The Effect of CuO/CeO$_2$ Preparation Methods on the HCN Catalytic Removal Efficiency

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Abstract: In this paper, the porous CeO$_2$ flowerlike spheres support and a series of CuO/CeO$_2$ prepared by different methods were synthesized. The SEM, XRD, BET, H$_2$-TPR and FT-IR characterization were conducted to probe the physicochemical properties of the samples. To evaluate the HCN catalytic removal efficiency over the prepared samples, the breakthrough time of HCN over different samples were investigated. The results implied the CuO/CeO$_2$ prepared by precipitation method (donated as Ce-5) showed highest catalytic activity, the breakthrough time of which was more than 70 min at 30 °C. It was proved the dispersion of CuO phase on the support, the redox properties and the interaction between CuO and CeO$_2$ support over CuO/CeO$_2$ played an important role in the HCN catalytic removal process. FT-IR analysis demonstrated the CuCN was generated due to the chemisorption of CuO and HCN.

1.Introduction

Hydrogen cyanide (HCN), which is colorless and poisonous with boiling point of 26 ℃, comes from various sources, including the combustion of fossil, selective reduction of NOx, polymer pyrolysis and yellow phosphorus production [1-3]. HCN can cause disability and even death by entering the human body through skin penetration and respiratory inhalation and reacting with Fe3+ in the cell to prevent cell respiration [4-6]. Due to the high vapor pressure and volatility and the low molecular weight of HCN, traditional protective materials are difficult to achieve ideal removal efficiency. Therefore, the development of new material which could achieve deep purification of HCN has caused intensive interests.

To our best knowledge, there are main four methods for the removal of HCN, including absorption, combustion, catalytic hydrolysis and catalytic oxidation [7]. Ning et al [8] prepared metal (Cu, Co, Zn) loaded ZSM-5 zeolite materials and investigated its removal ability toward HCN, when loaded with Cu, the HCN breakthrough capacity was enhanced significantly. Krocher [9] studied the HCN removal performance over various catalysts. TiO$_2$ anatase exhibited a high HCN hydrolysis activity and could attain 90% conversion at 400 °C. Wang [10] reported that La$_1$Cuy$_9$/TiO$_2$ showed the best performance for HCN removal, the removal rate of 100 ppm HCN over which could achieve 100%. The addition of La improved the reduction performance of the catalyst and the number of acid sites, which could accelerate the reduction of the hydrolysis by-product NH$_3$ by NH$_3$-SCR reaction. Ma [11] reported the DI-20Al-Ti prepared by self-assembly

method can achieve 100% HCN conversion and 90% CO selectivity at 250°C, which was attributed to its large specific surface area, high dispersion of micropore, and a mass of alkaline sites. Hu [12] prepared Fe-Cu/ HZSM-5 catalytic material by sol-gel method, the HCN conversion and N$_2$ selectivity over which were 100% and 80% at 250°C. The synergetic of bio-metal of Fe-Cu/ HZSM-5 enhance the reduction performance toward HCN due to the increase of dispersion of metal oxide compared with load single metal.

From above analysis, the catalytic materials reported need higher reaction temperature (>200°C) to achieve deep purification of HCN, which cost a lot of energy. Besides, these samples could not meet the requirements of gas mask which is usually employed in the temperature region of -20~30°C. It is urgent to develop a material to show high catalytic activity toward HCN at lower temperature (<30 °C) and could be employed in the gas mask.

CeO$_2$ possesses the property of n-type semiconductor. When loaded with metal oxide, CeO$_2$ can significantly improve catalytic activity, reaction selectivity and stability due to the synergy between metal oxide and CeO$_2$ support [13-14]. Compared with the traditional CeO$_2$, the porous CeO$_2$ flowerlike spheres prepared by hydrothermal method was covered with more oxygen vacancies and Ce^{3+}, and the storage capacity of oxygen was greatly improved. Sun [15] prepared CuO/CeO$_2$ (15 wt.%) and investigated its catalytic performance toward ethanol reforming. The selectively of H$_2$ was 74.1%, and the maximum conversion of ethanol was 88.3%, while the CO were less than 4% at whole reaction temperature range. Tan reported

the catalytic activity of CeO_2 loaded with metal oxide (CuO, Fe_2O_3, La_2O_3) toward styrene conversion. The results indicated that CuO/CeO_2 could achieve higher styrene conversion than other samples due to its more active oxygen species on the surface [16]. Although the CuO/CeO_2 exhibited excellent catalytic performance toward styrene and ethanol, there was hardly reports for the HCN removal. Based on the above analysis, we prepared porous CeO_2 flowerlike spheres and a series of CuO/CeO_2 with fixed mass ratio to investigate the impact of different preparation methods on HCN removal at room temperature, which provide better preparation method of catalytic material.

In this work, the porous CeO_2 flowerlike spheres loaded with CuO species were prepared and were applied for HCN removal at 30 °C. The physicochemical properties were probed by means of XRD, BET, SEM, H_2-TPR and FT-IR analysis, and the effect of preparation methods on samples' catalytic activity were investigated.

2. preparation of catalysts

2.1.preparation of support-CeO₂

In the typical experiment, $C_6H_{12}O_6 \cdot H_2O$ (3.5 g), acrylamide (3.5 g), $Ce(NO_3) \cdot 3H_2O$ (7 g) were dissolved into 180 ml deionized water with magnetic stirring. The ammonia solution (25 wt.%) was added into the solution to adjust the pH value. When the solution became suspension, the color of it became brown during the adding. the suspension was stirred for 3 h. After that, the suspension was transferred into the Teflon-lined autoclave (200 ml), which was sealed and kept at 180 ℃ for 72 h in the electric oven. After cooled to the room temperature. the obtained solution was centrifugally washed by deionized water and alcohol. The porous CeO_2 flowerlike spheres support could be obtained after the precipitate was dried at 80 ℃ for 12 h and calcinated at 550 ℃ for 4 h.

2.2.the preparation of CuO/CeO₂ catalytic material

2.2.1.chemical absorption method

In the typical experiment, ammonia solution (25 wt.%) was added into a 50ml $Cu(NO_3)_2$ solution (1.08 g $Cu(NO_3)_2 \cdot 3H_2O$) at rate of 1 drop/s with magnetic stirring to adjust the pH value of the solution to 9, then CeO_2 powder (4 g) was dispersed into the solution, followed by aging for 30 minutes in ice water. After that, deionized water (200 ml) was slowly added into the above solution with stirring. Upon the addition of the deionized water, the solution became murky, and then standed still for 2 h without stirring. After removing water layer, the precipitate was centrifugally washed with deionized water and alcohol until the upper liquid was colorless, and then dried at 80 ℃ for 12h. The catalytic material donated as Ce-1 was obtained after calcination at 450 ℃ for 4h.

2.2.2.K₂C₂O₄ impregnation method

In the typical experiment, CeO2 powder (4 g) and K2C2O4 (1.35 g) was dissolved into deionized water (50 ml) with magnetic stirring, which was followed by addition of 20 ml solution of Cu(NO3)2(1.08 g Cu(NO3)2·3H2O) at the rate of 1 drop/s with stirring. After titration of the solution of Cu(NO3)2, stirring for 4 h to get suspension. Then the suspension was washed by deionized water and alcohol until the upper liquid became colorless. The precipitate was dried 80℃ for 12 h, and then was calcined at 450℃ for 4 h. The acquired material was donated as Ce-2.

2.2.3.Equal volume impregnation method

The Cu(NO3)2 · 3H2O (1.08 g) was dissolved into deionized water (50ml), which was followed by addition of CeO2 powder (4 g) with magnetic stirring. Then solution was standed still for 24 h. After that, the upper liquid was evaporated, the material got by evaporation was dried at 80℃ for 12 h. Then the dried was calcined at 450 ℃ for 4 h. The catalytic material donated as Ce-3 was obtained after calcination at 450 ℃ for 4 h.

2.2.4.Coprecipitation method

The Cu(NO3)2 · 3H2O (1.08g) and Ce(NO3)3 · 6H2O (12.6g) were dissolved into deionized water(160ml) with magnetic stirring, subsequently adding C6H12O6·H2O (6.3g) and acrylamide (6.3g) to the solution. After that, ammonia solution (mass fraction of 25%) was injected into the above solution to adjust the PH value to 10. This solution mixture was stirred for 3 h before washed by deionized water and alcohol. The solution was washed until the upper liquid was colorless. Then the precipitate was dried at 80℃ for 12h, and then calcined at 450 ℃ for 4 h. The obtained catalytic material was donated as Ce-4.

2.2.5.Precipitation method

The CeO2 powder (4g) was impregnated into deionized water (40 ml) with magnetic stirring, which became the suspension. The 50ml solution of Cu(NO3)2·3H2O (1.08g) was added into the suspension at rate of 1 drop every second with stirring. After that, NaCO3 (1 mol/L) was added to the suspension to make the pH value to 9. Then acquired suspension was stirred for 5h at room temperature to guarantee the reaction was finished completely, and then standed still for 24 h. The acquired upper liquid was taken out, and the precipitate was washed by deionized water and alcohol till the upper liquid became colorless, and then dried at 80℃ for 12h. The Ceria-supported CuO was obtained by calcination at 450 ℃ for 4h. The catalytic material after calcination was donated as Ce-5.

2.3.The active evaluation of catalytic materials

The catalytic activity tests of the prepared samples toward HCN were carried out in a quartz tube (with an inner diameter of 5 mm) on a fixed bed loaded with 0.25 g samples. The whole device was self-made which was shown in Figure 1. The experimental processes were as followed: the air purified by the Quadruple Scrubber and HCN with certain flow rate were obtained by setting the Mass Flow Controller, by changing the flow rate of air, the water content could be adjusted via being diverted to the water bubbler, then 130 mg/m3 HCN with 5 vol.% H2O was introduced into the catalytic material bed. The exhaust gas was absorbed by the NaOH solution (1 mol/L).

The removal performance of all samples toward HCN was carried out at the condition of 20.4 vol.% O2, 5vol.% H2O and 61146 h-1. The concentration of HCN (mg/m3)

at the outlet was detected by Spectrophotometry of isonicotinic acid-pyrazolone solution, the detection limits of which was 0.005 mg/L. The catalytic activity of samples was evaluated by the breakthrough time when the HCN removal rate was lower than 100%. The HCN removal rate at different reaction time was calculated as follows:

$$Y = \left(1 - \frac{C}{C_0}\right) * 100\% \qquad (1)$$

the Y is the HCN removal rate, the C_0 (mg / m3) is the inlet concentration of HCN, the C (mg / m3) is the outlet concentration of HCN.
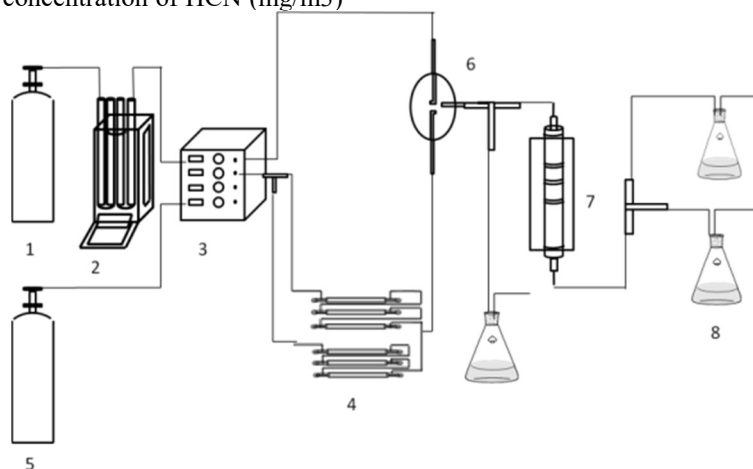

Figure 1 The device for active evaluation of catalytic materials.1. air cylinder, 2. Quadruple Scrubber 3. Mass Flow Controller, 4. Saturated Vapor Generator, 5. HCN cylinder, 6. Mixed ball, 7. Power Tube, 8. NaOH absorbent.

3.Results and Discussion

3.1 The results of SEM

SEM of CeO2 and catalytic materials prepared by different methods was shown in Figure 2. As presented in Figure 2(1), the CeO2 exhibited flowerlike mesoporous sphere with diameter of 2~3μm, which proved the CeO2 were synthesized successfully. After loaded with CuO species, all samples still showed sphere structure, indicating CuO loaded couldn't significantly change the structure of the CeO2 support. From the figure 2(2) and 2(6), it can be seen that pore structure was formed by interweaved nanosheets on the surface of support, which testified CuO particles were uniformly dispersed on the CeO2 support. Figure 2(3), 2(4) and 2(5) showed there are a mass of irregular particles on the support which confirmed CuO was agglomerated on the support and weren't uniformly dispersed. From SEM figures, we concluded that different preparation methods of catalytic materials can influence the dispersion of active species.

EDS of catalytic materials from different preparation methods was presented in Figure 3. The actual load amount of CuO from all samples were obtained from EDS analysis and listed in Table 1, which demonstrated actual
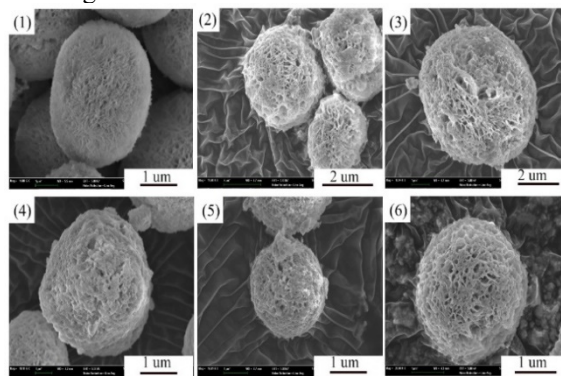
CuO loading were around 8%~10%.

Figure 2 SEM images of support and CuO/CeO₂ catalytic materials from different methods:(1) CeO₂ (2) Ce-1, (3) Ce-2, (4) Ce-3, (5) Ce-4, (6) Ce-5
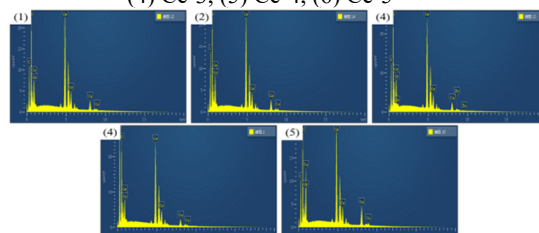

Figure 3 EDS of Cu/CeO₂ catalytic material from different methods: (1) C-1, (2) C-2, (3) C-3, (4) C-4, (5) C-5

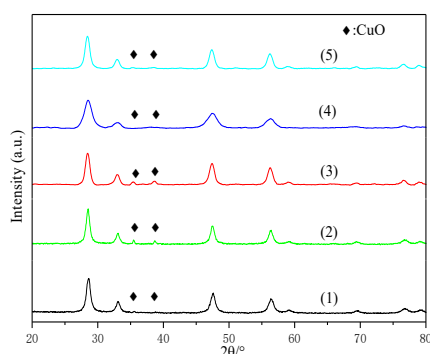## 3.2. The results of XRD and BET

Figure 4 XRD patterns of Cu/CeO₂ from different methods: (1) Ce-1, (2) Ce-2, (3) Ce-3, (4) Ce-4, (5) Ce-5

As observed in the Figure 4, all samples exhibited main reflections at 28.8 °, 33.1 °, 47.8 °, 56.5 °, 59.5 °, 69.3 °, 77.1 ° and 79.2 ° in the XRD patterns corresponding to the distinct cubic fluorite diffraction pattern of CeO2 (JCPDS 34-0394) which implied the structure of CeO2 was not changed after CuO loaded [17], the results were consistent with SEM analysis. The distinct characteristic diffraction peaks of CuO were observed at 2 θ=35.4° and 38.7°. According to the Scheler's formula, the crystal size of CuO particles were calculated and the results were listed in Table 1. It could be observed the crystal sizes of Ce-2 and Ce-3 were larger than others owing to the accumulation of CuO on the support. For Ce-4, the intensity of its diffraction peak were lower than others, and the crystal size of CuO particle was smallest, which might be explained the CuO doped into the lattice of CeO2, and formed the Cu-Ce-O solid solution [18]. The surface area of all samples was measured by BET. It could be observed that surface area of C-5 (61.478 m2/g) was the largest. The large surface area was beneficial to increase dispersion of CuO on the surface of support and enhanced the interaction between CuO and CeO2 support, which limited the accumulation of CuO.

Table 1 Actual load, surface area and crystallite size of samples

Sample	CuO loading[a] (wt.%)	Surface area/(m²/g)	Crystallite size[b]/nm
Ce-1	8.63	60.3	19.4
Ce-2	8.57	57.6	28.2
Ce-3	8.10	58.3	30.3
Ce-4	9.34	50.6	16.3
Ce-5	9.28	61.5	18.3

[a] Calculated by EDS [b] Calculated by Scheler's formula.

3.3. The results of H₂-TPR.

The H2-TPR of all samples were presented in the Figure 5. Three groups of characteristic peaks could be observed in each sample. The peak of α was attributed to the reduction of Cu2+ to Cu+. The peak of β could be ascribed to the reduction of Cu+ to Cu. The peak of γ came from the reduction of active oxygen species on CeO2 [15]. According to the literature [16], the reduction peak of CuO were located at 350 ℃, however, in Figure 5, the peaks from samples all transferred to the low temperature region. It could be explained that the reductive temperature of CuO was related to the dispersion of CuO on the support. The highly dispersed CuO can enhance the interaction between support and active species, and decrease the reductive temperature of CuO. It can be concluded that Ce-5 presented the best redox properties among all samples.
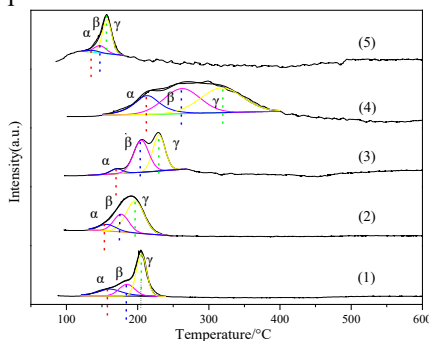

Figure 5 H₂-TPR of Cu/CeO₂ from different synthetic methods: (1) Ce-1, (2) Ce-2, (3) Ce-3, (4) Ce-4, (5) Ce-5

3.4. Catalytic activity

Figure 6 showed the HCN removal performance over different samples at the condition of 30 ℃, 61146 h-1and 5 vol.% H2O. As presented, the catalytic activity toward HCN of all samples followed this order: Ce-5 > Ce-1 > Ce-3 > Ce-2 > Ce-4. The breakthrough time of Ce-4, Ce-3 and Ce-2 were all less 40 min, and the C-4 showed the worst HCN removal activity, the removal rate of which was less than 100% after reaction for 20 min. Among all samples, Ce-5 showed the highest catalytic activity toward HCN, the breakthrough time of which was more than 70 min, even at 90 min, the HCN removal rate over Ce-5 was still more than 95%. In our previous study, the catalytic activity of CeO2 toward HCN was the lowest, the HCN

removal rate was lower than 10% when the reaction time exceeded 80 min. The CuO phase in the prepared samples played an important role in the HCN catalytic removal.
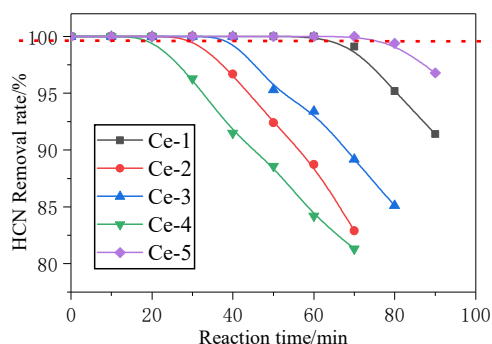

Figure 6 HCN removal rate of Cu/CeO_2 from different methods at the condition of 30°C, 61146h^{-1}, 5 vol.%H_2O

3.5.FT-IR analysis

Figure 6 implied that Ce-5 exhibited the highest catalytic activity, to examine the interaction between Ce-5 and HCN, the FT-IR analysis of Ce-5 before and after reaction were conducted and the results were shown in Figure 7.

The characteristic bonds at 3412.3 cm-1 and 1650.6 cm-1 were ascribed to the stretching vibration of -OH and the bending vibration of H2O adsorbed [19]. The absorption band at 774.2 cm-1 was assigned to the Ce-O asymmetric stretch [20]. And the absorption bond at 1319.2 cm-1 and 1108.2 cm-1 were attributed to the stretch vibration of CO_3^{2-} and stretch vibration of C-H [21].

In the spectra of Ce-5 after reaction, a new peak corresponding to the absorbance of CuCN could be observed at 2142.5 cm-1 [22], which indicated CuCN was generated on the surface of CuO/CeO2 due to the chemisorption.
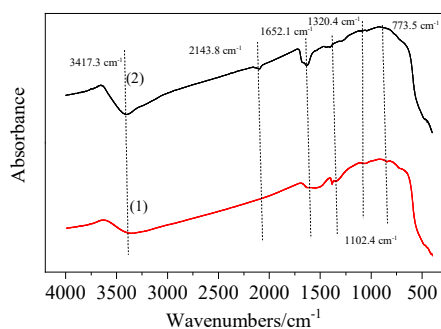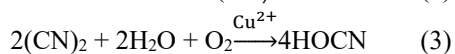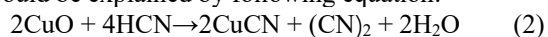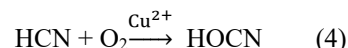

Figure 7 The FT-IR spectra of Ce-5: (1) before reaction (2) after reaction

3.6.Discussion

Based on above analysis, the CuO phase on the CeO2 support contributed to the high HCN removal efficiency over prepared samples, the interaction between CuO and HCN could be explained by following equation:

$$2CuO + 4HCN \rightarrow 2CuCN + (CN)_2 + 2H_2O \quad (2)$$

$$2(CN)_2 + 2H_2O + O_2 \xrightarrow{Cu^{2+}} 4HOCN \quad (3)$$

Besides, the HCN could also be converted directly to HOCN with the participation of O2 according to the literature reported.

$$HCN + O_2 \xrightarrow{Cu^{2+}} HOCN \quad (4)$$

The reason why Ce-5 showed the highest catalytic activity toward HCN among all samples prepared by different methods was analyzed based on the experimental results and the SEM, XRD, BET and H2-TPR characterization. The dispersion of CuO particles, the interaction between CuO and CeO2 support as well as redox properties all influenced the activity for HCN removal. The XRD results implied the CuO species had smaller crystal size (18.3 nm) due to the stronger interaction between CuO and CeO2 support. The SEM and BET analysis implied the CuO had high dispersion on the support. The lower reduction temperature of Ce-5 in the H2-TPR spectra showed the excellent redox properties as results of the reduction of easily reduced metal species and the stronger interaction between CuO and CeO2.

4.Conclusion

Experimental results indicated the catalytic activity of samples were influenced greatly by the preparation methods, among all methods, the precipitation method was proved to be suitable for preparing catalytic materials with high activity. The breakthrough time of HCN over Ce-5 was more than 70 min at the condition of 30 °C,61146 h-1 and 5 vol%H2O. Combined with the results of SEM, XRD, BET and H2-TPR, the HCN removal performance of catalytic materials was closely related to the dispersion of CuO species on the support, the interaction between CuO species and support as well as redox properties.

Acknowledge

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