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Simultaneous removal of Hg⁰ and HCN from the yellow phosphorus tail gas

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Abstract: Transition metal oxides supported on TiO₂ were synthesized by a sol-gel method and implied to simultaneous removal of Hg⁰ 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 (Hg⁰) 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/TiO₂ catalyst was demonstrated to a good catalytic oxidant for simultaneous removal of elemental mercury (Hg⁰) 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/m³. In various Hg⁰ species, such as elemental (Hg⁰), oxidized (Hg²⁺), and particle bound (Hg^p), Hg⁰ 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 Hg⁰ to Hg²⁺ 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, N₂O, NO₂ and NH₃, causing the secondary pollution, catalytic oxidation of HCN into nitrogen is also a potentially effective method.

To achieve HCN and Hg⁰ removal simultaneously, the MnOx/TiO₂ in the conversion of HCN and Hg⁰ is desirable, which could be as a candidate and propose for the treatment of yellow phosphorus tail gas in this work. The MnOx/TiO2 catalysts were prepared by sol-gel method and tested in various conditions. And oxygen species in the oxidation reaction of HCN and Hg⁰ was proposed.

2. Experimental Section

2.1. Samples preparation

 $MnOx/TiO_2$ catalysts were synthesized by the sol-gel method. Ti(OC₂H₅)₄ (Aldrich 97%) and

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manganese (II) acetate tetrahydrate ($Mn(CH_3COO)_2 \cdot 4H_2O$, 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_2H_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. Hg⁰ 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 %O₂, 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/m³. 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:

$$X = \frac{Qc_0 t - Q\int_0^t cd_t}{m}$$
(2)

Where C_0 and C represent the Hg⁰ concentration at inlet and outlet of the reactor, respectively. X is the Hg⁰ adsorption capacity, which is the Hg⁰ 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 m³/min and the unit of test time is min.

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

$$S_{HCN} = \frac{C_{HCN-in} - C_{HCN-out}}{C_{HCN-in}} \times 100\% \quad (3)$$
$$S_{N_2O} = 2\frac{C_{N_2O - out}}{C_{HCN-in} - C_{HCN-out}} \times 100\% \quad (4)$$

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 K α 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.

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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 Hg⁰ and HCN without O₂. For Hg⁰, Hg⁰ 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 TiO₂, Hg⁰ removal efficiency enhanced obviously when the active components were introduced. It was clear that the better performance of MnOx/TiO₂ on Hg⁰ removal among these catalysts. For HCN, the conversions of HCN and the product N₂ 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 N₂ yields within the whole reaction temperature. From the above mentioned, the added manganese oxide played a positive and synergetic role in simultaneous removal of Hg⁰ and HCN. In addition, in the absence of oxygen, the Hg⁰ 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 $150^{\circ}C$.



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.

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 N₂, 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 N₂ yields over the corresponding catalysts ascended too. But further increase the O_2 concentration to 1vol%, it had no pronouncedly change, suggesting that the O_2 concentration higher than 1% didn't have effect on HCN removal. So we choose 1vol% O_2 concentration to remove Hg⁰ and HCN simultaneously.



Fig.3 The effect of different O_2 concentration on removal efficiency of Hg^0 at the reaction temperature of $150^{\circ}C$



Fig.4 The effect of different O_2 concentration on removal efficiency of Hg^0 HCN conversion and N_2 yield at the reaction temperature ranged from 100 to 350°C

3.3. Effects of the reaction temperature on Hg^0 and the reaction time on HCN conversion

 Hg^0 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, Hg^0 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.



Fig.5 The effect of different reaction temperatures on removal efficiency of Hg⁰



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

3.4 Samples characteristics

3.4.1 BET analysis

The structural parameters for TiO₂, fresh MnOx/TiO₂, and used MnOx/TiO₂ 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 TiO₂. Both the specific surface areas of TiO₂ and MnOx/TiO₂ 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.

Table.1 Parameters of porous structure of catalysis			
Sample	Surface area(m ² /g)	Pore volume (cm^3/g)	Pore diameter (cm)
MnO _x /TiO ₂ -fresh	55.23	0.070	2.56
MnO _x /TiO ₂ - used	7.84	0.015	3.59
Pure TiO ₂	61.50	0.078	2.87

c ------. f 1 **T** 11

3.4.2 XPS analysis



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 O 1s 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 Hg^0 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 Hg^0 . Considering to all associated factors that the simultaneous removal of HCN and Hg^0 . 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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