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 N_2. The introduction of H_2O apparently inhibited the conversion efficiency of HCN, and the H_2O could restrain the production of N_2 yield at lower temperature but it nearly had no effect on N_2 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 NO_2, NO, N_2O, 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 N_2, which is harmless to the atmospheric environment. Therefore, it is imperative to develop an industrial technology that make HCN. conversion or selective conversion to N_2, 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 N_2 was investigated.

2. Experimental section

2.1. Samples preparation

Mn- based catalysts were made by a sol-gel method. $Ti(OC_2H_5)_4$ (Aldrich 97%) as the precursor of the carrier. First, a certain amount of Ti $(OC_2H_5)_4$ 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 NOx (NO and NO_2), and N_2O were detect 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 so-nicotinic-acid-3-methy-1-phenyl 5-yrazolone pectrophotometric method. NH_3 was determined by sodium hypochlorite-salicylic acid ectro-potometry. N_2 can be calculated by the N-balances and C- balances.

$$S_{HCN} = \frac{C_{HCN\ in} \quad C_{HCN\ out}}{C_{HCN-in}} \times 100\% \quad (1)$$

$$S_{N_2} = 2\frac{C_{N_2\ out}}{C_{HCN-in} \quad C_{HCN\ out}} \times 100\% \quad (2)$$

$$S_{NO_X} = \frac{C_{NO_X\ out}}{C_{HCN-in} \quad C_{HCN\ out}} \times 100\% \quad (3)$$

$$C_{N_2} = \frac{C_{HCN\ in} - C_{NH_3\ out} - C_{NO_X\ out} - C_{HCN\ out}}{2} - C_{N_2O\ out} \quad (4)$$

2.3. Characterization

X-ray photoelectron spectroscopy (XPS) analyses were conducted on a Thermo ESCALAB 250XI, with an Al Kα 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

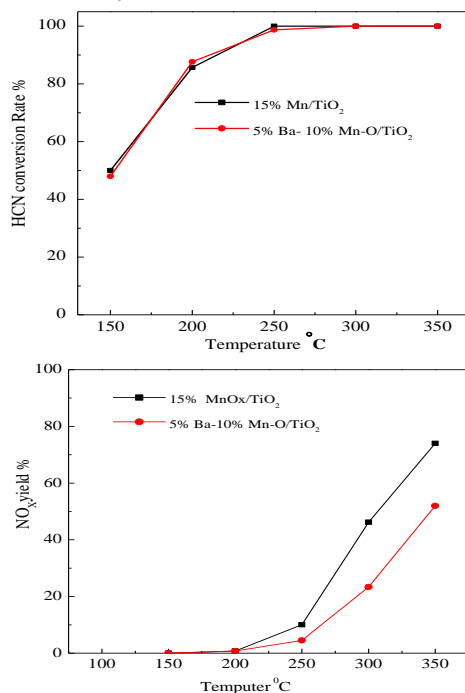### 3.1 Effect of different active components on HCN removal

In this experiment, pure TiO_2, pure TiO_2 modified by manganese and barium were selected as the catalysts for removal of HCN with $0.2vol\%O_2$ at the reaction temperature from150 to 350°C were investigated. As shown in the Fig.1, compared to the pure TiO_2, HCN conversion efficiency enhanced obviously when the active components were introduced, and the catalysis activity of pure TiO_2-Al_2O_3 catalyst can be neglected. The barium supported on TiO_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 $MnOx/TiO_2$ 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.
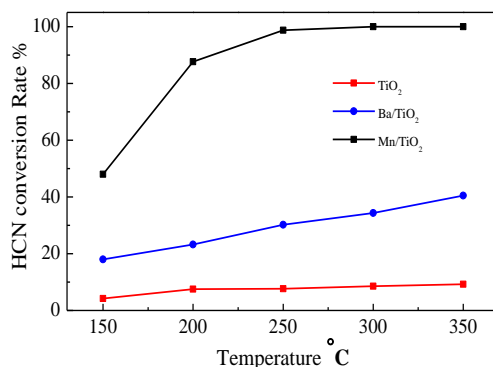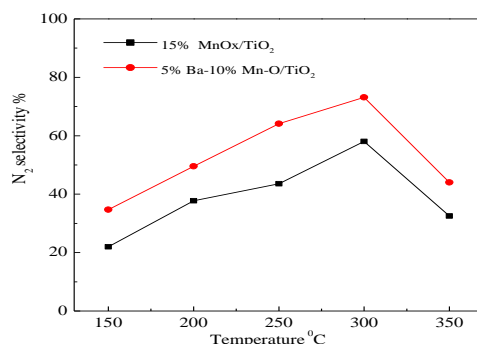
Fig.1 The removal of HCN in different active components at the reaction temperature from150 to 350°C

3.2 Effect of different active components on HCN conversion and the production distribution

HCN conversion, NOx and N_2 yield over 15%MnOx/TiO$_2$ and 5%Ba-10%Mn-O/TiO$_2$ catalysts under 0.2vol% O_2 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 N_2 yield, as observed in Fig. 2b and 2c, compared to that of MnOx/TiO$_2$ catalyst, the NO yield sequentially decreased with the temperature from 200 to 300 °C over the 5%Ba-10%Mn-O/TiO$_2$ 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 NH$_3$ to produce N_2, which is known as NOx nonselective catalytic reduction reaction. The NH$_3$ 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 N_2, which was in agreement with Xiao et al. concluded [14]. As expected above, the N_2 yield over 5%Ba-10%Mn-O/TiO$_2$ catalyst extremely was higher extremely than the MnOx/TiO$_2$ catalyst at all temperatures tested. Therefore, the added barium enhanced the HCN catalytic oxidation to N_2.
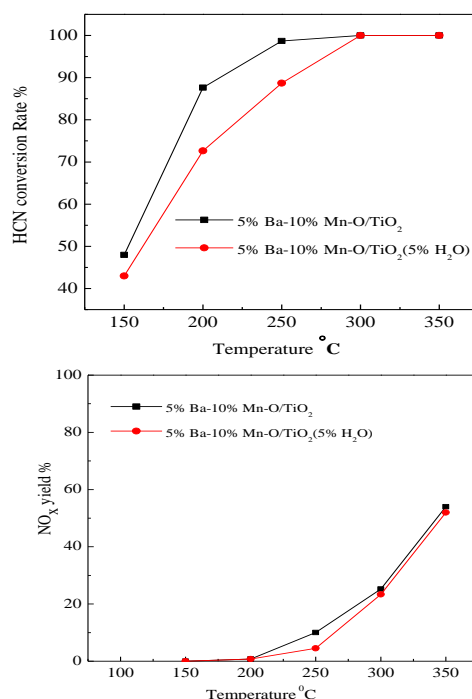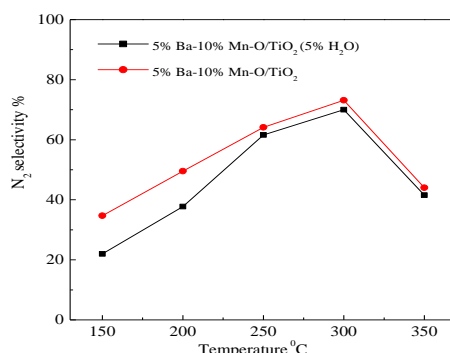
Fig.2 (a) (b) (c) the removal efficiency of HCN conversion, NOx and N2 yield over different active components at the temperature ranged from 100 to 350°C

3.3 Effect of H2O on HCN conversion and the production distribution

Compared to the condition that H_2O was absent, the effect of H_2O on HCN conversion, NOx and N_2 yield over 5%Ba-10%Mn-O/TiO$_2$ catalysts under 0.2vol% O$_2$ concentration are shown in Fig.3a, 3b and 3c. The introduction of H_2O apparently inhibited the conversion efficiency of HCN [15]. The presence of H_2O greatly increased the NO yield at lower temperatures from 150 to 250°C, which may be due to the completion adsorption from H_2O. But at higher temperatures, it was obvious that the HCN conversion in the presence of H_2O was nearly the same as in the absence of H_2O. This result may be because that the higher temperature will encouraged the H_2O to desorption from the surface of the catalyst. Concerning the N_2 yield, as observed in Fig. 3c, the N_2 yield sequentially decreased with the temperature from 150 to 250 °C and then nearly had no change above 250°C, which indicated that the H_2O could restrain the production of N_2 yield at lower temperature but it nearly had no effect on N_2 yield at higher temperatures.

Fig.3 (a) (b) (c) the effect of 5% H_2O 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_2O apparently inhibited the conversion efficiency of HCN, and the H_2O 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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