 500 °C in the DSC curve might be attributed to the oxidation Cu(NO₃)₂ to CuO, however, it had no effect on the activity of the Cu₈Mn₂/CeO₂.

![Fig. S3](image3.png)

**Fig. S3** The HCN removal rate over Cu₈Mn₂/CeO₂ pretreated at different temperature.

Reaction condition: 120000 h⁻¹, 5 vol.% H₂O, 120 °C.

|          | H-ZSM-5 | Cu-ZSM-5 | Cu₈Mn₂/ CeO₂ |
|----------|---------|----------|--------------|
| ppm      | 50      | 52 000   | 500          |
| ppm      | 1200    | 20 000   | 350          |
| mg/m³    |         | 120 000  | 90           |

Present work

2.3 Stability of the Cu₈Mn₂/CeO₂ in multiple cycles

To evaluate the behavior of Cu₈Mn₂/CeO₂ under recycling in consecutive catalytic runs, the samples were regenerated after calcinated at 450 °C for 4 h. As shown in Fig. S5, the catalytic activity of Cu₈Mn₂/CeO₂ decreased
slightly as recycling runs increased. The Cu₈Mn₂/CeO₂ could still achieve nearly 90% HCN removal rate even after 4 runs.

![HCN Removal rate](image)

**Fig. S5** The HCN removal rate over Cu₈Mn₂/CeO₂ at different repeated used times.

Reaction condition: 120000 h⁻¹, 5 vol.% H₂O, 120 °C.

### 2.4 Analysis of HCN reaction products over Cu₈Mn₂/CeO₂

Then reaction products concentration of HCN over Cu₈Mn₂/CeO₂ was listed in Table S1.

#### Table S2 The balance data of C and N elements

| Temperature/°C | CO  | CO₂ | NH₃ | NO  | NO₂ | CN⁻ | N₂  | HCN_inlet | HCN_outlet |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----------|------------|
| 30            | 3   | 35  | 3.5 | 0   | 0   | 254 | 17.3 | 400       | 108        |
| 60            | 7.6 | 209 | 19.4| 4.3 | 0   | 143.4| 96.5| 400       | 40         |
| 90            | 0   | 356 | 34.8| 15.2| 5.6 | 44  | 150.2| 400       | 0          |
| 120           | 0   | 400 | 47.2| 16.4| 19.2| 0   | 158.6| 400       | 0          |
| 150           | 0   | 400 | 59.6| 0   | 8.4 | 0   | 166  | 400       | 0          |

### 2.5 Breakthrough behaviors of HCN over Cu₈Mn₂/CeO₂

Fig. S6 showed the breakthrough behaviors of HCN over Cu₈Mn₂/CeO₂ samples at the temperature region of 0–30 °C. It could be observed the breakthrough time (C/C₀ was below 0.1) of HCN over Cu₈Mn₂/CeO₂ decreased as temperature increased. When the temperature was below 10 °C, the breakthrough curve changed not obviously. However, with temperature increased further, the breakthrough curve became steeper and the breakthrough time got shorter. In our previous studies, the breakthrough time of HCN over CuO/CeO₂ increased as temperature increased from 15 °C to 30 °C. The different results between CuO/CeO₂ and Cu₈Mn₂/CeO₂ could be attributed to the following reason: the HCN concentration in our previous studies was 136 mg/m³, much lower than the HCN (400 mg/m³) used in this experiment, as temperature increased, the number of activated HCN increased further and accelerated the saturation of activated sites of Cu₈Mn₂/CeO₂, leading the breakthrough time becoming shorter. While the HCN concentration was 136 mg/m³, the saturation rate of activated sites was much slower, in addition, the catalytic activity of CuO/CeO₂ also promoted the conversion of CN⁻, which leading the breakthrough time of HCN increased as temperature increasing.
**Fig. S6** The HCN removal rate over CeO$_2$, CuO/CeO$_2$, MnO$_x$/CeO$_2$ and Cu$_8$Mn$_2$/CeO$_2$ samples.

**Table S3** The parameters of Yoon and Nelson model for HCN adsorption on Cu$_8$Mn$_2$/CeO$_2$

| Temperature/°C | $k$/min$^{-1}$ | $r$/min$^{-1}$ | $R^2$ |
|----------------|---------------|--------------|--------|
| 10             | -0.0354       | 157          | 0.999  |
| 20             | -0.04845      | 104.3        | 0.994  |
| 30             | -0.06194      | 93.8         | 0.981  |

2.6 SEM analysis of the CeO$_2$ loaded with different bimetal oxides

The SEM images for Cu$_8$Zn$_2$/CeO$_2$, Cu$_8$Ni$_2$/CeO$_2$, Cu$_8$Co$_2$/CeO$_2$, Cu$_8$Fe$_2$/CeO$_2$ and Cu$_8$Ag$_2$/CeO$_2$ were shown in Fig. S7. It could be observed all samples exhibited monodisperse spherical particles and the porous structure of CeO$_2$ was covered by the metal oxides. The EDS analysis was conducted to investigate the actual loading of metal oxides on CeO$_2$ support, which was shown in Fig. S8.

**Fig. S7** The SEM images of CeO$_2$ loaded with different bimetal oxides, (1) (6) Cu$_8$Zn$_2$/CeO$_2$; (2) (7) Cu$_8$Ni$_2$/CeO$_2$; (3) (8) Cu$_8$Co$_2$/CeO$_2$; (4) (9) Cu$_8$Fe$_2$/CeO$_2$; (5) (10) Cu$_8$Ag$_2$/CeO$_2$. 
The EDS analysis of CeO$_2$ loaded with different bimetal oxides (1) Cu$_8$Mn$_2$/CeO$_2$; (2) Cu$_8$Zn$_2$/CeO$_2$; (3) Cu$_8$Ni$_2$/CeO$_2$; (4) Cu$_8$Co$_2$/CeO$_2$; (5) Cu$_8$Fe$_2$/CeO$_2$; (6) Cu$_8$Ag$_2$/CeO$_2$.

2.7 XRD analysis

The XRD patterns of CeO$_2$, CuO/CeO$_2$ and MnO$_x$/CeO$_2$ were shown in Fig. S9. For CuO/CeO$_2$, the two obvious characteristic diffraction peaks of CuO at 35.4° and 38.7° belonged to the (002), (311) crystal planes. It could be observed a diffraction peak at 37.3° in the MnO$_x$/CeO$_2$, which was attributed to the Mn$_2$O$_3$.

Fig. S9 The XRD patterns of CeO$_2$, CuO/CeO$_2$, MnO$_x$/CeO$_2$ and Cu$_8$Mn$_2$/CeO$_2$ samples.

2.8 H$_2$-TPR

Table S4 Temperature of peaks position and quantitative analysis of H$_2$ consumption

| Samples         | Peak temperature/°C | H$_2$ consumption/(cm$^3$/g) |
|-----------------|----------------------|------------------------------|
|                 | I       | II      | III     | V       |                 |
| CuO/CeO$_2$     | 158     | 181     | 212     |         | 27.67            |
| Cu$_8$Mn$_2$/CeO$_2$ | 164     | 183     | 228     | 274     | 32.95            |

2.9 NH$_3$-TPD
**Table S5** The quantitative analysis of desorbed NH$_3$ at corresponding temperature region.

| Samples            | Region and NH$_3$ desorption (100%) |
|--------------------|-------------------------------------|
|                    | 100–200 °C | 200–500 °C | Above 500 °C |
| CeO$_2$            | 46         | 14         | 40           |
| CuO/CeO$_2$        | 35         | 65         | —            |
| MnO$_x$/CeO$_2$    | 1          | 41         | 58           |
| Cu$_8$Mn$_2$/CeO$_2$ | 48         | 16         | 38           |

**2.10 XRD and ICP analysis**

The XRD and ICP analysis were also conducted to further investigate the performance of Cu$_8$Mn$_2$/CeO$_2$ in the reaction system. Fig. S10 displayed the XRD spectra of Cu$_8$Mn$_2$/CeO$_2$ before and after reaction. It could be observed the diffraction peaks corresponding to CeO$_2$ were not influenced and the CuO and MnO$_x$’s peak still could not be founded, which indicating the CuO and MnO$_x$ always had high dispersion on the CeO$_2$ support. After reacted with HCN, the content of Cu, Mn changed little according to the XRD results, indicating the Cu$_8$Mn$_2$/CeO$_2$ exhibited high stability in the reaction system.

![XRD spectra of fresh and used Cu$_8$Mn$_2$/CeO$_2$](image)

**Fig. S10** The XRD patterns of fresh and used Cu$_8$Mn$_2$/CeO$_2$, the used Cu$_8$Mn$_2$/CeO$_2$ referred to samples reacted at 120 °C.

**Table S6** The ICP analysis of fresh and used Cu$_8$Mn$_2$/CeO$_2$

| Samples | Cu$_8$Mn$_2$/CeO$_2$ Cu/wt.% | Mn wt.% |
|---------|-----------------------------|---------|
| Fresh   | 7.81                        | 7.69    |
| used$^a$| 2.1                         | 2.05    |

$^a$Cu$_8$Mn$_2$/CeO$_2$ reacted at 120 °C
Fig. S11 The schematical diagram of the HCN reaction mechanism over Cu₈Mn₂/CeO₂.

Reference

1. O. KROCHER and M. ELSENER, Hydrolysis and oxidation of gaseous HCN over heterogeneous catalysts, Appl. Catal. B., 2009, 92, 75-89.

2. L.L. Wang, X.Q. Wang and X.L. Jing, Efficient removal of HCN through catalytic hydrolysis and oxidation on Cu/CoSpc/Ce metal-modified activated carbon under low oxygen conditions, RSC Advances., 2016, 6, 113834-113843.

3. Y.J. Li, H. Yang, Y.C. Zhang, J. Hu, J.H. Huang, P. Ning and S.L. Tian, Catalytic decomposition of HCN on copper manganese oxide at low temperatures: Performance and mechanism, Chem. Eng. J., 2018, 346, 621-629.

4. Q. Wang, X. Wang, L. Wang, Y.N. Hu, P. Ning, Y. X. Ma and L. M. Tan, Catalytic oxidation and hydrolysis of HCN over LaₓCuᵧ/TiO₂ catalysts at low temperatures, Microporous. Mesoporous. Mater., 2019, 282, 260-268.

5. N. Liu, X.N. Yuan, B.H. Chen, Y.X. Li and R.D. Zhang, Selective catalytic combustion of hydrogen cyanide over metal modified zeolite catalysts: From experiment to theory, Catal. Today., 2017, 297, 201-210.

6. Z.H. Yi, J. Sun, J.G. Li, T. Zhou, S P. Wei, H.J. Xie and Y.L. Yang, High efficient removal of HCN over porous CuO/CeO₂ micro-nano spheres at lower temperature range, Chin. J. Chem. Eng., 2020, Doi: 10.1016/j.cjche.2020.08.029.

7. D. Gamarra, G. Munuera, A.B. Hungría, M.J. Fernández-Garcia, C. Conesa and P.A. Midgley, Structure-activity relationship in nano-structured copper-ceria based preferential CO oxidation catalysts, J. Phys. Chem. C., 2007, 111, 11026-11038.

8. Z. Wang, G.L. Shen, J.Q. Li, H.D. Liu, Q. Wang and Y.F. Chen, Catalytic removal of benzene over CeO₂-MnOₓ composite oxides prepared by hydrothermal method, Appl. Catal. B., 2013, 138, 253-259.

9. X.F. Tang, Y.G. Li, X.M. Huang, Y.D. Xu, H.Q. Zhu, J.G. Wang and W.J. Shen, MnOₓ-CeO₂ mixed oxide catalysts for complete oxidation of formaldehyde: Effect of preparation method and calcination temperature, Appl. Catal. B., 2006, 62, 265-273.