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# The highly efficient removal of HCN over $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$ catalytic material†

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In this work, porous  $\text{CeO}_2$  flower-like spheres loaded with bimetal oxides were prepared to achieve effective removal of HCN in the lower temperature region of 30–150 °C. Among all samples, the  $\text{CeO}_2$  loaded with copper and manganese oxides at the mass ratio of 8/2 ( $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$ ) exhibited the highest catalytic activity: the HCN removal rate was nearly 100% at 90 °C at the conditions of 120 000  $\text{h}^{-1}$  and 5 vol%  $\text{H}_2\text{O}$ , the catalytic activity of which was higher than for other reported catalysts. The introduction of  $\text{MnO}_x$  could improve the dispersion of  $\text{CuO}$  particles and increase the total acid sites of the prepared samples. It was proved that the synergy between  $\text{CuO}$  and  $\text{MnO}_x$ , the chemisorption oxygen, the oxygen vacancies, the  $\text{Cu}^{2+}$  and  $\text{Mn}^{4+}$  all played an important role in determining the good catalytic activity of the prepared samples.  $\text{NH}_3$ -TPD analysis indicated the introduction of  $\text{MnO}_x$  promoted the conversion of  $\text{NH}_3$  and  $\text{N}_2$  selectivity by increasing the acid sites of the sample. According to the C, N balance data and FT-IR results, when the temperature was below 30 °C, the removal of HCN over  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  was mainly by chemisorption and the HCN breakthrough behaviors corresponded to the Yoon and Nelson's model. When temperature was above 120 °C, the HCN was totally removed by catalytic hydrolysis and catalytic oxidation.

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## 1 Introduction

Hydrogen cyanide (HCN) is a kind of highly toxic and volatile compound, with a boiling point of 26 °C, which is widely used in the laboratory and chemical industry.<sup>1</sup> HCN could inhibit the enzyme cytochrome oxidase, and interfere with aerobic respiration at cellular level, which poses a threat to human health.<sup>2</sup> Significantly, as the precursor of nitrogen oxides such as  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{N}_2\text{O}$ , HCN could also lead to the greenhouse effect and generation of photochemical fumes.<sup>3</sup> In addition to laboratory synthesis, there is a fair chance to produce HCN including the processing of cyanide-containing chemicals,<sup>4</sup> processing tail gas of calcium and yellow phosphorus,<sup>5</sup> fossil fuels and biomass combustion,<sup>6</sup> selective catalytic reduction of  $\text{NO}_x$  as well as the well-established three-way-catalyst process.<sup>7</sup> To relieve or reduce the negative effect on both the human body and the environment caused by HCN, it is essential to develop highly efficient dicyanide methods. Based on the above discussion, the removal of HCN has been paid more and more attention and the treatment of HCN has important prospects.

Diverse strategies have been reported to remove HCN from gas which involves absorption, adsorption, combustion, catalytic hydrolysis and catalytic oxidation.<sup>8</sup>

Liu *et al.*<sup>9</sup> studied the catalytic combustion of HCN over ZSM-5 catalysts loaded with Cu, Co, Fe, Mn, Ni species. Among all samples, Cu-ZSM-5 exhibited excellent HCN conversion activity ( $T_{90} = 350$  °C) and high  $\text{N}_2$  yield (>95%). Nickolov *et al.*<sup>10</sup> reported the adsorption characteristics of modified activate carbons (AC) toward HCN. When loaded with Cu (5.6 wt%), Zn (5.24 wt%), Ag (0.61 wt%), the AC material (VSZC) showed enhanced HCN removal ability, which was proved to be comparable with the standard ASC Whetlerite carbon. The Zn phase deposited near the external surface of the sample was consumed first to reduce the production of cyanogen. It has also been proved that the addition of negligible amount of  $\text{Cr}^{6+}$  (3.5 times lower than that in ASC Whetlerite carbon) could enhance the conversion of cyanogen. Hudson *et al.*<sup>11</sup> synthesized an SBA-15 material modified with the BBOP and equilibrated with copper (ii) nitrate. Owing to the greater accessibility of the functional groups, the doddered nature of the interconnected porous network and large mesopores, The SBA-15 material showed an improved breakthrough time for HCN (36 min) which was closed to the reference AC adsorbents. Ma *et al.*<sup>12</sup> investigated the Nb/La- $\text{TiO}_x$  catalyst's activity for the hydrolysis of HCN, the conversion of HCN over which could reach 100% accompanied with more than 90%  $\text{NH}_3$  selectivity. They proposed following mechanism of HCN hydrolysis over Nb/La- $\text{TiO}_x$  catalyst: HCN was first converted to

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intermediated  $\text{CHONH}_2$  under the function of catalyst, subsequently, the  $\text{CHONH}_2$  was continually hydrolyzed to  $\text{NH}_4^+$  and  $\text{HCOOH}$  with the participation of acid sites of the catalyst. Finally, the  $\text{NH}_4^+$  was converted into  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , and simultaneous  $\text{HCOOH}$  was decomposed to  $\text{CO}$  and  $\text{H}_2\text{O}$  or  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Hu<sup>13</sup> reported the metal oxides (Fe, Cu) modified HZSM-5 catalysts synthesized by incipient wetness method showed improved performance toward HCN removal (100% conversion of HCN and 80% selectivity of  $\text{N}_2$ ), the high catalytic activity of which could be attributed to the highly dispersed iron and copper composites on the surface of the catalyst support, the excellent redox ability and regulated acid properties. Wang *et al.*<sup>14</sup> carried out a detail investigation on coupling catalytic hydrolysis and oxidation of HCN over a serious  $\text{MnO}_x/\text{TiO}_2\text{-Al}_2\text{O}_3$  prepared *via* sol-gel method. 15 wt%  $\text{MnO}_x/\text{TiO}_2\text{-Al}_2\text{O}_3$  showed the best performance on HCN oxidation, and nearly 100% HCN conversion and 70%  $\text{N}_2$  yield were obtained at 200 °C.

From these above statements, it could be observed the catalytic hydrolysis and oxidation based on these catalysts require relatively higher temperature (>200 °C) to achieve deep purification of HCN, which might cost a lot of energy. Adsorbent materials showed excellent removal efficiency toward HCN at room temperature while the incomplete conversion of HCN and the secondary pollution caused by the desorption products limit the further application of this method. Therefore, it is necessary to develop novel catalytic materials to obtain high HCN removal rate at lower temperature range (30–150 °C).

$\text{CeO}_2$  has been widely used in various fields including low-temperature water-gas shift reaction, fuel cells, phosphors, catalysts, cocatalysts, catalyst supports as well as hydrogen storage materials due to the high oxygen storage/release capacity (OSC) and high oxygen mobility arising from facile redox cycle between  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$ .<sup>15,16</sup> In recent reports,  $\text{CeO}_2$  materials with different structure and morphologies has been prepared and evidenced to exhibit unique properties differing from common  $\text{CeO}_2$ .<sup>17,18</sup> The porous  $\text{CeO}_2$  flowerlike sphere has attracted lots of interest for its larger pore volume, higher surface area and marked hydrothermal stability when used as supports.<sup>19,20</sup> Tan *et al.*<sup>21</sup> conducted the oxidation of styrene on the porous  $\text{CeO}_2$  flowerlike sphere loaded with  $\text{CuO}$ ,  $\text{La}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , and found the  $\text{CuO}/\text{CeO}_2$  showed the highest activity. Sun *et al.*<sup>22</sup> examined the catalytic activities and hydrothermal stability of  $\text{Cu}/\text{CeO}_2$  for ethanol stream reforming. At 300 °C, the  $\text{H}_2$  selectivity could reach 74.9% while the  $\text{CO}$  was below the detection line.

In this work, the porous  $\text{CeO}_2$  flowerlike spheres modified with a series of bimetallic oxides ( $\text{Cu-Ag}$ ,  $\text{Cu-Mn}$ ,  $\text{Cu-Zn}$ ,  $\text{Cu-Ni}$ ,  $\text{Cu-Co}$ ,  $\text{Cu-Fe}$ ) were prepared and their catalytic activity for HCN removal were evaluated under lower temperature region (30–150 °C). The reaction kinetics and the mechanism of HCN removal over the synthesized samples were analyzed.

## 2 Experimental

### 2.1 Catalytic materials preparation

**2.1.1 Porous  $\text{CeO}_2$  flowerlike spheres preparation.** The synthesis of porous  $\text{CeO}_2$  flowerlike spheres was according to our previous method, which were reported in the literature.<sup>22</sup>

**2.1.2 Catalytic materials preparation.**  $\text{CeO}_2$  loaded with copper and manganese oxides were prepared by precipitation method. The  $\text{CeO}_2$  sample was dissolved into deionized water with magnetic stirring, followed by the addition of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  at the mass ratio of 8 : 2. The total content of Cu and Mn oxides always accounted for 10 wt% of the  $\text{CeO}_2$  support. Then the  $\text{Na}_2\text{CO}_3$  solution ( $0.5 \text{ mol L}^{-1}$ ) was added at the speed of 1 drop/s until the pH value of the solution reached 9. After being stirred for 4 h, the suspension and precipitate were separated by centrifugation and the precipitate was washed with deionized water and ethanol for three times respectively. Finally, the samples donated as  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  were obtained after undergoing such steps: calcination, grinding, pelletizing and sieving. The total metal mass percentage was calculated by the equation  $(M/(M + \text{CeO}_2))$ ,  $M = \text{Cu, Mn}$ , in which wt% means the mass percentage. The  $\text{Cu}_8\text{Ag}_2/\text{CeO}_2$ ,  $\text{Cu}_8\text{Ni}_2/\text{CeO}_2$ ,  $\text{Cu}_8\text{Co}_2/\text{CeO}_2$ ,  $\text{Cu}_8\text{Zn}_2/\text{CeO}_2$  and  $\text{Cu}_8\text{Fe}_2/\text{CeO}_2$  samples were also prepared by the same method by changing the nitrate solution of metal species.

### 2.2 Experimental setup

The catalytic activity test of the prepared samples was evaluated in a fixed-bed reactor, and the reaction scheme was shown in Fig. S1.† The prepared sample (0.25 g) was placed in a quartz tube (with an inner diameter of 5 mm) for each reaction. The mixed gases containing  $400 \text{ mg m}^{-3}$  HCN and 5 vol%  $\text{H}_2\text{O}$  were introduced into the fixed-bed quartz tubular reactor at a total flow rate of  $400 \text{ mL min}^{-1}$  ( $\text{GHSV} = 120\,000 \text{ h}^{-1}$ ). The exhaust gas from the sample bed was first analyzed (as described below) and then absorbed and discharged.

### 2.3 Detection and analysis of reacted products

The outlet gas from the sample bed was first analyzed and then absorbed by the  $\text{NaOH}$  solution ( $1 \text{ mol L}^{-1}$ ). The HCN and  $\text{NH}_3$  were determined by iso-nicotinic-acid-3-methyl-1-phenyl-5-pyrazolone spectrophotometric method and sodium hypochlorite-salicylic acid spectrophotometric method respectively, the detection limits of which were  $0.005 \text{ mg L}^{-1}$  and  $0.0025 \text{ mg L}^{-1}$  respectively. The concentration of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NO}$  and  $\text{NO}_2$  ( $\text{mg m}^{-3}$ ) were measured using a flue gas analyzer (DeTu, 350, German) after the gas stabilized for 80 min at the corresponding temperature. The HCN removal rate and reaction products selectivity were calculated according to the eqn (S1)–(S8).†

### 2.4 Characterization

The related characterization information was detailed in the ESI.†

## 3 Results and discussion

### 3.1 Catalytic activity of $\text{CeO}_2$ loaded with copper and manganese oxides

In order to evaluate the catalytic activity of  $\text{CeO}_2$  and the  $\text{CeO}_2$  loaded with copper and manganese oxides, the four prepared samples including  $\text{CeO}_2$ ,  $\text{CuO}/\text{CeO}_2$ ,  $\text{MnO}_x/\text{CeO}_2$  as well as  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  were tested for the HCN catalytic removal and the results were shown in Fig. 1. It could be observed the HCN

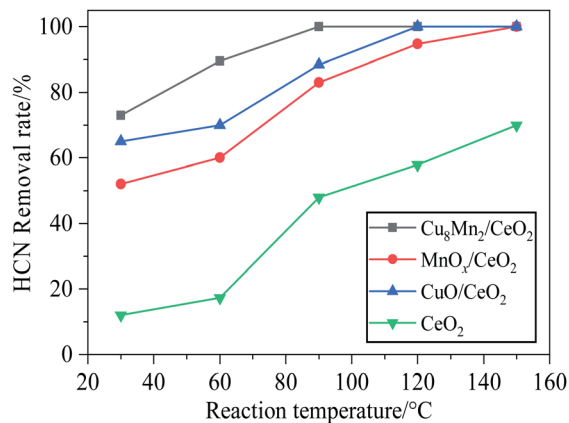
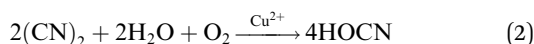
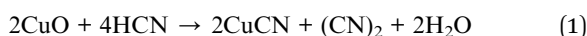
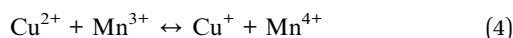


Fig. 1 The HCN removal rate over CeO<sub>2</sub>, CuO/CeO<sub>2</sub>, MnO<sub>x</sub>/CeO<sub>2</sub> and Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> samples. Reaction condition: 120 000 h<sup>-1</sup>, 5 vol% H<sub>2</sub>O.

removal rate of all samples increased with increasing the reaction temperature from 30 °C to 150 °C. The CeO<sub>2</sub> support showed the lowest activity toward HCN, even at 150 °C, the HCN removal rate was still below 70%. The HCN removal rate over CuO/CeO<sub>2</sub> were higher than MnO<sub>x</sub>/CeO<sub>2</sub> throughout the reaction temperature region, indicating the CuO phase on the CeO<sub>2</sub> played an important role in the HCN catalytic removal. The reason why CuO exhibited good catalytic performance could be explained by the interaction between CuO and HCN which was demonstrated in following equations.<sup>23,24</sup>



The highest HCN removal rate was obtained for Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub>: it was equal to 73% at 30 °C and reached nearly 100% at 90 °C. To determine the optimal Cu/Mn mass ratio, a series of Cu<sub>x</sub>Mn<sub>y</sub>/CeO<sub>2</sub> materials including Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub>, Cu<sub>6</sub>Mn<sub>4</sub>/CeO<sub>2</sub>, Cu<sub>4</sub>Mn<sub>6</sub>/CeO<sub>2</sub> and Cu<sub>2</sub>Mn<sub>8</sub>/CeO<sub>2</sub> were prepared and the catalytic activity of these samples were compared with CuO/CeO<sub>2</sub> and MnO<sub>x</sub>/CeO<sub>2</sub>. As presented in Fig. S2,† the Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> still exhibited the highest activity and the optimal Cu/Mn ratio was 8 : 2. The addition of a small amount of MnO<sub>x</sub> could enhanced the catalytic activity of CuO/CeO<sub>2</sub> and the results might be attributed to the synergy between copper and manganese oxides, which was in accordance with the study of Li and Njagi *et al.* who studied the catalytic activity of Cu–Mn–O catalysts toward HCN and CO respectively.<sup>25,26</sup>



### 3.2 Catalytic activity of CeO<sub>2</sub> loaded with different bimetal oxides

Fig. 2 investigated the HCN catalytic removal rate over CeO<sub>2</sub> loaded with different bimetal oxides including Cu<sub>8</sub>Fe<sub>2</sub>/CeO<sub>2</sub>,

Cu<sub>8</sub>Ni<sub>2</sub>/CeO<sub>2</sub>, Cu<sub>8</sub>Co<sub>2</sub>/CeO<sub>2</sub>, Cu<sub>8</sub>Ag<sub>2</sub>/CeO<sub>2</sub> and Cu<sub>8</sub>Zn<sub>2</sub>/CeO<sub>2</sub> samples. All samples exhibited the same HCN removal trend as Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> at the temperature region of 30–150 °C: the HCN removal rate increased as temperature improving. Cu<sub>8</sub>Ni<sub>2</sub>/CeO<sub>2</sub> and Cu<sub>8</sub>Fe<sub>2</sub>/CeO<sub>2</sub> showed the similar catalytic performance and their activity were both stronger than CuO/CeO<sub>2</sub>. The results indicated the introduction of iron and nickel species could generated good synergy with copper oxide species. Significantly, the addition of iron species could strengthen the redox properties of catalysts and increase the dispersion of copper species by inhabiting the particles agglomeration.<sup>27</sup> For Cu<sub>8</sub>Co<sub>2</sub>/CeO<sub>2</sub>, it exhibited the same catalytic activity toward HCN as CuO/CeO<sub>2</sub>. Noteworthy, when cobalt and silver oxides were introduced, the activity of two samples were lower than CuO/CeO<sub>2</sub>, this might be ascribed to the weaker synergy and lower CuO active sites on the support surface. Among all samples, the Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> still showed the most remarkable catalytic performance toward HCN, implying the synergy between copper and manganese was stronger than other bimetal oxides. Table S1† showed the comparison of HCN catalytic removal activity over various catalysts, indicating the Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> exhibited the lowest T<sub>100%</sub> temperature, at which HCN could be totally removed.

In order to investigate the thermal stability of Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub>, the Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> pretreated at 200 °C, 400 °C and 600 °C were tested for the HCN removal and the results shown in Fig. S3† indicated the catalytic activity of Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> were not influenced when the pretreated temperature varied. Further TG-DCS analysis shown in Fig. S4† also proved the Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> showed high thermal stability.

It was necessary to know whether the Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> could be recycled. The regeneration of the Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> were performed by the calcination of the samples at 450 °C for 4 h. Four recycling runs for the Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> were carried out, the results shown in Fig. S5† indicated the Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> could still achieve nearly 80% removal rate toward HCN even after 4 runs.

### 3.3 Analysis of HCN reaction products over Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub>

The HCN removal rate and the reaction products over Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> were investigated at the temperature region of 30–150 °C

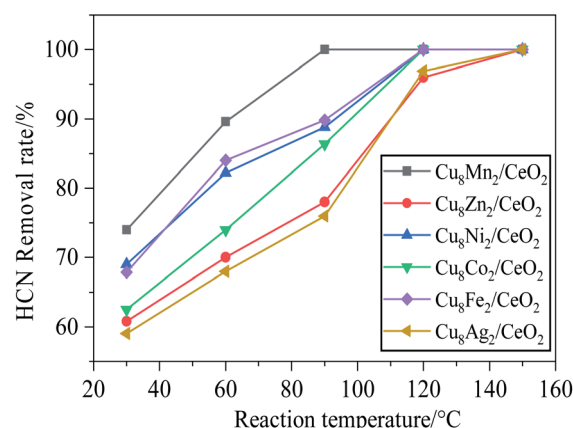
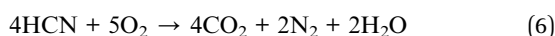
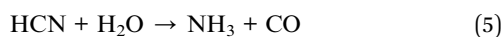


Fig. 2 The HCN removal rate over CeO<sub>2</sub> loaded with different bimetal oxides. Reaction condition: 120 000 h<sup>-1</sup>, 5 vol% H<sub>2</sub>O.



and the results were shown in Fig. 3. The products detected in the outlet gas involved CO, CO<sub>2</sub>, NH<sub>3</sub>, NO and NO<sub>2</sub>. The selectivity of CN<sup>−</sup> and N<sub>2</sub> were calculated according to the C-balance N-balance data and the concentration of all reaction products were listed in Table S2.†

At 30 °C, the selectivity of CO and CO<sub>2</sub> were not in line with the HCN removed, which implied most HCN were converted to CN<sup>−</sup> due to the chemical interaction between CuO and MnO<sub>x</sub> phase on the CeO<sub>2</sub> support (eqn (1)) and the HCN was mainly removed by chemisorption. The small amount of CO and NH<sub>3</sub> might be attributed to the catalytic hydrolysis reaction of HCN (shown in eqn (5)), while the CO<sub>2</sub> were assigned to the catalytic oxidation (shown in eqn (6)). In addition, the oxidation of CO could also generate CO<sub>2</sub>.



The catalytic hydrolysis of HCN over Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> showed low activity at the temperature region of 30 °C–60 °C, the NH<sub>3</sub> yield changed little with temperature increasing. However, the high CO<sub>2</sub> selectivity indicated the catalytic oxidation of HCN was enhanced, the CN<sup>−</sup> was oxidized to CO<sub>2</sub> and released more active sites, which could strengthen the HCN removal rate.

The selectivity of NH<sub>3</sub> and CO<sub>2</sub> increased significantly from 60–150 °C as results of catalytic hydrolysis and catalytic oxidation of HCN showing high activity. The generated NO and NO<sub>2</sub> might be attributed to the byproducts of catalytic oxidation of HCN. Compared with NH<sub>3</sub> generated by catalytic hydrolysis, the amount of CO disappeared with temperature increasing due to the oxidation of CO to CO<sub>2</sub>. When the temperature reached 120 °C and increased further, the CO<sub>2</sub> selectivity stayed 100%, implying the HCN was completely removed by catalytic hydrolysis and oxidation.

More significantly, the NH<sub>3</sub> selectivity generated by catalytic hydrolysis was below than 20% at the whole reaction temperature, which were lower than the reported literature.<sup>12,13</sup> It might

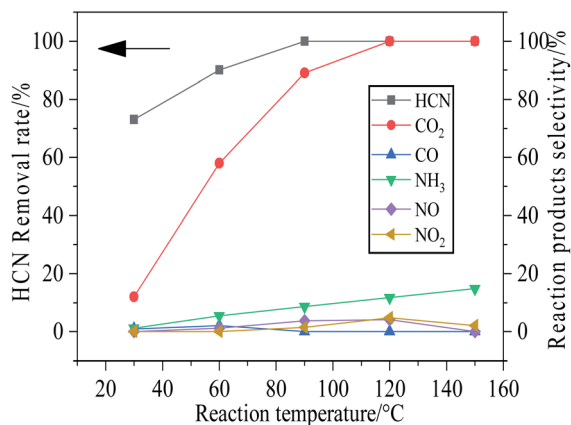


Fig. 3 The removal rate of HCN and selectivity of reacted products over Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> at different temperature. Reaction condition: 120 000 h<sup>−1</sup>, 5 vol% H<sub>2</sub>O.

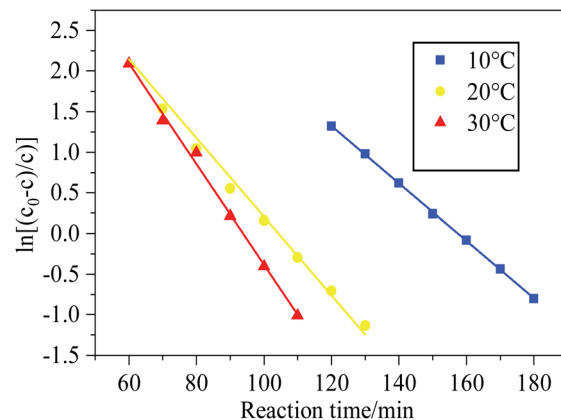


Fig. 4 Plot of  $\ln\left(\frac{C_0 - C}{C}\right) - t$  for Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> bed at temperature region of 10–30 °C. Reaction condition: 120 000 h<sup>−1</sup>, 5 vol% H<sub>2</sub>O.

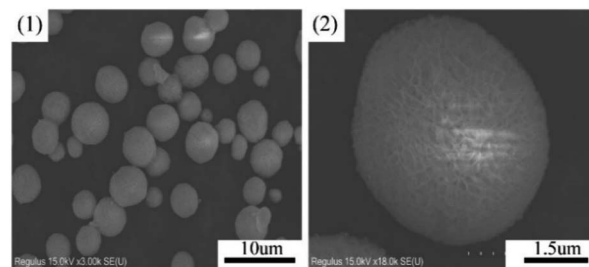


Fig. 5 The SEM images of the CeO<sub>2</sub>. (1) and (2) Low and high magnification SEM images of CeO<sub>2</sub>.

be attributed to the increase of acid sites on the Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> after MnO<sub>x</sub> introduced and the generated NH<sub>3</sub> could be absorbed on the Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> samples and converted into N<sub>2</sub>.

### 3.4 Breakthrough behaviors of HCN over Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub>

By analyzing the reaction products of HCN, it was concluded that the HCN was mainly removed by chemisorption at 30 °C. To study the catalytic materials' adsorption performance, the breakthrough behaviour of HCN over Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> was investigated and the breakthrough curves were shown in Fig. S6.†

The Yoon and Nelson's equation was introduced to describe the breakthrough behaviour of HCN over Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub>.<sup>28</sup>

$$\ln\left(\frac{C_0 - C}{C}\right) = k(\tau - t) \quad (7)$$

where  $C_0$  was the inlet concentration of HCN, mg m<sup>−3</sup>;  $C$  referred to the breakthrough concentration of HCN, mg m<sup>−3</sup>;  $t$  was the breakthrough time, min;  $\tau$  was the time required to obtain 50% breakthrough, min<sup>−1</sup>;  $k$  was the lumped shape factor of breakthrough, min<sup>−1</sup>.

Fig. 4 demonstrated the experimental results of the  $\ln\left(\frac{C_0 - C}{C}\right)$  and  $t$  curves, the values of  $k$  and  $\tau$  at different temperature were calculated and the results were listed in Table S3.† With temperature increased, the thermal motion of HCN





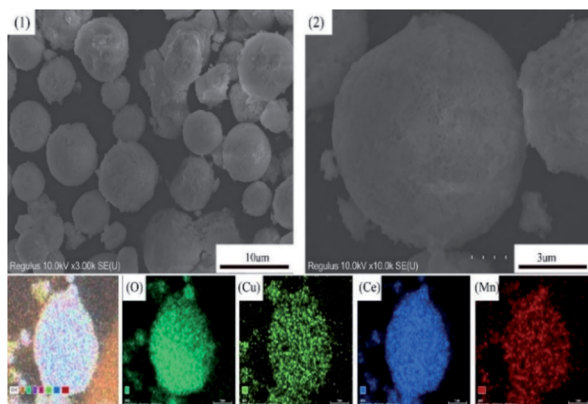


Fig. 6 The SEM images of the  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  and the corresponding elements (O, Cu, Ce, Mn) mapping. (1) and (2) Low and high magnification SEM images of  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$ .

Table 1 The structural parameters of the  $\text{CeO}_2$  loaded with different bimetal oxides

Samples	CuO (wt%)	$\text{M}_x\text{O}_y$ (wt%)	Crystal size <sup>a</sup>
$\text{Cu}_8\text{Mn}_2/\text{CeO}_2$	9.7	1.8	—
$\text{Cu}_8\text{Zn}_2/\text{CeO}_2$	9.3	2.1	30
$\text{Cu}_8\text{Ni}_2/\text{CeO}_2$	9.5	2.3	17
$\text{Cu}_8\text{Co}_2/\text{CeO}_2$	9.3	2.3	22
$\text{Cu}_8\text{Fe}_2/\text{CeO}_2$	10.7	2.0	—
$\text{Cu}_8\text{Ag}_2/\text{CeO}_2$	9.4	1.7	41

<sup>a</sup> Crystallite sizes calculated from the line broadening of the (002) plane of CuO.

became intense, and the number of activated molecules increased, which accelerated the saturation of activated sites on the  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$ . HCN was absorbed on the samples' surface in the form of  $\text{CN}^-$  and could not be converted further. The activated sites could not be released, as a result, the breakthrough curve became steeper and breakthrough time became shorter as temperature increased.

### 3.5 SEM and TEM analysis

The morphological properties of samples were characterized by SEM analysis. As presented in Fig. 5, the  $\text{CeO}_2$  support exhibited flowerlike mesoporous microspheres with average diameter of 2–4  $\mu\text{m}$  and dispersed evenly. There were many petal-like nanosheets on the microsphere surface and these nanosheets interweaved together to form the porous structure.<sup>29</sup> Fig. 6 showed the morphology and size of  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  materials, it could be observed the metal oxide particles were loaded dispersively on the  $\text{CeO}_2$  supports and the porous structure were covered after metal oxide species loaded. EDS analysis shown in Fig. S6† implied the Cu and Mn elements had uniform distribution on the  $\text{CeO}_2$  surface. The SEM images for  $\text{Cu}_8\text{Zn}_2/\text{CeO}_2$ ,  $\text{Cu}_8\text{Ni}_2/\text{CeO}_2$ ,  $\text{Cu}_8\text{Co}_2/\text{CeO}_2$ ,  $\text{Cu}_8\text{Fe}_2/\text{CeO}_2$  and  $\text{Cu}_8\text{Ag}_2/\text{CeO}_2$  were shown in Fig. S7.† The actual metal oxides loading of all samples were calculated according to EDS analysis shown in Fig. S8† and the results were listed in Table 1, which

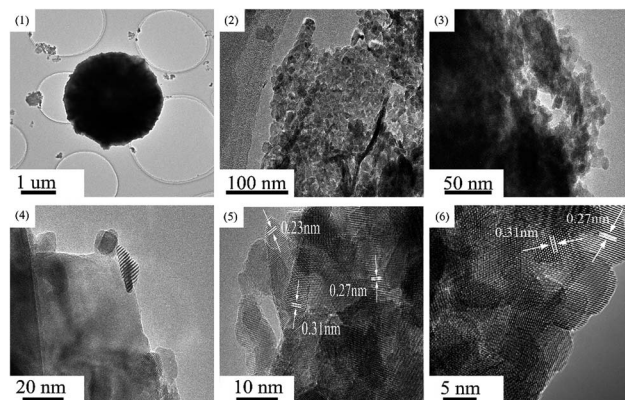


Fig. 7 The HR-TEM images of the  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  at different magnification. (1) The overall  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  morphology; (2) and (3) the polycrystalline structure of  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$ ; (4) the CuO phases; (5) the crystal planes of  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$ ; (6) the crystal planes of  $\text{CeO}_2$ .

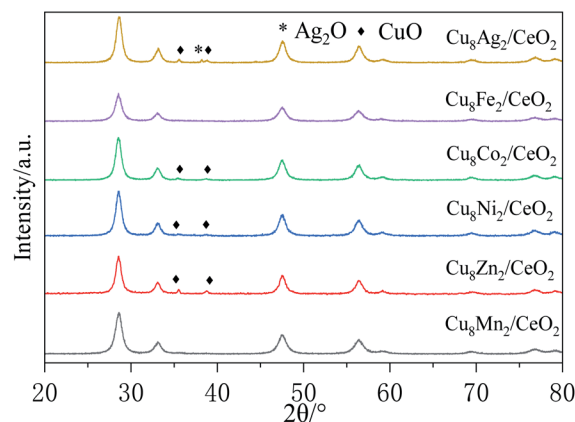


Fig. 8 The XRD patterns of  $\text{CeO}_2$  loaded with different bimetal oxides.

demonstrated the actual metal oxides loading were in accordance with theoretical value.

In order to analyze the microstructure and crystallinity of the  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  samples, the HR-TEM characterization was carried out and the results were shown in Fig. 7. As shown in Fig. 7(1), it could be seen the  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  exhibited a sphere structure with diameter of 2–3  $\mu\text{m}$ , which was consistent with SEM characterization. Fig. 7(2) indicated the  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  was polycrystalline structure composed of many nanocrystals at different orientations.<sup>30</sup> The nanocrystals marked in Fig. 7(4) was assigned to CuO species loaded on  $\text{CeO}_2$  support, the crystal size of which were around 10–15 nm. Three interplanar spacings of the ordered stripes marked in Fig. 7(5) were 0.27 nm, 0.31 nm and 0.23 nm, corresponding to the (200) and (111) lattice planes of  $\text{CeO}_2$  and (111) lattice planes of CuO.<sup>31</sup> However, there no  $\text{MnO}_x$  phase observed in Fig. 7(5), this could be explained by the high dispersion of  $\text{MnO}_x$  due to the low loading. Fig. 7(6) displayed the TEM image for  $\text{CeO}_2$ , it could be concluded the structure of  $\text{CeO}_2$  was not changed after metal oxides loaded and still exposed (200) and (111) lattice planes.



**Table 2** The textural data and crystallite size of the CeO<sub>2</sub>, CuO/CeO<sub>2</sub>, MnO<sub>x</sub>/CeO<sub>2</sub>, Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub>

Samples	Surface area/ (m <sup>2</sup> g <sup>-1</sup> )	Pore volume/ (cm <sup>3</sup> g <sup>-1</sup> )	Pore size/ nm
CeO <sub>2</sub>	104.4	0.12	4.6
CuO/CeO <sub>2</sub>	59.1	0.23	14.3
MnO <sub>x</sub> /CeO <sub>2</sub>	96.3	0.16	6.5
Cu <sub>8</sub> Mn <sub>2</sub> /CeO <sub>2</sub>	40.1	0.22	24

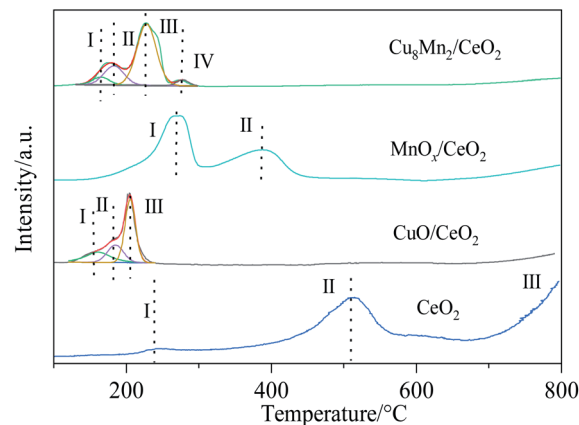
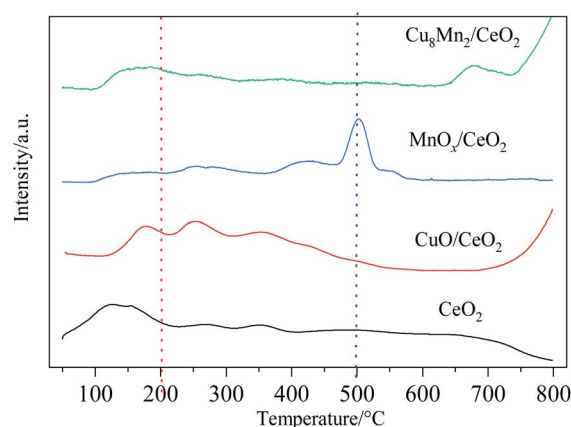
### 3.6 XRD analysis

Fig. 8 showed the XRD patterns of CeO<sub>2</sub> loaded with different bimetal oxides. The main diffraction peaks at 28.8°, 33.1°, 47.8°, 56.5°, 59.5°, 69.3°, 77.1° and 79.2° were ascribed to the cubic fluorite cerium oxide and the peaks at 35.4° and 38.7° were attributed to the CuO (JCPDS 34-0394).<sup>32</sup> Except Cu<sub>8</sub>Ag<sub>2</sub>/CeO<sub>2</sub> exhibited the Ag<sub>2</sub>O diffraction peak at 38.2°, no diffraction peaks derived from other metal or metal oxides (Mn, Zn, Ni, Co, Fe) were observed in the XRD patterns.<sup>33</sup> The results implied these metal oxides were well dispersed on the CeO<sub>2</sub> support due to their low loading. The crystal size of CuO loaded on CeO<sub>2</sub> in all samples was calculated according to the Scherrer equation and the results were listed in Table 1. It could be seen the introduction of ZnO or Ag<sub>2</sub>O promoted the agglomeration of CuO on the surface of supports and increased the crystal size. For NiO or Co<sub>3</sub>O<sub>4</sub>, they showed little effect toward the crystal size of CuO. When introduced MnO<sub>x</sub> or Fe<sub>2</sub>O<sub>3</sub>, the diffraction peaks of CuO disappeared, indicating the CuO species were dispersed well as amorphous oxides or some Cu species doped into the lattice of CeO<sub>2</sub> and formed Cu–Ce–O solid solution.<sup>31</sup> CuO and MnO<sub>x</sub> species could strengthen the synergy between CuO and CeO<sub>2</sub> support to restrain the growth of CuO particles. Combined with catalytic activity test results, it could be deduced the bimetal synergistic effect could improve samples' activity by strengthening the interaction between metal oxides and supports. The XRD patterns of CeO<sub>2</sub>, CuO/CeO<sub>2</sub> and MnO<sub>x</sub>/CeO<sub>2</sub> were shown in Fig. S9,<sup>†</sup> and the crystal size of metal oxide particles calculated were also listed in Table 2.

### 3.7 H<sub>2</sub>-TPR

The reduction properties of CeO<sub>2</sub>, CuO/CeO<sub>2</sub>, MnO<sub>x</sub>/CeO<sub>2</sub> and Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> were investigated by H<sub>2</sub>-TPR analysis and the results were shown in Fig. 9. The reduction peaks of CeO<sub>2</sub> have been detailed discussed in our previous work.<sup>8</sup>

After peak fitting process, three reduction peaks were observed in the CuO/CeO<sub>2</sub> spectra. The first peak at 158 °C were attributed to the reduction of finely dispersed CuO species on the CeO<sub>2</sub> supports, the second peaks at 181 °C came from the reduction of CuO with moderate crystal size which interacted with the oxygen vacancies of CeO<sub>2</sub> and the third peak at 212 °C was related to the reduction of a part of the surface ceria, the copper oxide incorporated into the ceria lattice and the large copper oxide phase. Compared with CeO<sub>2</sub>, the surface ceria reduction peak shifted to lower temperature, which could be

**Fig. 9** The H<sub>2</sub>-TPR profiles of the prepared CeO<sub>2</sub>, CuO/CeO<sub>2</sub>, MnO<sub>x</sub>/CeO<sub>2</sub> and Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> samples.**Fig. 10** The NH<sub>3</sub>-TPD profiles of CeO<sub>2</sub>, CuO/CeO<sub>2</sub>, MnO<sub>x</sub>/CeO<sub>2</sub> and Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> samples.

assigned to the presence of hydrogen spillover process from metal Cu surface and the interaction between CuO and CeO<sub>2</sub>.<sup>34</sup>

For MnO<sub>x</sub>/CeO<sub>2</sub>, the first reduction peak at 250 °C was assigned to the reduction of MnO<sub>2</sub> or Mn<sub>2</sub>O<sub>3</sub> to Mn<sub>3</sub>O<sub>4</sub>, the second peak at 410 °C was related to the reduction of Mn<sub>3</sub>O<sub>4</sub> to MnO and surface Ce<sup>4+</sup> to Ce<sup>3+</sup>.<sup>35</sup> The results indicated the interaction of MnO<sub>x</sub> and CeO<sub>2</sub> were weaker than CuO and CeO<sub>2</sub>, which might help explain why CuO/CeO<sub>2</sub> showed high catalytic activity than MnO<sub>x</sub>/CeO<sub>2</sub>. When loaded with MnO<sub>x</sub>, the Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> not only exhibited the three reduction peaks corresponding to CuO/CeO<sub>2</sub> but also showed the reduction peak of MnO<sub>2</sub> or Mn<sub>2</sub>O<sub>3</sub> to Mn<sub>3</sub>O<sub>4</sub>, while the reduction peak of Mn<sub>3</sub>O<sub>4</sub> to MnO was not observed, implying the Mn<sup>4+</sup> were more actively than Mn<sup>3+</sup> or Mn<sup>4+</sup>. Combining with the XRD analysis, the MnO<sub>x</sub> had a high dispersion on the CeO<sub>2</sub> support due its low content and the interaction between MnO<sub>x</sub> and CeO<sub>2</sub> prevented the reduction of Mn<sub>3</sub>O<sub>4</sub> to MnO. Compared with CuO/CeO<sub>2</sub>, the peak intensity of Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> was improved and the H<sub>2</sub> consumption also increased, which implied the Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> showed high catalytic activity. The TPR peaks and H<sub>2</sub> consumption of CuO/CeO<sub>2</sub> and Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> were summarized



in Table S4.† In addition, the reduction peaks of  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  were shifted to higher temperature region, which might be attributed to the formation of polymeride.<sup>36</sup>

### 3.8 $\text{NH}_3$ -TPD

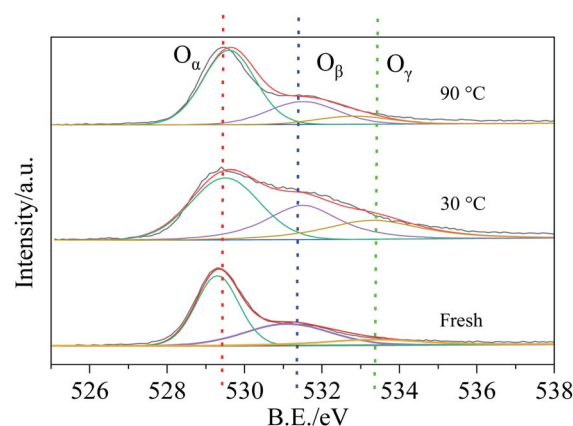
In order to probe the acidity of  $\text{CeO}_2$ ,  $\text{CuO}/\text{CeO}_2$ ,  $\text{MnO}_x/\text{CeO}_2$  and  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  samples, the  $\text{NH}_3$ -TPD analysis were carried out. As presented in Fig. 10, the  $\text{NH}_3$  desorption peaks could be divided into three parts: peaks at 100–200 °C were corresponded to the desorption of physically absorbed  $\text{NH}_3$  and  $\text{NH}_3$  absorbed on the weak Brønsted acid sites, the peaks at 200–500 °C were attributed to the desorption of  $\text{NH}_4^+$  absorbed on the strong Brønsted acid sites and the peaks at above 500 °C were related to the desorption of  $\text{NH}_3$  absorbed on the weak and strong Lewis acid sites.<sup>37,38</sup> The area of the  $\text{NH}_3$  desorption peaks directly related to the amount of acidic sites and their acidic strength, respectively. Quantitative analysis of  $\text{NH}_3$  desorption at corresponding temperature over all samples were calculated and the results were listed in Table S5.† It could be observed the total amount of acid sites of  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  at lower temperature were improved and a desorption peak at above 500 °C region was observed, indicating the acidic strength of samples was enhanced when  $\text{MnO}_x$  was introduced. Significantly, the  $\text{NH}_3$  desorption amount of  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  was higher than  $\text{CuO}/\text{CeO}_2$  at 100–200 °C region, which implied the  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  could bind more  $\text{NH}_3$  at lower temperature than  $\text{CuO}/\text{CeO}_2$ . The stronger  $\text{NH}_3$  adsorption capacity of samples could enhance the absorption ability toward  $\text{NH}_3$  generated by catalytic hydrolysis and promote the conversion of  $\text{NH}_3$  to  $\text{N}_2$  which was consistent with the results of Fig. 3.

### 3.9 BET analysis

The  $\text{N}_2$  desorption–desorption isotherms of  $\text{CeO}_2$ ,  $\text{CuO}/\text{CeO}_2$ ,  $\text{MnO}_x/\text{CeO}_2$  as well as  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  were displayed in Fig. 11. The adsorption–desorption isotherms of all samples showed a type IV trend with a  $\text{H}_2$ -type hysteresis loop, implying the typical mesoporous structure of  $\text{CeO}_2$  was not influenced after

**Table 3** The surface atom types and atomic ratio among  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  samples

Samples	O (100%)			Cu (100%)		Ce (100%)		Mn (100%)		
	$\text{O}_\alpha$	$\text{O}_\beta$	$\text{O}_\gamma$	$\text{Cu}^{2+}$	$\text{Cu}^+$	$\text{Ce}^{4+}$	$\text{Ce}^{3+}$	$\text{Mn}^{4+}$	$\text{Mn}^{3+}$	$\text{Mn}^{2+}$
Fresh	54	35	11	31	44	73	27	21	54	0
30 °C	47	31	22	25	52	68	32	18	33	19
90 °C	65	26	9	19	58	65	35	14	48	11



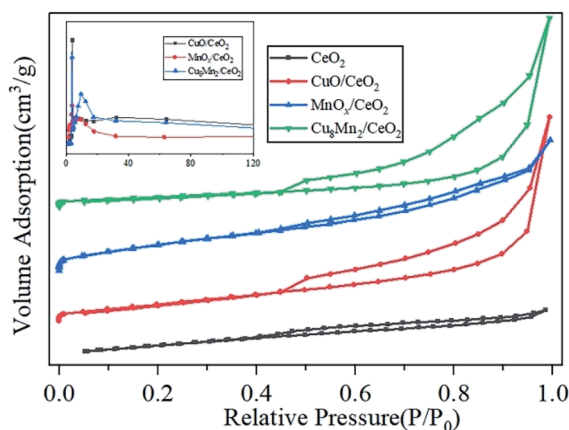
**Fig. 12** The O 1s spectra of  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  samples.

metal oxides loaded.<sup>29</sup> The pore size distribution of three catalytic materials were calculated and the results were shown as the insert part in Fig. 11. The textural properties including the specific surface area, pore volumes, and pore size were listed in Table 2. The specific surface area of three catalytic materials decreased while the pore volumes and pore size increased and  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  showed the smallest specific surface area  $40.1 \text{ m}^2 \text{ g}^{-1}$  and largest pore size 24 nm respectively. These might be assigned to the fact that copper and manganese oxides covered the external surface of  $\text{CeO}_2$ , and block the micropores structure, which was consistent with SEM analysis.<sup>13</sup>

### 3.10 XPS analysis

By analyzing the reaction products, it could be obtained the HCN was mainly removed by catalytic hydrolysis and catalytic oxidation when the reaction temperature was higher than 90 °C. To further investigate the reaction mechanism between HCN and  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$ , the XPS characterization was carried out to analyze the chemical state, surface atomic concentration and the dispersion of main elements of the samples before and after reaction and the results were summarized in the Table 3.

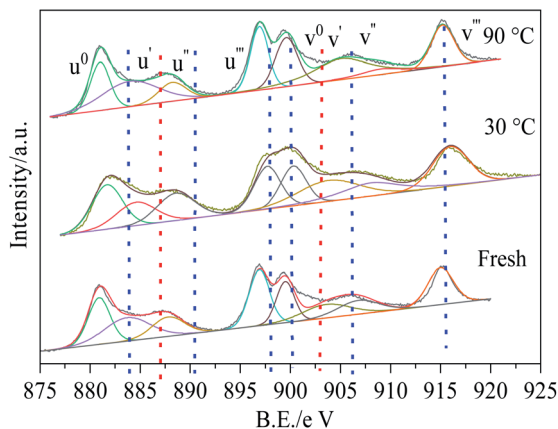
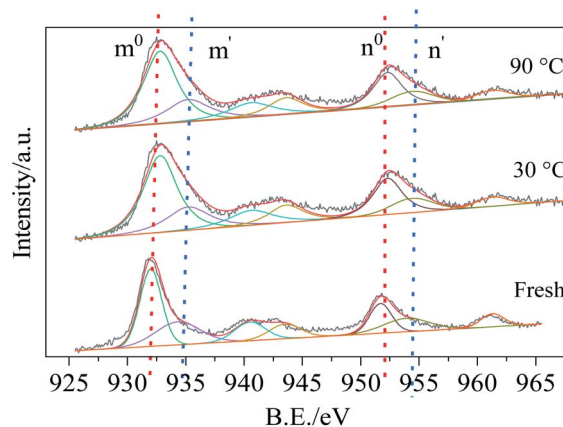
Fig. 12 showed the O 1s XPS spectra of the fresh samples and samples reacted at 30 °C and 90 °C. It could be observed an asymmetrical peak at the bonding energy range of 528–536 eV, which could be resolved into three distinct peaks: peak located at 529.5 eV (denoted as  $\text{O}_\alpha$ ) was ascribed to the lattice oxygen, peak located at 531.1 eV (denoted as  $\text{O}_\beta$ ) was corresponded to



**Fig. 11** The nitrogen adsorption–desorption isotherms and pore size distributions of  $\text{CeO}_2$ ,  $\text{CuO}/\text{CeO}_2$ ,  $\text{MnO}_x/\text{CeO}_2$  and  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  samples.

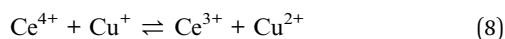




Fig. 13 The Ce 3d spectra of Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> samples.Fig. 14 The Cu 2p spectra of Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> samples.

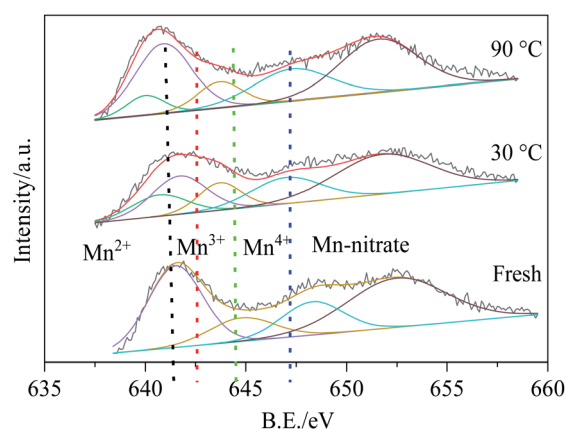
the surface chemisorption oxygen and the peak at 532.2 eV (denoted as O<sub>γ</sub>) was assigned to the adsorbed water or surface OH species on the samples.<sup>39</sup> The content of the O<sub>α</sub>, O<sub>β</sub> and O<sub>γ</sub> were calculated and listed in the Table 3. As presented in Table 3, after reacted with HCN at 30 °C, the O<sub>β</sub> content of Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> decreased from 35% to 31% which indicated the O<sub>β</sub> took part in the HCN catalytic removal over the samples due to its higher mobility. The increase of O<sub>γ</sub> content was attributed to the H<sub>2</sub>O in the reaction system absorbed on the surface of samples. With temperature increased further, the O<sub>β</sub> content decreased continuously and O<sub>γ</sub> content also decreased, implying the catalytic hydrolysis activity enhanced, the O<sub>β</sub> and H<sub>2</sub>O absorbed worked together to contribute to the HCN catalytic removal over Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub>.

Ce 3d XPS spectra of Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> were displayed in Fig. 13. After peak fitting process, it could be observed eight binding energy peaks at the bonding energy region of 875–925 eV. The binding energy peaks of u' and v' were assigned to the Ce<sup>3+</sup> species while others were related to Ce<sup>4+</sup> ions and the content of Ce<sup>3+</sup> and Ce<sup>4+</sup> were listed in the Table 3.<sup>40</sup> With reaction temperature increased from 30 to 90 °C, the Ce<sup>3+</sup> content increased from 27% to 35%, while the Ce<sup>4+</sup> content decreased from 73% to 65%, owing to the synergy between Cu<sup>2+</sup> and Cu<sup>3+</sup> shown as following equation.<sup>41</sup>



Oxygen vacancies could be generated as a function of surface Ce<sup>3+</sup> on the samples, which could avoid the CuO particles agglomeration and improve its dispersion on CeO<sub>2</sub> support by enhancing the synergy between CuO and CeO<sub>2</sub>.<sup>40</sup> This could help explain why no diffraction peak of CuO was observed in the XRD patterns of Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub>.

Cu 2p spectra were fitted with four energy peaks and the results were shown in Fig. 14, the bonding energy peaks m<sup>0</sup>, n<sup>0</sup> represented Cu<sup>+</sup> while m', n' peaks were related to Cu<sup>2+</sup>. After reacted with HCN, the Cu<sup>2+</sup> decreased from 31% to 19% while Cu<sup>+</sup> increased from 44% to 58%.<sup>42</sup> It might be ascribed to the chemical interaction between CuO phase and HCN: HCN

Fig. 15 The Mn 2p spectra of Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> samples.

bonded with Cu<sup>2+</sup> and generated CuCN due to chemisorption, and promote the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>, which implied the Cu<sup>2+</sup> played an important role in the HCN catalytic removal over Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub>.

Fig. 15 demonstrated the Mn 2p spectra of all samples, there were two main peaks at 642 eV and 653 eV, which were ascribed to the Mn 2p<sub>3/2</sub> and Mn 2p<sub>1/2</sub> respectively. The Mn 2p<sub>3/2</sub> spectra could be decomposed into four bonding energy peaks: 640.3, 641.6, 643.2 and 646.2 eV, corresponding to Mn<sup>2+</sup>, Mn<sup>3+</sup>, Mn<sup>4+</sup> and manganese nitrate.<sup>43</sup> For the fresh Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub> samples, Mn<sup>3+</sup> and Mn<sup>4+</sup> peaks were observed while Mn<sup>2+</sup> peak was not founded. When reacted with HCN at 30 °C, the Mn<sup>2+</sup> content increased to 19% while Mn<sup>3+</sup> and Mn<sup>4+</sup> content all decreased, indicating the Mn<sup>3+</sup> and Mn<sup>4+</sup> participated in the HCN catalytic removal over Cu<sub>8</sub>Mn<sub>2</sub>/CeO<sub>2</sub>, and the reaction system referred the reduction of Mn<sup>4+</sup> to Mn<sup>3+</sup> and Mn<sup>3+</sup> to Mn<sup>2+</sup>. With reaction temperature increased to 90 °C, the Mn<sup>3+</sup> content still increased, while Mn<sup>3+</sup> and Mn<sup>2+</sup> content decreased, which demonstrated the HCN catalytic removal at 90 °C was mainly attributed to the reduction of Mn<sup>4+</sup> to Mn<sup>3+</sup>. It could be deduced that Mn<sup>4+</sup> played an important role in the investigated reactions, and the results were consistent with the H<sub>2</sub>-TPR analysis.





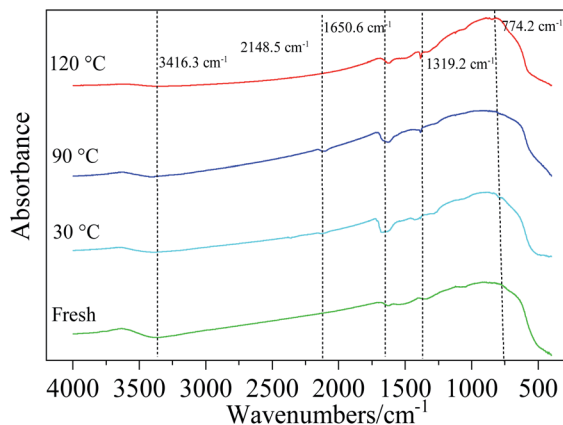
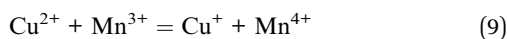


Fig. 16 The FTIR spectra of  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  samples.

Besides, the redox couple shown in following equation could also strengthen the samples' activity toward HCN.<sup>44</sup>



### 3.11 The results of FT-IR

The FT-IR spectra of fresh and used  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  which reacted with HCN at 30 °C, 90 °C and 120 °C were analyzed to investigate the reaction mechanism of HCN over prepared samples. As presented in Fig. 16, all samples exhibited two characteristic bonds at  $3416.3 \text{ cm}^{-1}$  and  $1650 \text{ cm}^{-1}$  corresponding to the stretching vibration of surface OH groups and the bending vibration of  $\text{H}_2\text{O}$  adsorbed, which were beneficial to the HCN catalytic hydrolysis and oxidation.<sup>45</sup> The absorption peak at  $774.2 \text{ cm}^{-1}$  was assigned to the Ce–O asymmetric vibrational stretch and peak at  $1319.2 \text{ cm}^{-1}$  might be attributed to the  $\text{CO}_3^{2-}$  vibrational stretch.<sup>29</sup> After reacted at 30 °C, a new peak appeared at  $2148.5 \text{ cm}^{-1}$  which was ascribed to the  $\text{CN}^-$  vibrational stretch, indicating the HCN bonded with  $\text{Cu}^{2+}$  and generated CuCN due to chemisorption.<sup>46</sup> When the reaction temperature increased to 90 °C, the peak at  $2148.5 \text{ cm}^{-1}$  could still be observed, which implied the chemisorption were still involved in the reaction system for removal of HCN. With temperature increased further, the peak corresponding to  $\text{C}\equiv\text{N}$  vibrational stretch disappeared while other peaks were not changed, indicating the  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  exhibited high stability in the reaction system, and the results were consistent with the XRD and ICP analysis shown in Fig. S10 and Table S6† respectively. The  $\text{CN}^-$  absorbed might be converted into  $\text{N}_2$ ,  $\text{NH}_3$  and  $\text{CO}_2$  with the participation of  $\text{O}_2$ ,  $\text{H}_2\text{O}$  and OH species. As a result, the active site on the  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  was supplemented, which could capture more HCN molecular to strengthen the catalytic activity of the samples.

## 4 Discussion

Based activity test results, the  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  was chosen as the ideal catalytic material. It was believed the  $\text{CeO}_2$  still played an important role in the HCN catalytic removal over  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$ .

Combing the SEM and TEM analysis, the  $\text{CeO}_2$  exhibited a 3D porous structure which was beneficial for gas transport.<sup>29</sup> The flowerlike sphere structure of  $\text{CeO}_2$  could also improve the dispersion of metal species.<sup>21</sup> Besides, the addition of  $\text{MnO}_x$  could restrain the growth of CuO particles and improve their dispersion on the  $\text{CeO}_2$  by the synergistic effect according to the XRD results, which promoted the removal of HCN over  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  sample.  $\text{H}_2$ -TPR analysis indicated the redox ability of  $\text{CeO}_2$  was enhanced after CuO and  $\text{MnO}_x$  loaded, as reported, the excellent activity of  $\text{CeO}_2$  based catalysts derived from the reversible  $\text{Ce}^{3+}$ – $\text{Ce}^{4+}$  transition in  $\text{CeO}_2$  support associated with oxygen vacancy formation and migration which might strengthen the interaction between CuO,  $\text{MnO}_x$  and  $\text{CeO}_2$  support and promoted its redox ability.<sup>47</sup>

The CuO phase on the  $\text{CeO}_2$  played an important role in the HCN removal process, the HCN was absorbed on the  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  to generate CuCN by the reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$ . The reaction products of HCN over  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  at the temperature region of 30–150 °C indicated the catalytic hydrolysis and catalytic oxidation improved as temperature increasing. Combing the XPS analysis, the chemisorption oxygen, the oxygen vacancies, the  $\text{Cu}^{2+}$  and  $\text{Mn}^{4+}$  all played an important role in determining the excellent HCN removal performance of  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$ .  $\text{NH}_3$ -TPD characterization indicated the addition of  $\text{MnO}_x$  could increase the acid sites of  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$ , which could strengthen the absorption ability of  $\text{NH}_3$  and promoted its conversion.

Based the FT-IR results, the  $\text{CN}^-$  absorbed on the samples disappeared when the reaction temperature was above 120 °C, this could be explained by the totally conversion of  $\text{CN}^-$ . At this moment, the HCN removal was completely in the form of catalytic hydrolysis and catalytic oxidation. When the temperature was lower than 30 °C, the removal of HCN was mainly attributed to the sample's chemisorption. The HCN breakthrough behavior on the catalytic materials bed was corresponded to the Yoon and Nelson's model.

Based above analysis, the HCN reaction mechanism over  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  at 30–150 °C was described as follows: HCN was first absorbed and then decomposed into  $\text{CN}^-$  on the surface of  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  due to the chemisorption of bimetal oxides on the  $\text{CeO}_2$ . With reaction temperature increased, the  $\text{CN}^-$  could be oxidized into  $-\text{NCO}$  with the participation of  $\text{O}_2$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{4+}$  and oxygen vacancies.<sup>10,12</sup> The formed  $-\text{NCO}$  were further converted into  $\text{NH}_3$  and CO by catalytic hydrolysis. On the other hand, the generated  $-\text{NCO}$  species were oxidized to form  $\text{CO}_2$ ,  $\text{N}_2$  and byproducts such as NO and  $\text{NO}_2$  by catalytic oxidation. The schematical diagram of the HCN reaction mechanism over  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  was shown in Fig. S11.†

## 5 Conclusions

The  $\text{Cu}_x\text{Mn}_y/\text{CeO}_2$  catalytic material was synthesized by precipitation method to achieve deep purification of HCN at the lower temperature region of 30–150 °C. By investigating the effect of different metal oxide species and the Cu/Mn mass ratio on the sample's catalytic activity, the  $\text{Cu}_8\text{Mn}_2/\text{CeO}_2$  sample was chosen as the ideal catalytic material, which could obtain



almost 100% removal rate toward  $400 \text{ mg m}^{-3}$  HCN at  $90^\circ\text{C}$ . The introduction of  $\text{MnO}_x$  could improve the dispersion of CuO particles and increase the total acid sites of the prepared samples. It was proved the synergy between CuO and  $\text{MnO}_x$ , the chemisorption oxygen, the oxygen vacancies, the  $\text{Cu}^{2+}$  and  $\text{Mn}^{4+}$  all played an important role in determining the good catalytic activity of the prepared samples.

## Author contributions

Z. H. Yi: conceptualization, formal analysis, investigation, writing original draft. J. Sun: funding acquisition, formal analysis, Resources, writing review and editing. Y. L. Yang: data curation. J. G. Li: investigation. T. Zhou: investigation. S. P. Wei: investigation. A. N. Zhu: investigation.

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 P. Dagaut, P. Glarborg and M. U. Alzueta, The oxidation of hydrogen cyanide and related chemistry, *Prog. Energy Combust. Sci.*, 2008, **34**, 1–46.
- 2 T. M. Oliver, K. P. Aleksandar and D. Nikola, Synthetic activated carbons for the removal of hydrogen cyanide from air, *Chem. Eng. Process.*, 2005, **44**, 1181–1187.
- 3 M. M. Baum, J. A. Moss, S. H. Pastel and G. A. Poskrebyshv, Hydrogen Cyanide Exhaust Emissions from In-Use Motor Vehicles, *Environ. Sci. Technol.*, 2007, **41**, 857–862.
- 4 J. P. Hämäläinen, M. J. Aho and J. L. Tummavuori, Formation of nitrogen oxides from fuel-N through HCN and  $\text{NH}_3$ : a model-compound study, *Fuel*, 1994, **73**, 1894–1898.
- 5 M. Jiang, Z. H. Wang, P. Ning, S. L. Tian, X. F. Huang, Y. W. Bai, Y. Shi, X. G. Ren and W. Chen, Dust removal and purification of calcium carbide furnace off-gas, *J. Taiwan Inst. Chem. Eng.*, 2014, **45**, 901–907.
- 6 J. A. Miller and C. T. Bowman, Mechanism and modeling of nitrogen chemistry in combustion, *Prog. Energy Combust. Sci.*, 1989, **15**, 287–338.
- 7 M. Devadas, O. Kroeher, M. Elsener and A. Wokaun, Influence of  $\text{NO}_2$  on the selective catalytic reduction of NO with ammonia over Fe-ZSM5, *Appl. Catal., B*, 2006, **67**, 187–196.
- 8 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/ $\text{CeO}_2$  micro-nano spheres at lower temperature range, *Chin. J. Chem. Eng.*, 2020, DOI: 10.1016/j.cjche.2020.08.029.
- 9 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.
- 10 R. N. Nickolov and D. R. Mehandjiev, Comparative study on removal efficiency of impregnated carbons for hydrogen cyanide vapors in air depending on their phase composition and porous textures, *J. Colloid Interface Sci.*, 2004, **273**, 87–94.
- 11 M. J. Hudson, J. P. Knowles and P. J. F. Harris, The trapping and decomposition of toxic gases such as hydrogen cyanide using modified mesoporous silicates, *Microporous Mesoporous Mater.*, 2004, **75**, 121–128.
- 12 Y. X. Ma, F. Wang, X. Q. Wang, P. Ning, X. Jing and J. H. Cheng, The hydrolysis of hydrogen cyanide over Nb/La- $\text{TiO}_x$  catalyst, *J. Taiwan Inst. Chem. Eng.*, 2017, **70**, 141–149.
- 13 Y. N. Hu, J. P. Liu, J. H. Cheng, L. L. Wang, L. Tao, Q. Wang, X. Q. Wang and P. Ning, Coupling catalytic hydrolysis and oxidation of HCN over HZSM-5 modified by metal (Fe,Cu) oxides, *Appl. Surf. Sci.*, 2017, **427**, 843–850.
- 14 X. Q. Wang, J. H. Cheng, X. Y. Wang, Y. Z. Shi, F. Y. Chen, X. L. Jing, F. Wang, Y. X. Ma, L. L. Wang and P. Ning, Mn based catalysts for driving high performance of HCN catalytic oxidation to  $\text{N}_2$  under micro-oxygen and low temperature conditions, *Chem. Eng. J.*, 2018, **333**, 402–413.
- 15 Y. S. She, Q. Zheng and L. Li, Rare earth oxide modified CuO/ $\text{CeO}_2$  catalysts for the water-gas shift reaction, *Int. J. Hydrogen Energy*, 2009, **34**, 8929–8936.
- 16 E. S. Ranganathan, S. K. Bej and L. T. Thompson, Methanol steam reforming over Pd/ZnO and Pd/ $\text{CeO}_2$  catalysts, *Appl. Catal., A*, 2005, **289**, 153–162.
- 17 J. Lu, H. Gao, S. Shaikhutdinov and H. J. Freund, Morphology and defect structure of the  $\text{CeO}_2(111)$  films grown on Ru(0001) as studied by scanning tunneling microscopy, *Surf. Sci.*, 2006, **600**, 5004–5010.
- 18 N. Singhania, E. A. Anumol, N. Ravishankar and G. Madras, Influence of  $\text{CeO}_2$  morphology on the catalytic activity of  $\text{CeO}_2$ -Pt hybrids for CO oxidation, *Dalton Trans.*, 2013, **42**, 15343–15354.
- 19 J. F. Chen and H. Yi, Self-assembly of flower-like  $\text{CeO}_2$  microspheres via a template-free synthetic approach and its use as support in enhanced CO and benzene oxidation activity, *Adv. Mater. Res.*, 2011, **310**, 656–661.
- 20 H. Li, G. Lu, Y. Wang and Y. Guo, Synthesis of flower-like La or Pr-doped mesoporous ceria microspheres and their catalytic activities for methane combustion, *Catal. Commun.*, 2010, **11**, 946–950.
- 21 L. Tan, Q. Tao, H. Gao and J. Li, Preparation and catalytic performance of mesoporous ceria-base composites CuO/ $\text{CeO}_2$ ,  $\text{Fe}_2\text{O}_3/\text{CeO}_2$  and  $\text{La}_2\text{O}_3/\text{CeO}_2$ , *J. Porous Mater.*, 2016, **24**, 795–803.
- 22 C. W. Sun, H. Li and L. Q. Chen, Study of flowerlike  $\text{CeO}_2$  microspheres used as catalyst supports for CO oxidation reaction, *J. Phys. Chem. Solids*, 2007, **68**, 1785–1790.
- 23 G. K. Prasad, J. P. Kumar and P. V. R. K. Ramacharyulu, Impregnated charcoal cloth for the treatment of air



- polluted with hydrogen cyanide, *Environ. Prog. Sustainable Energy*, 2013, **32**, 715–720.
- 24 R. N. Nickolov and D. R. Mehandjiev, Comparative study on removal efficiency of impregnated carbons for hydrogen cyanide vapors in air depending on their phase composition and porous textures, *J. Colloid Interface Sci.*, 2004, **273**, 87–94.
  - 25 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.
  - 26 E. C. Njagi, C. H. Chen, H. Genuino, H. Galindo, H. Huang and S. L. Suib, Total oxidation of CO at ambient temperature using copper manganese oxide catalysts prepared by a redox method, *Appl. Catal., B*, 2010, **99**, 103–110.
  - 27 L. Chmielarz, P. Kuśtrowski, R. Dziembaj and E. F. Vansant, Catalytic performance of various mesoporous silicas modified with copper or iron oxides introduced by different ways in the selective reduction of NO by ammonia, *Appl. Catal., B*, 2006, **62**, 369–380.
  - 28 P. W. Ye, Z. Q. Luan and K. Li, The use of a combination of activated carbon and nickel microfibers in the removal of hydrogen cyanide from air, *Carbon*, 2009, **47**, 1799–1805.
  - 29 C. W. Sun, J. Sun, G. L. Xiao, H. R. Zhang, X. P. Qiu, H. Li and L. Q. Chen, Mesoscale organization of nearly monodisperse flowerlike ceria microspheres, *J. Phys. Chem. B*, 2006, **110**, 13445–13452.
  - 30 J. F. Li, G. Z. Lu, H. F. Li, Y. Q. Wang and Y. Guo, Facile synthesis of 3D flowerlike CeO<sub>2</sub> microspheres under mild condition with high catalytic performance for CO oxidation, *J. Colloid Interface Sci.*, 2011, **360**, 93–99.
  - 31 B. Yang, W. Deng, L. Guo and T. Ishihara, Copper–ceria solid solution with improved catalytic activity for hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH, *Chin. J. Catal.*, 2020, **41**, 1348–1359.
  - 32 A. Zhou, J. Wang and H. Wang, Effect of active oxygen on the performance of Pt/CeO<sub>2</sub> catalysts for CO oxidation, *J. Rare Earths*, 2018, **36**, 257–264.
  - 33 R. Xu, X. Wang, D. S. Wang, K. B. Zhou and Y. D. Li, Surface structure effects in nanocrystal MnO<sub>2</sub> and Ag/MnO<sub>2</sub> catalytic oxidation of CO, *J. Catal.*, 2006, **237**, 426–430.
  - 34 W. J. Shen, C. Liu, H. J. Guo, L. H. Yang, X. N. Wang and Z. C. Feng, Synthesis of Zero, One, and Three Dimensional CeO<sub>2</sub> Particles and CO Oxidation over CuO/CeO<sub>2</sub>, *Chin. J. Catal.*, 2011, **32**, 1136–1141.
  - 35 B. Guan, H. Lin, L. Zhu and Z. Huang, Selective Catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> over Mn Ce substitution Ti<sub>0.9</sub>V<sub>0.1</sub>O<sub>2–δ</sub> nanocomposites catalysts prepared by self-propagating high-temperature synthesis method, *J. Phys. Chem. C*, 2011, **15**, 12850–12863.
  - 36 X. Chen, S. A. C. Carabineiro and P. B. Tavares, Catalytic oxidation of ethyl acetate over La–Co and La–Cu oxides, *J. Environ. Chem. Eng.*, 2014, **1**, 344–355.
  - 37 L. Chmielarz, R. Dziembaj, T. Grzybek, J. Klinik, T. Łojewski, D. Olszewska and H. Papp, Pillared smectite modified with carbon and manganese as catalyst for SCR of NO<sub>x</sub> with NH<sub>3</sub>. Part I. General characterization and catalyst screening, *Catal. Lett.*, 2000, **68**, 95–100.
  - 38 Q. Jin, Y. He, M. Miao, C. Guan, Y. Du, J. Feng and D. Li, Highly selective and stable PdNi catalyst derived from layered double hydroxides for partial hydrogenation of acetylene, *Appl. Catal., A*, 2015, **500**, 3–11.
  - 39 W. J. Zhu, X. Chen, J. H. Jin, X. Di, C. H. Liang and Z. M. Liu, Insight into catalytic properties of Co<sub>3</sub>O<sub>4</sub>–CeO<sub>2</sub> binary oxides for propane total oxidation, *Chin. J. Catal.*, 2020, **41**, 679–690.
  - 40 X. J. Yao, L. Chen, T. T. Kong, S. M. Ding, Q. Luo and F. M. Yang, Support effect of the supported ceria-based catalysts during NH<sub>3</sub>–SCR reaction, *Chin. J. Catal.*, 2017, **38**, 1423–1430.
  - 41 R. W. Tarnuzzer, J. Colon, S. Patil and S. Seal, Vacancy engineered ceria nanostructures or protection from radiation-induced cellular damage, *Nano Lett.*, 2005, **5**, 2573–2577.
  - 42 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 La<sub>x</sub>Cu<sub>y</sub>/TiO<sub>2</sub> catalysts at low temperatures, *Microporous Mesoporous Mater.*, 2019, **282**, 260–268.
  - 43 B. R. Strohmeier and D. M. Hercules, Surface spectroscopic characterization of manganese/aluminum oxide catalysts, *J. Phys. Chem.*, 1984, **88**, 4922–4929.
  - 44 W. S. Kijlstra, J. C. M. L. Daamen, J. M. Graaf, E. K. Poels and A. Blik, Inhibiting and deactivating effects of water on the selective catalytic reduction of nitric oxide with ammonia over MnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, *Appl. Catal., B*, 1996, **7**, 337–357.
  - 45 G. D. Ramis, L. Yi, G. D. Busca, M. Turco, E. Kotur and R. J. Willey, Adsorption, activation, and oxidation of ammonia over SCR catalysts, *J. Catal.*, 1995, **157**, 523–535.
  - 46 J. J. Zhang, Z. G. Feng, J. T. Lu and C. S. Cha, Ex situ FTIR reflection–absorption spectroscopic studies of surface films on copper electrode formed in cyanide and thiocyanate solutions, *Chin. J. Inorg. Chem.*, 1990, **6**, 319–323.
  - 47 N. V. Skorodumova, S. I. Simak, B. I. Lundqvist and B. Johansson, Quantum origin of the oxygen storage capability of ceria, *Phys. Rev. Lett.*, 2002, **89**, 166601–166604.

