Removal of HCN over Mn based catalysts under low temperatures

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Abstract. Mn-based catalysts were synthesized by a sol-gel method and implied to removal of HCN under low temperature and micro-oxygen conditions. The results show the catalysts that modified by manganese oxide have superior catalytic oxidation activity for HCN conversion. Furthermore, the introduction of barium can promote the selective catalytic oxidation of HCN to N₂. The introduction of H₂O apparently inhibited the conversion efficiency of HCN, and the H₂O could restrain the production of N₂ yield at lower temperature but it nearly had no effect on N₂ yield at higher temperatures.

1. Introduction

Hydrogen cyanide (HCN) is a very toxic and harmful gas, which discharges directly will cause serious harm to the atmospheric environment and human health. When HCN enters human body through human organs such as skin, respiratory tract or digestive tract, which will lead to a variety of diseases that effect the normal function of the human body [1, 2]. A short time inhalation of high concentrations of hydrogen cyanide gas can make human death immediately [3]. In general, HCN usually have a variety of sources, including the exhaust of existing motor vehicles [4], nitrogen oxides and hydrocarbons (HC-SCR) selective catalytic reduction [5], Three-Way catalyst TWC) [9], urea-SCR processes [6], biological and fossil fuels such as coal combustion and petroleum processing [7]. Yellow phosphorus tail gas and calcium carbide furnace exhaust also contain a small amount of HCN, in which a lot of CO simultaneously exists that can be used as a chemical raw material (C1) or high-quality fuel [8]. However, HCN in the tail gas will poison significantly the carbonyl synthesis catalyst and the shift catalyst [5] and produce slow and long-term corrosion of industrial pipelines. It greatly reduces the exhaust gas utilization and recycling of resources. In order to make full use of CO to synthesize various and valuable organic compounds, it is necessary to remove the HCN out of the exhaust gas. In addition, HCN is considered to be the main intermediate of nitrogen oxides, such as NO₂, NO, N₂O, which lead to the secondary pollution [10], Aho et al. [11], like greenhouse effect and photochemical smog, etc [12]. Thus far, only few studies focused on the conversion of HCN to N₂, which is harmless to the atmospheric environment. Therefore, it is imperative to develop an industrial technology that make HCN conversion or selective conversion to N₂, which the subject we study is of great significance.

Mn-based catalysts, which could be treated as a candidate for the removal of HCN in this work, was due to its high catalytic activities and unique redox properties under low temperatures. In this study, Mn-based catalysts were prepared by sol-gel method and tested in various conditions. Furthermore, the effect of the introduction of barium on the selective catalytic oxidation of HCN to N₂ was investigated.
2. Experimental section

2.1. Samples preparation
Mn-based catalysts were made by a sol-gel method. Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} (Aldrich 97%) as the precursor of the carrier. First, a certain amount of Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} was added to the anhydrous ethanol, and then the corresponding proportions of citric acid (citric acid / M = 1, molar ratio), acetic acid, and were successively added to the mixture. After vigorous stirring at 40°C in a magnetic stirrer for about 1 h, a yellow liquid obtained. Then the hydrolyzed manganese acetate and barium chloride solution was slowly added dropwise. The mixture was stirred at 60°C until it became a viscous gel and vaporized at 80-120°C for 6-7 days until the dry-gel was obtained. Finally, the xerogel was calcined at 550 °C for 5 h in a muffle furnace. The ratio of butyl titanate, deionized water, glacial acetic acid and absolute ethanol was 1: 1: 0.5: 5.

2.2. HCN removal measurement
In order to obtain more precise experimental data, the effluent gas was analyzed after a continuous reaction for 10 min at each temperature. The production that NO\textsubscript{x} (NO and NO\textsubscript{2}), and N\textsubscript{2}O were detected by a gas chromatography (FULI, 9790Ⅱ). The tail gas was absorbed after for 10 min at each continuous reaction temperature, then the HCN was measured through the snicoticinic-acid-3-methyl-1-phenyl 5-yrazolone pectrophotometric method. NH\textsubscript{3} was determined by sodium hypochlorite-salicylic acid clectrophotometry. N\textsubscript{2} can be calculated by the N-balances and C-balances.

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S_{\text{HCN}} = \frac{c_{\text{HCN in}} - c_{\text{HCN out}}}{c_{\text{HCN in}}} \times 100\% \quad (1)
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\[
S_{\text{N}_2} = 2 \frac{c_{\text{N}_2 \text{ out}}}{c_{\text{HCN in}} - c_{\text{HCN out}}} \times 100\% \quad (2)
\]
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S_{\text{NO}_x} = \frac{c_{\text{NO}_x \text{ out}}}{c_{\text{HCN in}} - c_{\text{HCN out}}} \times 100\% \quad (3)
\]
\[
c_{\text{N}_2} = \frac{c_{\text{HCN in}} + c_{\text{NH}_3 \text{ out}} + c_{\text{NO}_x \text{ out}} + c_{\text{HCN out}}}{2} \times c_{\text{N}_2 \text{O out}} \quad (4)
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2.3. Characterization
X-ray photoelectron spectroscopy (XPS) analyses were conducted on a Thermo ESCALAB 250XI, with an Al K\textalpha anode (hv =1486.6 eV). The O 1s photoelectron lines were measured in XPS mode. The photon energy scale was calibrated using C 1s of saturated carbon at 284.8 eV.

3. Results and discussion

3.1 Effect of different active components on HCN removal
In this experiment, pure TiO\textsubscript{2}, pure TiO\textsubscript{2} modified by manganese and barium were selected as the catalysts for removal of HCN with 0.2vol%O\textsubscript{2} at the reaction temperature from150 to 350°C were investigated. As shown in the Fig.1, compared to the pure TiO\textsubscript{2}, HCN conversion efficiency enhanced obviously when the active components were introduced, and the catalysis activity of pure TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} catalyst can be neglected. The barium supported on TiO\textsubscript{2} showed a little higher activity, which reached the highest HCN conversion about 40% at 350°C. Compared to the barium-based catalyst, it can be observed that the excellent performance of MnOx/TiO\textsubscript{2} on HCN removal at the whole reaction temperature ranged from 100 to 350°C, of which the HCN conversion activity approximate 1-3 times higher than that of the corresponding catalysts in this experiment. From the above mentioned, the introduction of manganese oxide played a positive role in removal of HCN.
3.2 Effect of different active components on HCN conversion and the production distribution

HCN conversion, NOx and N₂ yield over 15%MnOₓ/TiO₂ and 5%Ba-10%Mn-O/TiO₂ catalysts under 0.2vol% O₂ concentration are presented in Fig.2a, 2b and 2c. From the results provided in Fig.2a, there was almost no difference between these two catalysts on HCN catalytic activity under the reaction temperatures, and nearly full HCN conversion were obtained above 250°C. But concerning NOx and N₂ yield, as observed in Fig. 2b and 2c, compared to that of MnOₓ/TiO₂ catalyst, the NO yield sequentially decreased with the temperature from 200 to 300 °C over the 5%Ba-10%Mn-O/TiO₂ catalysts. This result that may be attributed to the introduction of BaO significantly enhanced the NOx storage capacity, which could offer relatively high thermal stability to nitrate by its strong surface basicity [13]. The storage NOx could react with NH₃ to produce N₂, which is known as NOx nonselective catalytic reduction reaction. The NH₃ was produced by the re-absorbed water produced by the HCN oxidation reaction hydrolyzed HCN simultaneously. So barium as the NOx storage component and the manganese as the component for NO oxidation significantly improved the HCN oxidation to N₂, which was in agreement with Xiao et al. concluded [14]. As expected above, the N₂ yield over 5%Ba-10%Mn-O/TiO₂ catalyst extremely was higher extremely than the MnOₓ/TiO₂ catalyst at all temperatures tested. Therefore, the added barium enhanced the HCN catalytic oxidation to N₂.
3.3 Effect of H2O on HCN conversion and the production distribution

Compared to the condition that H2O was absent, the effect of H2O on HCN conversion, NOx and N2 yield over 5%Ba-10%Mn-O/TiO2 catalysts under 0.2vol%H2 concentration are shown in Fig.3a, 3b and 3c. The introduction of H2O apparently inhibited the conversion efficiency of HCN [15]. The presence of H2O greatly increased the NO yield at lower temperatures from 150 to 250°C, which may be due to the completion adsorption from H2O. But at higher temperatures, it was obvious that the HCN conversion in the presence of H2O was nearly the same as in the absence of H2O. This result may be because that the higher temperature will encouraged the H2O to desorption from the surface of the catalyst. Concerning the N2 yield, as observed in Fig. 3c, the N2 yield sequentially decreased with the temperature from 150 to 250 °C and then nearly had no change above 250°C, which indicated that the H2O could restrain the production of N2 yield at lower temperature but it nearly had no effect on N2 yield at higher temperatures.
Fig. 3 (a) (b) (c) the effect of 5% H$_2$O on removal efficiency of HCN conversion, NOx and N$_2$ yield over 5% Ba-10%Mn-O/TiO$_2$ at the temperature ranged from 100 to 350°C

4. Conclusions
We have studied HCN removal behavior on Mn- based catalysts under low temperature and micro-oxygen conditions. We found that the pure TiO$_2$ modified by manganese oxide has greatly enhanced the sample removal ability for HCN. In addition, considering the products of HCN, the introduction of barium promoted the selective catalytic oxidation of HCN to N$_2$. The added H$_2$O apparently inhibited the conversion efficiency of HCN, and the H$_2$O could restrain the production of N$_2$ yield at lower temperature but it nearly had no effect on N$_2$ yield at higher temperatures.

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