Removal of NO by synergistic oxidation of electrocatalytic oxidation and persulfate

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ABSTRACT

Traditional NO removal technology was restricted in many special industries and fields. In this study, electrochemically-activated persulfate (EC/PS) system was selected to carry out NO removal research. Influencing factors such as anode, gas flow, reaction temperature, current density, PS concentration, etc. have been studied. It was found that the EC/PS system has a stable removal effect of NO, and the removal rate can be stabilized above 60% under optimal conditions. The Ti/SnO₂ anode shows excellent oxidation performance in the EC/PS system. Reaction temperature and gas flow are the main factors that affect the NO removal effect of the EC/PS system. The findings of this research might provide a practical reference for promoting the removal of NO.

Keywords: NO removal, electrocatalytic oxidation, persulfate, EC/PS system

1. INTRODUCTION

The NOx (NO account for more than 90%)emitted from stationary sources and mobile sources has been widely concerned for a long time because of its harm to humans and the environment (e.g., acid rain, ozone pollution and photochemical smog)^[1]. Traditional denitrification processes represented by SCR and SNCR have been widely used in the thermal power industry and large coal-fired boilers. However, due to their complex system, large footprint, high investment and operating costs, their application in special fields such as small/ medium enterprises and ships is greatly restricted. Meanwhile, as emission standards become more and more stringent, the denitrification of flue gas from non-

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electric industries and marine vessels has gradually become the focus of emission reduction. Thus it is urgent to develop a flue gas denitrification technology with high efficiency, low cost, wide application range and no secondary pollution.

The wet oxidation methods for NOx abatement aim at oxidizing insoluble NO into soluble higher order nitrogen oxides and then remove it by absorption. A series of oxidation has been investigated that include ozone (O_3) , hydrogen peroxide (H_2O_2) , chlorine dioxide (ClO₂), potassium permanganate (KMnO₄), sodium chlorite (NaClO₂), sodium hypochlorite (NaClO), potassium persulfate (K₂S₂O₈). Persulfate was considered to be an excellent advanced oxidant due to its ability to generate $SO_4^{\bullet-}$ ($E^{\theta} = 2.60 V$) with strong oxidizing ability and relatively long life $(3 \sim 4 \times 10^{-5} s)$ and no secondary pollution. However, the formation of $SO_4^{\bullet-}$ from persulfate often requires certain activation methods, such as heat, UV light, microwave, ultrasound and transition metal. Adewuyi et al^[2] introduced Fe2+ and Fe-EDTA to Na₂S₂O₈ solution to realize the NO removal at a relatively lower flow rate (0.1 standard liters per min). Wang et al^[3] studied the NO removal from flue gas using the developed microwave-activated H2O2/PS oxidation system. Liu et al^[4] also adopted an integrated activation method of ultrasound(US)/Fe²⁺/heat for persulfate system activation on simultaneous absorption of SO₂ and NO from flue gas. Although these activation methods have shown great activation efficiency, they present many disadvantages. Electrochemical process as another persulfate activation technology has been widely studied in the wastewater treatment field due to its advantages of small reactor, low investment cost and no secondary pollution. Meanwhile, electrochemical systems using certain anodes also exhibit electrocatalytic oxidation performance, and have been researched and applied as an advanced oxidation method in organic wastewater treatment ^[5]. Therefore, this study combined the electrocatalytic oxidation method with persulfate to remove NO, provide a new method for flue gas denitrification in special fields and occasions.

MATERIALS AND METHODS 2.

2.1 DSA anodes preparation

2.1.1 Titanium surface treatment

Pure titanium sheets (99.9%, 30 mm × 50 mm × 1 mm) and titanium mesh (60% porosity) were polished on abrasive papers from 360-mesh to 1200-mesh accordingly, then rinsed with deionized water, and then degreased in 40% NaOH at 80 °C for 60 min. Afterwards, the samples were etched in 12% oxalic acid solution for about 120 min until the titanium surface reached a uniform gray tone to obtain a rough and uniform surface with no oxides. Finally, all the matrixes were thoroughly washed with deionized water.

2.1.2 Preparation of electrodes

After sonicated in ultrapure water for 20 min, the pretreated Ti substrates were dip-coated with mixed solution of isopropanol and N-butanol containing 80% RuCl₄+ 20% IrCl₂ and SnCl₄, respectively. The Ti substrates were dipped in the coating solutions, sequentially dried at 90 °C for 10 min and calcined in furnace for 10 min at 550 °C. The coating cycle was repeated 20 times. Finally, the anodes were annealed at 550 °C for 1 h.

2.2 Analytical methods

The crystallographic structure of the coating was determined by X-ray diffraction (XRD) on a Philips X'Pert Diffractometer in Bragg–Brentano geometry using Cu Ka radiation (1.542 Å) in the 20 range from 10 to 80 with 0.03 as step size and 10 s holding time.

The electrochemical performance of the prepared DSA anodes were tested on a standard three-electrode system by using an electrochemical analyzer (CS 2350H, Wuhan CorrTest Instruments Corp., Ltd, China). The prepared DSA anode was used as the working electrode. The auxiliary electrode was a pure titanium plate, and the reference electrode was a Ag/AgCl electrode. The linear polarization curve was tested in a 0.5 mol/L Na₂SO₄ solution, and the scan rate was set at 20 mV/s.

2.3 NO removal experiment

200 mL of sodium sulfate (Na₂SO₄) or/and persulfate (PS) solution was prepared and added in to a 250ml sealed electrolytic cell. NO generated by self-made NO

generator was bubbled into the solution after measured the concentration by gas analyzer (KANE 950, KANE International LTD, UK). The concentration of the reacted gas is also determined. Removal rate of NO was calculated by the following equation: R

Removal rate=
$$(C_{in} - C_{out})/C_{in} \times 100\%$$
 (1)

Other experimental conditions were listed as the Table 1.

lable 1 Experimental conditio	ons for	NO	remova
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Reaction conditions	1#	2#	3#	4#	5#		
Anode	No	Ti(p)/ RuO ₂ - IrO ₂	Ti(p)∕ SnO₂	Ti(m)∕ SnO₂			
Flow rate(ml/min)	200	400	600	800	1000		
Reaction temperature(°C)	30	50	70	90			
Current density(mA/cm ²)	40	60	80	100	120		
Oxidant concentration(mol/L)	0	0.05	0.1	0.15	0.2		

RESULTS AND DISCUSSION 3.

3.1 Electrode characterization

3.1.1 XRD analysis

The physical characterizations of the electrodes after the heat treatments were performed initially by XRD in order to detect the crystalline phases formed onto electrodes surfaces. It is believed that the electrocatalytic performance of anodes depends heavily on the crystal patterns and composition of electrodes.





Fig 1 XRD patterns of prepared electrodes (a) Ti/RuO₂-IrO₂, (b) Ti/SnO₂

The XRD pattern of prepared Ti/RuO2-IrO2 electrode was presented in Fig 1(a). Comparing the XRD patterns to Joint Committee on Powder Diffraction Standards (JCPDS), it could be concluded that the prepared electrodes presented the crystalline structure of RuO₂ and IrO_2 . Peaks at 20 value of 37.2°, 53.6°, 63.8° correspond to the (200), (220) and (311) planes, respectively, of RuO₂ phase (JCPDS: 00-050-1428). Meanwhile, peaks placed at 20 value of 28.0°, 34.7°, 40.0°, 53.9° are assigned to the (110), (101), (200) and (211) planes of IrO₂ (JCPDS: 01-088-0288), respectively. In addition, a series of characteristic diffraction peaks of Ti were detected, because the X-ray penetrate the coating^[6]. Rutile IrO₂ and RuO₂ solid solutions are indicated to be formed during the calcination process because of the deviation of the characteristic peaks of IrO₂ and RuO₂, and it is believed that the electro-catalytic activity and stability of the electrode would be improved accordingly^[7].

Fig 1(b) shows the X-ray diffractogram of the Ti/SnO₂ electrode. XRD determined the crystalline nature of the structures of the oxide films coated on the titanium substrate. It was possible to distinctively identify the presence of Ti, TiO₂, SnO₂ in the rutile structure. The peaks at 2θ =35.09°, 38.43°, 40.18°, 53.02° and 70.68° correspond to metallic titanium (JCPDS, No.65-3362). Clearly, several peaks at 2θ =26.61°, 33.89°, 51.78° 54.77°, 61.89° and 64.77° (JCPDS, No.72-1147) can be assigned well to the characteristic peaks of SnO₂ with a rutile type structure. 3.1.2 LSV test

The linear scan voltammetry (LSV) curve of Ti/RuO₂ - IrO_2 and Ti/SnO₂ anode in 0.5 M Na₂SO₄ solution at 30 °C in a potential range of 1- 1.8V at a scanning rate of 20 mV s⁻¹ was given in Fig 2. By fitting and analyzing the curve, it can be seen that the oxygen evolution overpotential of Ti/RuO₂-IrO₂ and Ti/SnO₂ is about 1.34V and 1.46V (vs Ag/AgCl), respectively. Moreover, the oxygen evolution overpotential of the prepared Ti/SnO₂ anode is significantly higher than that of the Ti/RuO₂-IrO₂ anode.



Fig 2 LSV curve of Ti/IrO₂-RuO₂ anode in 0.5 M H₂SO₄.

3.2 NO removal experiment

3.2.1 Effect of anode

The removal effects with different anodes was shown in Fig 3. The removal rate of NO has been enhanced by the adoption of electrochemical method. As a representative inactive anode, the efficiency of SnO₂ electrode was significantly better than that of RuO₂-IrO₂ anode which is classified as active anode in NO removal. It was indicated that the indirect oxidation process is more effective in the electrochemical oxidation removal of NO than that of direct oxidation. Meanwhile, It was found that the NO removal efficiency of SnO₂ anode with the matrix of Ti plate is better than that with the Ti mesh matrix. In all tested electrodes, SnO₂ anode with Ti plate matrix show the best NO removal efficiency.



Fig 3 Removal of NO in the EC/PS system with different anode. Experimental conditions: Current density= 100 mA/cm², flow rate= 200 ml/min, T=50 °C, [PS]=0.1 mol/L. 3.2.2 Effect of flow rate

S.Z.Z Effect of flow rate

Fig 4 showed the removal of NO in different gas flow rate. As the gas flow rate increases, the NO removal rate decreases gradually. This is because, with the increase of gas flow rate, the residence time in the sealed electrolytic cell of gas is shorter and the contact time with oxidizing electrolyte is shorter, so the removal efficiency is decreasing. This is because with the increase of gas flow rate, the residence time of gas in the sealed electrolytic cell and contact time with oxidizing electrolyte become shorter, so the removal efficiency decreases continuously.



Fig 4 Removal of NO in the EC/PS system with different gas flow rate. Experimental conditions: Current density= 100 mA/cm², Ti/SnO₂, T=50 °C, [PS]=0.1 mol/L.

3.2.3 Effect of reaction temperature

The effects of reaction temperature were shown in Fig5. With the increase of reaction temperature, NO removal rate showed a trend of first increasing and then

decreasing. Higher temperature is conducive to the activation of persulfate to produce sulfate radical, thus improving the oxidation process of the solution. However, the resistance of the electrode increases with the increase of temperature, thus reducing its conductivity and weakening electrocatalytic oxidation.



Fig 5 Removal of NO in the EC/PS system with different temperature. Experimental conditions: Current density= 100 mA/cm2, flow rate= 200 ml/min, Ti/SnO2, [PS]=0.1 mol/L.

3.2.4 Effect of current density

The removal effect of NO under different current density was shown in Fig 6. It can be seen from the figure that the effect of current density on NO removal is not obvious. This maybe because factors such as PS concentration dominate the system, and the oxidation of PS plays a major role.



Fig 6 Removal of NO in the EC/PS system with different current density. Experimental conditions: flow rate= 200 ml/min, Ti/SnO_2 , T=50 °C, [PS]=0.1 mol/L.

3.2.5 Effect of persulfate concentration

Fig7 Showed the NO removal efficiency with different potassium persulfate concentration. The removal rate of NO increased significantly with the increase of persulfate concentration, because more persulfate could produce more $SO_4^{\bullet-}$, thus improving the oxidation of the solution. However, when the concentration of potassium persulfate exceeded 0.1M, NO removal rate changed little with the further increase of the concentration. This may be due to the change of system control factors to other factors such as mass transfer and potassium persulfate activation efficiency.



Fig 7 Removal of NO in the EC/PS system with different persulfate concentration. Experimental conditions: Current density= 100 mA/cm², flow rate= 200 mI/min, Ti/SnO₂, T=50 °C.

4. CONCLUSIONS

The electrocatalysis and persulfate synergistic oxidation process proved to be an effective NO removal method, the system has a stable removal effect of NO, and the removal rate can be stabilized above 60% under optimal conditions. The Ti/SnO₂ anode in the EC/PS system is better than Ti/RuO₂-IrO₂ anode in removing NO. Reaction temperature and gas flow are the main factors that affect the NO removal effect of the EC/PS system.

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