Simultaneous removal of Hg\(^0\) and HCN from the yellow phosphorus tail gas

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Abstract: Transition metal oxides supported on TiO\(_2\) were synthesized by a sol-gel method and implied to simultaneous removal of Hg\(^0\) and HCN under low temperature and micro-oxygen conditions. The results show that catalysts that modified by manganese oxide have superior catalytic oxidation activity for both the removal of elemental mercury (Hg\(^0\)) and HCN. Furthermore, the O\(_2\) can promote in the removal reaction process. The fresh and used catalysts were characterized by BET and XPS. The catalyst characterization indicated that the catalyst possessed a large specific surface area and the chemisorbed oxygen participated in the catalytic oxidation reaction. The MnOx/TiO\(_2\) catalyst was demonstrated to a good catalytic oxidant for simultaneous removal of elemental mercury (Hg\(^0\)) and HCN under micro-oxygen conditions.

1 General Instructions
Mercury has attracted more and more worldwide attention in recent years, which was because of its high bioaccumulation, toxicity and irreversibility to humans and the environment [1]. Smelting flue and coal-fired flue gas were accounted for the main emissions sources of mercury in China [2]. In addition, the amounts of Hg\(^0\) released from yellow phosphorus tail off-gas must not be ignored [3]. According to the "Emission Standard of Air Pollutants for Thermal Power Plants" (GB13223-2011), which have been published by China, states that mercury discharge concentration is not permitted more than 0.03mg/m\(^3\). In various Hg\(^0\) species, such as elemental (Hg\(^0\)), oxidized (Hg\(^{2+}\)), and particle bound (Hg\(^p\)). Hg\(^0\) as the primary species is easy to escape into the atmosphere because of its properties of high volatile, thermodynamically stable and slight water solubility [4, 5]. Hence, the transformation of Hg\(^0\) to Hg\(^{2+}\) by catalytic oxidation technology over the metallic oxides catalysts needs to be developed. The produced Hg\(^{2+}\) can be removed effectively by existing APCDs mentioned later [6]. Meanwhile, a small quantity of Hydrogen cyanide (HCN) can also be measured from the yellow phosphorus tail gas, which is a toxic and harmful gas that needs to be removed. In order to avoid especially the productions of HCN, such as NO, N\(_2\)O, NO\(_2\) and NH\(_3\), causing the secondary pollution, catalytic oxidation of HCN into nitrogen is also a potentially effective method.

To achieve HCN and Hg\(^0\) removal simultaneously, the MnOx/TiO\(_2\) in the conversion of HCN and Hg\(^0\) is desirable, which could be as a candidate and propose for the treatment of yellow phosphorus tail gas in this work. The MnOx/TiO\(_2\) catalysts were prepared by sol-gel method and tested in various conditions. And oxygen species in the oxidation reaction of HCN and Hg\(^0\) was proposed.

2. Experimental Section

2.1. Samples preparation

MnOx/TiO\(_2\) catalysts were synthesized by the sol-gel method. Ti(OC\(_2\)H\(_5\))\(_4\) (Aldrich 97%) and
manganese (II) acetate tetrahydrate (Mn(CH$_3$COO)$_2$·4H$_2$O, 99.9%, Aldrich) was selected as the precursors of the carrier and active component, respectively. Firstly, appropriate amount of citric acid, after it was sufficiently dissolved in the beaker containing absolute alcohol with a known amount of Ti (OC$_2$H$_5$)$_4$. The solution was maintained at 60°C for 20 min under mild stirring. Then necessary a certain volume of glacial acid and was added slowly by stirring with magnetic stirring to form A solution. After that, doping the appropriate amount of manganese acetate solution one by one in the A solution slowly to form B solution. Water bath temperature of 40-60°C conditions, the B solution to slowly drop into the Continue stirring the B solution to obtain a viscous gel. Put the gel in an oven and dry at a temperature for 5-7 days. At last, dry-gel was calcined at 550°C for 5 hours in muffle furnace. In this process, the volume ratio of butyl titanate, deionized water, glacial acetic acid and absolute ethanol was 1: 1: 0.5: 5. The total metal mass percentage of each catalyst is calculated as (M/(M + Ti), M is metal). Here we choose 15wt.% of the activity component quantity.

2.2. Hg$^0$ and HCN removal measurement

All the activity test of the catalysts for Hg$^0$ and HCN removal in our work were performed in a fixed-bed quartz reactor (inner diameter of 6 mm and a length of 60 cm), whose temperature was controlled by a tubular furnace. The inlet gas N$_2$ transported Hg$^0$ vapor into the system by passing through the mercury permeation U-tube, which placed in a constant water bath system. CVAAS (SG921; Jiangfen, China) was used to measure the Hg$^0$ concentrations before and after the reaction. The simulated flue gas included 0-1vol %O$_2$, 100 ppm HCN and N$_2$ as a balance gas, which were controlled by adjusted mass flow controllers. The initial concentration of mercury was 18mg/m$^3$. In the experiment, the total flow rate was 400 mL/min, all the gas components were mixed and then passed through the quartz reactor.

For Hg$^0$, the “breakthrough time” is the time that the Hg$^0$ outlet concentration reach to 10% of the inlet concentration. The breakthrough time and Hg$^0$ removal efficiency was calculated by formula (1) and (2) below:

\[ \eta = \frac{C}{C_0} \]  
\[ X = \frac{Qc_0t - Q \int_{0}^{t} cd_t}{m} \]  

Where C$_0$ and C represent the Hg$^0$ concentration at inlet and outlet of the reactor, respectively. X is the Hg$^0$ adsorption capacity, which is the Hg$^0$ adsorption capacity of the catalysts at the point of 10% breakthrough; m is the weight of the samples in the fixed-bed; Q is the gas flow in m$^3$/min and the unit of test time is min.

For HCN, the conversion and products yields of HCN were calculated by the following equations:

\[ S_{HCN} = \frac{C_{HCN-out}}{C_{HCN-in}} \times 100\% \]  
\[ S_{N_2O} = 2 \frac{C_{N_2O-out}}{C_{HCN-in}} \times 100\% \]  

2.3. Characterization

The textural structures were measured by nitrogen adsorption/desorption using a Micromeritics Tristar II 3020 at -196°C. The specific surface areas of catalysts were measured using a Brunauer-Emmett-Teller (BET) method. Pore volumes and average pore diameters were calculated by the Barrett–Joyner–Halenda (BJH) method from the desorption branches of the isotherms.

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 Hg\(^0\) and HCN removal without O\(_2\)

In this experiment, TiO\(_2\) modified by iron, manganese, cobalt and nickel were selected as the catalysts for simultaneous removal of Hg\(^0\) and HCN without O\(_2\). For Hg\(^0\), Hg\(^0\) removal efficiency changed with the time at the reaction temperature of 150°C over the samples were investigated. As shown in the Fig.1, compared to the pure TiO\(_2\), Hg\(^0\) removal efficiency enhanced obviously when the active components were introduced. It was clear that the better performance of MnOx/TiO\(_2\) on Hg\(^0\) removal among these catalysts. For HCN, the conversions of HCN and the product N\(_2\) yields over the corresponding catalysts at the temperature ranged from 100 to 350°C were seen in Fig.2. The Mn based catalyst showed the excellent activity both on HCN conversion and N\(_2\) yields within the whole reaction temperature. From the above mentioned, the added manganese oxide played a positive and synergetic role in simultaneous removal of Hg\(^0\) and HCN. In addition, in the absence of oxygen, the Hg\(^0\) and HCN removal could occurred maybe due to the lattice oxygen existed between the metal oxide [7], which indicated that the active component could increase the oxygen storage capacity.

![Fig.1 The removal efficiency of Hg\(^0\) in different active components at the reaction temperature of 150°C.](image1)

![Fig.2 The removal efficiency of HCN conversion and N\(_2\) yield in different active components for in the temperature ranged from 100 to 350°C.](image2)

3.2 Effect of different active components on Hg\(^0\) and HCN removal with different O\(_2\) concentration

In order to investigate the effect of O\(_2\) on the Hg0 and HCN removal, the experiments under pure N\(_2\), 0.5vol% O\(_2\) and 1 vol% O\(_2\) were carry out. For Hg\(^0\), as presented in Fig.3, Hg\(^0\) removal efficiency increased apparently with the O\(_2\) concentration increasing from 0 to 1 vol%. For HCN, as shown in Fig.4, Increasing the O\(_2\) concentration from 0 to 0.5 vol%, the conversions of HCN and the product N\(_2\)
yields over the corresponding catalysts ascended too. But further increase the O₂ concentration to 1vol%, it had no pronouncedly change, suggesting that the O₂ concentration higher than 1% didn’t have effect on HCN removal. So we choose 1vol% O₂ concentration to remove Hg⁰ and HCN simultaneously.

![Graph](image1)

**Fig.3** The effect of different O₂ concentration on removal efficiency of Hg⁰ at the reaction temperature of 150°C

![Graph](image2)

**Fig.4** The effect of different O₂ concentration on removal efficiency of Hg⁰ HCN conversion and N₂ yield at the reaction temperature ranged from 100 to 350°C

### 3.3 Effects of the reaction temperature on Hg⁰ and the reaction time on HCN conversion

Hg⁰ breakthroughs were investigated under conditions of a range of the reaction temperature from 100 to 300 °C over 15wt.% MnOx/TiO₂ with 1% O₂ and the result was given in Fig.5. From the Fig 5 it could be seen that increasing the temperature from 100 to 150°C, Hg⁰ removal efficiency increased vastly. However, when the reaction temperature reached from 150 to 300°C, the mercury removal efficiency decreased. Thus, the best reaction temperature was 150°C. For HCN, the HCN removal with the reaction time at the reaction temperature of 200°C was shown in Fig.6, we could reach a conclusion that the continuous operation of 48 hours, the catalyst maintained a high activity has not been any impact for the continuous operation of 48 hours, indicating that the catalyst had a good activity stability.
3.4 Samples characteristics

3.4.1 BET analysis

The structural parameters for TiO$_2$, fresh MnOx/TiO$_2$, and used MnOx/TiO$_2$ were summarized in the table 1, which was to identify the change of the physical properties of particles. Compared to the pure TiO$_2$, the specific surface area (BET) of the modified TiO$_2$(MnOx/TiO$_2$) was a slight reduce, and the supported active component did not affect the specific surface area of the TiO$_2$. Both the specific surface areas of TiO$_2$ and MnOx/TiO$_2$ were quite high, which may be due to roasting. In general, it is a major factor in the expansion of the surface area. The result that the surface area and pore volume decreased dramatically after the experiment, which could be owing to the considerable pore blockage on the catalyst.

| Sample               | Surface area (m$^2$/g) | Pore volume (cm$^3$/g) | Pore diameter (cm) |
|----------------------|------------------------|------------------------|-------------------|
| MnOx/TiO$_2$-fresh   | 55.23                  | 0.070                  | 2.56              |
| MnOx/TiO$_2$-used    | 7.84                   | 0.015                  | 3.59              |
| Pure TiO$_2$         | 61.50                  | 0.078                  | 2.87              |

Fig.5 The effect of different reaction temperatures on removal efficiency of Hg$^0$

Fig.6 The removal efficiency of HCN with reaction time at the reaction temperature of 200°C
3.4.2 XPS analysis

![XPS Spectra](image)

Fig.7 XPS spectra of O1s of the fresh and used MnOx/TiO2 catalysts at 200 °C

In order to make clear that the oxygen species that played important role in the oxidation reaction, comparative XPS spectra analysis of O1s of the fresh and used 15wt.% of MnOx/TiO2 catalysts at 150 °C were evaluated. As shown in Fig. 7, for both of the samples, the O1s spectra of the samples could be fitted into two regions: one was the peaks lower binding energy value located in 529.4-530.1eV [10],as expected for the lattice oxygen from transition metal oxides; the other higher one located in 531.3-531.7eV was chemisorbed oxygen assigned to OH, which played an important role as active oxygen in oxidation reaction. Compared to the fresh sample, chemisorbed oxygen decreased after the catalytic oxidation reaction [11, 12]. But the lattice oxygen increased, which suggested that chemisorbed oxygen participated in the catalytic oxidation reaction at 200°C.

4. Conclusions

We have studied HCN and Hg0 removal behavior on MnOx/TiO2 under low temperature and micro-oxygen conditions. We found that the pure TiO2 modified by manganese oxide has greatly enhanced the sample removal ability for both HCN and Hg0. Considering to all associated factors that the simultaneous removal of HCN and Hg0. O2 can the catalytic oxidation reaction and 1vol% O2 exhibits the good performance. In addition, the chemisorbed oxygen played the important role in the reaction process.

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