

# Hydrolysis and oxidation on AC–Cu–CoSPc–Ce catalyst for removal of HCN

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**Keywords:** HCN; hydrolysis; oxidation; Modified activated carbon

**Abstract :** A series of catalysts were studied for removal efficiency of hydrogen cyanide (HCN) under micro-oxygen conditions. It was found that activated carbon modified by Cu, Ce, and cobalt sulfonated phthalocyanine (CoSPc) denoted as AC–Cu–CoSPc–Ce showed significantly enhanced catalysis ability. The influences of preparation conditions on catalytic activity were studied, which were the kinds of additive, calcination temperatures, and oxygen concentration. The effects of the calcination temperatures on the catalyst were characterized by scanning electron microscopy (SEM). The AC–Cu–CoSPc–Ce catalyst showed >98% conversion of HCN at 200–350 °C. We concluded that AC–Cu–CoSPc–Ce could be used as a catalyst for the removal of HCN by simultaneous hydrolysis and oxidation.

## Introduction

Hydrogen cyanide (HCN) is a type of colorless and acutely poisonous compounds existing in vehicle exhaust emissions [1–2], chemical processing [3], and typical industrial tail gas [4,5] etc. In addition, HCN is observed as an unfortunate byproduct of NO<sub>x</sub> removal processes [6,7,8]. As HCN in various gases not only pollute the environment but also poison the catalysts [7], many methods have been developed to remove HCN from tail gas. The main technologies for HCN removal include adsorption [9,10,11,12], combustion [6], catalytic oxidation [4,8] and catalytic hydrolysis [13,14], etc. Among these methods, the adsorption method is widely used for HCN removal, especially aiming at the development of new adsorbents, particularly supported metal oxides [10,11]. Recently, catalytic method was recognized as the most promising process due to the harmless, no secondary pollution, and higher conversion efficiency. However, only a few reports could be found focused on the catalytic decomposition of HCN.

O.Kröcher and co-workers [7] carried out a detailed investigation of the HCN hydrolysis and oxidation over heterogeneous catalysts. With O<sub>2</sub> and H<sub>2</sub>O present, the maximum selectivity of N<sub>2</sub> was about 40% using Cu-ZSM-5 at 400 °C. Zhao et al tested a 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> oxidation catalyst [8]. They found that in the presence of excess oxygen, the strongly bound reaction intermediate CN<sup>–</sup> is fully oxidized only above 400°C. Nanba et al. found that H-ferrierite coated on cordierite monoliths

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converted about 78% of 250 ppm HCN at a GHSV of 21,200 h<sup>-1</sup> and a temperature of 500 °C in the presence of water and oxygen [15]. The main reaction was the hydrolysis of HCN to NH<sub>3</sub> and CO, but above 400 °C, small amounts of CO<sub>2</sub> were also found, pointing to the partial oxidation of HCN at these temperatures.

In this study, the simultaneous hydrolysis and oxidation of HCN is investigated using AC-supported catalysts at micro-oxygen conditions. In the present work, Cu is chosen as the active ingredient. It was found that activated carbon modified by sulfonated cobalt phthalocyanine (CoPcS) showed significantly enhanced catalytic activity. Mei and Wang reported that CoPcS could create additional oxidation sites [16,17]. CeO<sub>2</sub>, which possesses high oxygen storage capacity and excellent redox property [18], is also investigated as one of the catalyst active ingredient for HCN removal. For the assessment of the catalytic materials, scanning electron microscopy (SEM) was accomplished.

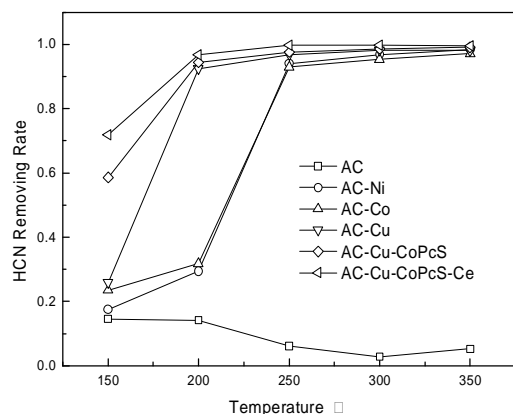
## Materials and methods

**Catalyst preparation.** All catalysts have been prepared by impregnation method. Activated carbon (AC) prepared from commercial coal-derived carbon was used as catalyst supports in the experiments. AC samples were impregnated with the Cu(NO<sub>3</sub>)<sub>2</sub> solution (0.1 mol/L, 50 mL), Ni(NO<sub>3</sub>)<sub>2</sub> solution (0.1 mol/L, 50 mL), Ni(NO<sub>3</sub>)<sub>2</sub> solution (0.1 mol/L, 50 mL), the combination of Cu(NO<sub>3</sub>)<sub>2</sub> solution (0.1 mol/L, 50 mL) and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution (0.01 mol/L, 50 mL), or the combination of Cu(NO<sub>3</sub>)<sub>2</sub> solution (0.1 mol/L, 50 mL), Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution (0.01 mol/L, 50 mL), and CoSPc solution (0.05 g/ 50 mL·10% NaOH), respectively. The impregnation was carried out under stirring for 24 h, and then the reaction solution was filtered to give the catalyst, which was dried at 110 °C for 12 h, followed by calcination at a specific temperature (250–450 °C) in a muffle furnace. Samples impregnated with different impregnants were denoted as AC–Cu, AC–Ni, AC–Co, AC–Cu–CoPcS and AC–Cu–CoPcS–Ce, respectively.

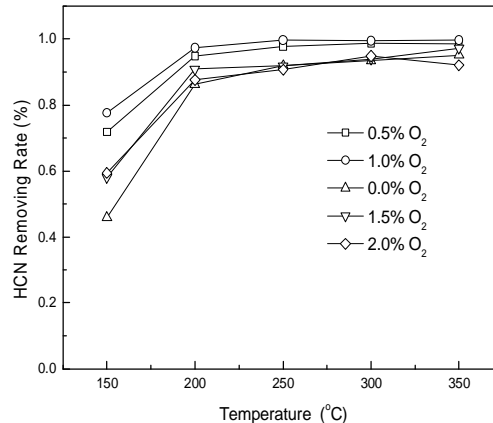
**Catalytic Activity Measurement.** The experiments were carried out in a fixed bed quartz reactor with a temperature range of 150–350 °C. HCN was measured through the iso-nicotinic-acid-3-methy-1-phenyl-5-pyrazolone spectrophotometric method. The component distribution and analysis on the surface of samples was studied by SEM. SEM produced by the Japanese Hitachi electronic and field emission of S4800.

## Results and discussion

**Effects of modifiers on HCN simultaneous hydrolysis and oxidation.** Six catalysts modified with different impregnants, denoted as AC, AC–Cu, AC–Ni, AC–Co, AC–Cu–CoPcS, AC–Cu–CoPcS–Ce, were studied and their catalysis capacities were measured and compared in dynamic removal capacity tests of HCN. The HCN removal rate curves of the above catalysts are plotted in Fig. 1. Compared with AC, AC–Ni, and AC–Co, sample AC–Cu displayed a significant improvement on HCN removal. What's more, it can be seen that the ability of HCN removal displayed a further improvement after the addition of CoPcS and Ce. This might because CoPcS can increase the oxidation function of catalyst, and Ce can further improve its redox property. Thus, the removal efficiency of AC–Cu–CoPcS–Ce was improved.



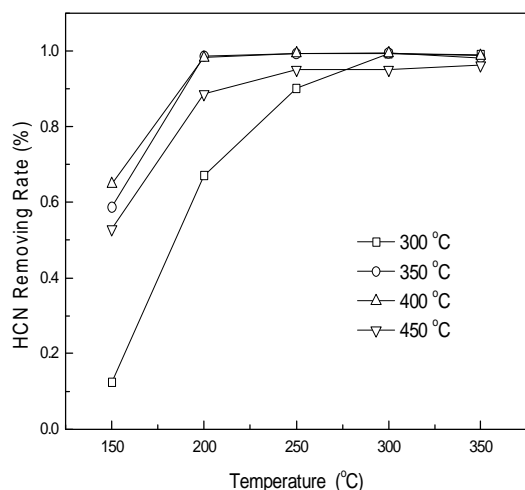
**Fig. 1.** Catalytic performance of HCN on different catalysts. Reaction conditions: 5% H<sub>2</sub>O, and 0.5% O<sub>2</sub>. AC was included as reference samples.



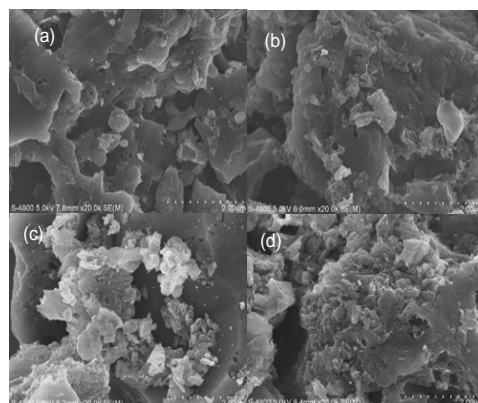
**Fig. 2.** Catalytic performance of HCN over AC-Cu-CoPcS-Ce with different oxygen contents. Reaction conditions: 5% H<sub>2</sub>O.

**Effects of the oxygen content.** Fig. 2 shows how the oxygen content affects the coupled catalysis of HCN on AC-Cu-CoPcS-Ce at a variety of temperatures between 150 and 300 °C. It was found that the removal rate of HCN with 1.0% O<sub>2</sub> is the highest compared to than that with other oxygen contents. The oxygen content is also one of the important factors that influence HCN purification efficiency, and we sought to identify the optimal O<sub>2</sub> content for AC-Cu-CoPcS-Ce catalytic activity. The reason that the highest removal rate of HCN was achieved with 1.0% O<sub>2</sub> is that AC-Cu-CoPcS-Ce catalysis is limited at lower oxygen content and thermally unstable at higher oxygen content.

**Effects of calcination temperature.** AC-Cu-CoPcS-Ce catalysts prepared at different calcination temperatures (300 °C, 350 °C, 400 °C, 450 °C) were selected for study. The effects of calcination temperatures on the AC-Cu-CoPcS-Ce catalysts for HCN removal are shown in Fig. 3. These data show that the calcination temperature is an important factor that influences the HCN removal efficiency. As the calcination temperature increased from 300 °C to 400 °C, the removal rate of HCN increased markedly. The AC-Cu-CoPcS-Ce catalyst calcined at 400 °C exhibited the best catalytic activity. However, when the calcination temperature was higher than 400 °C, the HCN removal efficiency decreased with increasing calcination temperature. If the calcination temperature is too high, it can accelerate carbon decomposition, which leads to a reduction of the activity of the catalyst [19].



**Fig. 3.** Catalytic performance of HCN over AC-Cu-CoPcS-Ce at different calcination temperatures. Reaction conditions: 5% H<sub>2</sub>O, and 1% O<sub>2</sub>.



**Fig. 4.** SEM images of AC-Cu-CoPcS-Ce calcined at different temperatures: (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C.

**SEM analysis.** The qualitative elemental analysis of SEM on part of the catalyst surface are shown in Fig. 4. SEM micrographs showed that the AC had rough areas containing various irregularly-shaped particles. Comparing the four catalysts of different calcination temperature, after calcined at 400 °C, the AC-Cu-CoPcS-Ce surface showed more bright areas with various dimensions and shapes in the SEM micrographs (Fig. 4(c)). There was a relatively large AC surface area covered by modifier during the calcination, indicating better active phase dispersion on this support. Therefore, the brighter area shown in the SEM of Fig. 4(c) represents components with higher atomic number, and the darker area corresponds to carbon. There is not much difference between Fig. 4(a) and Fig. 4(b), which correspond to the SEM image of activated carbon calcined at 300 °C and 400 °C, respectively. However, slight ashing could be seen in Fig. 4(d), which may be due to carbon decomposition caused by a higher temperature calcination.

## Conclusions

In order to develop highly efficient and stable catalysts for the decomposition of HCN by simultaneous hydrolysis and oxidation, AC based catalysts loaded with metal oxides were prepared in this study and their catalytic activity was tested. Comparing with other catalysts, Cu, Ce, and CoSPc modified AC showed a significant improvement on HCN catalysis. The AC-Cu-CoSPc-Ce catalyst showed >98% conversion of HCN at 200–350 °C. By exploring different reaction conditions, the optimal oxygen content was determined as 1.0% O<sub>2</sub>. The AC-Cu-CoPcS-Ce catalyst calcined at 400 °C exhibited the best catalytic activity. The SEM results illustrate that the calcination temperature can control the formation of the crystalline phase. It was concluded that Cu, Ce, and CoSPc modified AC promises a good candidate for hydrolysis and oxidation of HCN.

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