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Research Article

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Using blast furnace gas to remove NO of sinter band flue gas over the copper-based catalyst

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ABSTRACT

This paper investigated the catalytic reduction reaction of NO by CO over Cu Catalyst with Chemical simulation software Chemkin. And it determined the major step of reduction reaction through the analysis of the surface coverage and reaction sensitivity over the catalyst surface. Then we carried on the experimental study of using blast furnace gas to remove NO of sintering flue gas through laboratory Simulation prepared gas. And we investigated the relationship between temperature and Denitration efficiency. The simulation results show that NO participated the reduction reaction as NO and* $(NO)_2$** which are absorbed by the copper-based catalyst. CO covered almost the whole surface of the catalyst in the form of pioneer chemical adsorption when the reaction temperature is lower than 200 ℃ and almost no reduction reaction exist at the low-temperature. As the temperature getting higher, the coverage rate of CO* reduced, and the coverage rate of NO* and N* increased gradually and the conversion rate of reduction reaction increased gradually. The simulation results are consistent with the experimental results when the reaction temperature is between 200～450 ℃.*

Key words: Sinter Band Flue Gas; Denitrification; Carbon Monoxide; Nitrogen oxides

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INTRODUCTION

As one of the major air pollutants, Nitrogen oxides (NO_X) emissions from the sinter band flue gas arouses earthling attention, it not only pollutes the ecological environment but also endangers the human health. The proportion of NO is more than 90% among the total amount of nitrogen oxides (NO_X) of sinter band flue gas emissions. Thus, the denitrification project of sinter band flue gas is considered to be another important environmental protection project follows the desulfurization of sinter band flue gas. To develop novel technology of denitrification of sinter band flue gas is very important at present.

Currently, Selective Catalytic Reduction (SCR) process and Selective Non-Catalytic Reduction (SNCR) process are the most important denitrification processes. The two processes are the hot topic in the field of denitrification which attracted much attention of researchers all over the world in this area. NH_3, H_2, CO and hydrocarbons are generally used as reductive agents [1]. CO is one of these active reducing agents, and it is also a common associated gas of industrial process, such as blast furnace gas (BFG), coke oven gas (COG) etc. Blast furnace gas is one of the byproducts of steelmaking, and the volume percentage of CO is more than 30%. NO will be reduced to N_2 at a suitable temperature with the catalysis of catalyst [2]. Some researchers have focused on the reduction reaction of NO and CO of automobile exhaust [3],[4]. YANG [5], Lambert [6], Costa [7] had researched the reaction conditions and the initial reaction mechanism between H_2 and NO or CO and NO system of automobile exhaust on palladium-based catalysts. Sinter band flue gas has its own characteristics such as the large gas emissions, low nitrogen oxide concentrations, high dust content, and high oxygen content et al compared with other flue gas. That means the treatment of sinter band flue gas is more difficult than other flue gas.

In this paper, the reaction mechanism of CO and NO on the copper-based catalyst was analyzed in detail by chemical simulation and verified through experiment.

INTRODUCTION OF SIMULATION AND EXPERIMENTAL METHODS

1. Chemical Simulation Methods

Chemical Kinetics Simulator is used as the chemical simulation software [8] and the method of stochastic simulation is used to describe the main reaction process in this paper. Elementary reaction activation energy (Ea) is calculated through the unity bond index-quadratic exponential potential approach (UBI-QEP) [9]. Pre-exponential factor A can be calculated according to the transition state theory and the statistical thermodynamics methods [10]. Then the pre-exponential factor A of the reverse elementary reaction and positive elementary reaction can be calculated. Since the concentration of main reactant is low, the heat of reaction can be ignored and it is considered that the system temperature is constant along the catalyst bed temperature gradient. The activation energy and the pre-exponential factor A of elementary reactions do not change in the reaction process.

2. Experimental Methods and Experimental Process

Using Al_2O_3 as catalyst carrier and the diameter of Al_2O_3 particle is about 280~600μm. The equal volume of uniform dip pretreatment method is used as the main method for the preparation of catalyst. Using $CuSO_4$ solution as the impregnation solution and the loading amount is about 0.5%. The Al_2O_3 particle after dipping pretreatment was dried for more than 2h at 120℃ in the thermostatic oven. The catalyst particle after baking in the thermostatic oven was dried for about 6h at 600℃ in the Muffle furnace. Then the finished catalyst was manufactured finally.

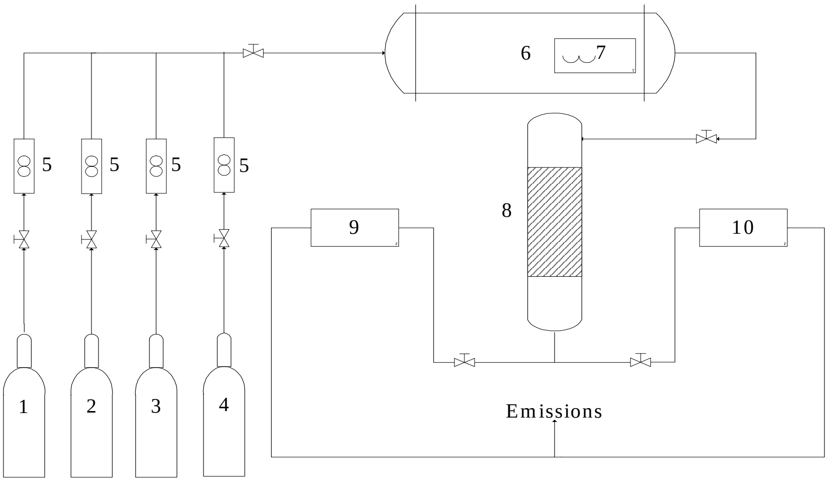

Fig.1 Experimental flow diagram

1,2,3,4 Gas cylinder，5 Mass flow meter，6 Electrical heater，7 Temperature controller，8 Reactor，9 CO2 Infrared detector，10 NO Detector

As is shown in fig 1, the raw material gas and dilution gas were accurately measured by mass flow meter then were heated by a gas heater. The heated mixed gas completed the reduction reaction in the quartz glass tube reactor which is filled with catalyst layer. The main components of clean gas after denitrification were measured respectively through the measuring instrument. Then the flue gas after denitrification was discharged through vent pipe.

Experimenter used a quartz tube as fixed bed reactor to check the performance of catalyst. The inside diameter of quartz tube reactor is 20mm and the filling amount of catalyst is about 5g.

The sinter band flue gas was simulated by cylinders gas. The volume percentage of O_2 is about 15%, the volume percentage of H_2O is about 10%, the volume concentration of NO is 800mg/Nm³, and the rest gas is N_2. The experimenter ignored the effect of SO_2 of the flue gas in order to study the reduction reaction mechanism of CO and NO. The flue gas analyzer KM9106E was used to test the concentration of NO, NO_2 and O_2 continuously. The analyzer accuracy of NO and NO_2 is up to 1×10^{-6}, and the accuracy of O_2 is up to 0.1%. The concentration of CO_2 after reaction was tested by portable infrared CO_2 analyzer GXH-3010F.

ANALYSIS OF SIMULATION AND EXPERIMENT RESULTS

1. The Simulation of Reaction Mechanism

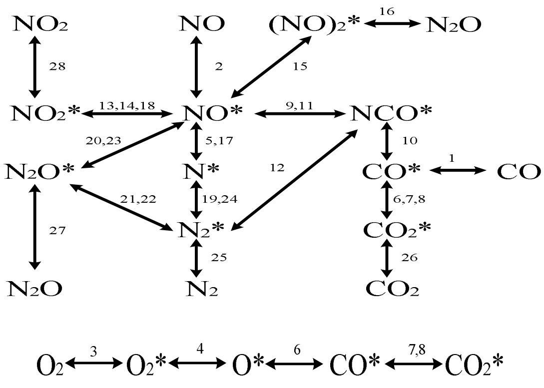

Fig.2 Reduction reaction network

The results of the simulation shows that the active adsorption species of NO* and $(NO)_2$* is the main form of NO which participate the reduction reaction, and the adsorption reaction of NO is the control step of the reduction reaction. The main adsorption route of reaction has the reaction 2,5,15. The reaction 2 and 15 are the main adsorption form of NO when the reaction temperature is under the 200℃. The reaction 5 and 15 are the main adsorption form of NO when the reaction temperature is between 200℃ and 300℃. The reaction 5 will be the main adsorption form of NO when the reaction temperature is over 300℃.

The reaction formulas 11, 16, 20, 23 are the main reaction step which the reaction product is N_2O. The reaction 16 is the most important step when the reaction temperature is lower than 200℃ because this reaction has lower activation energy. The reaction 20 will be the main step to generate N_2O with the reaction temperature rising to 300℃ since the coverage of NO* and N* is higher than other spices. The reaction 16 and 23 will be reacted preferentially with the reaction temperature rising continually and the reaction 16 will be the dominant step.

The reaction formulas 12, 19, 21, 22 and 24 are the main reaction step which the reaction product is N_2. The chemical simulation shows that the oxidation reaction of CO was the dominant reaction when the reaction temperature is lower than 200℃. In this condition, a small part of the NO is reduced to N_2O and no N_2 is generated. The main product of reduction reaction is N_2 when the temperature is between 200~320. The reaction 21, 22, 24 will be occurred preferentially and the reaction 21 is the dominant reaction. But the reaction 12 and 19 will be predominated as the temperature is raised continually. So the reaction selectivity of N_2 is improved greatly for the reaction 19.

The reaction 13, 18 are the main reaction step which the reaction product is NO_2 and these reactions are occurred only at lower temperature. These two reactions are tended to be inhibited when the temperature exceeds 200℃. In addition to these reactions, there is no other reaction which the reaction product is NO_2 occurred.

2. The analysis of main species surface coverage on the surface of the catalyst

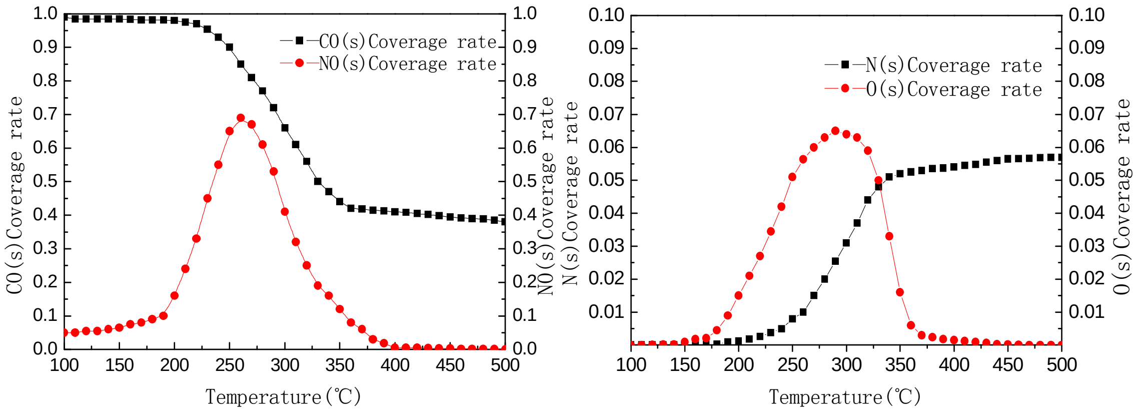

Fig.3 The relationship between temperature and species coverage on the Catalyst

The results of the simulation shows that the active adsorption species of NO* and $(NO)_2$* is the main form of NO which participate the reduction reaction, and the adsorption reaction of NO is the control step of the reduction reaction. The main adsorption route of reaction has the reaction 2,5,15. The reaction 2 and 15 are the main adsorption form of NO when the reaction temperature is under the 200℃. The reaction 5 and 15 are the main adsorption form of NO when the reaction temperature is between 200℃ and 300℃. The reaction 5 will be the main adsorption form of NO when the reaction temperature is over 300℃.

Figure 3 shows the surface coverage rate of major species on the copper-based catalyst with the change of reaction temperature. The surface coverage of CO(s) is nearly 1, which means CO(s) occupied most of the catalyst surface when the temperature is lower than 200℃. And CO(s) was adsorbed on the copper-based catalyst as chemical adsorption pioneer state. So the oxidation reaction of CO was the dominant reaction when the reaction temperature is lower than 200℃. There is competitive adsorption between the reactive species N(s) and CO(s) in the course of the reaction with the change of temperature. The coverage of CO(s) is reduced quickly with increasing temperature and the coverage of NO(s) and N(s) are increased gradually. The coverage of NO(s) reached maximum at 250℃ and then decreased quickly. That is consistent with the change of the concentration of N_2O. The change of the coverage of NO(s) and N(s) indicates that the reaction 20 and 23 are dominated step. The coverage of NO(s) is reduced to zero quickly when the temperature is raised from 250℃ to 380℃. And the coverage of N(s) is increased continually with the reaction temperature raised gradually. The reaction 20 is exacerbated and the main reduction product is N_2. The coverage of each species shows that the overall simulation results and experimental results are consistent with each other.

3. The Experimental results contrast with the simulation results

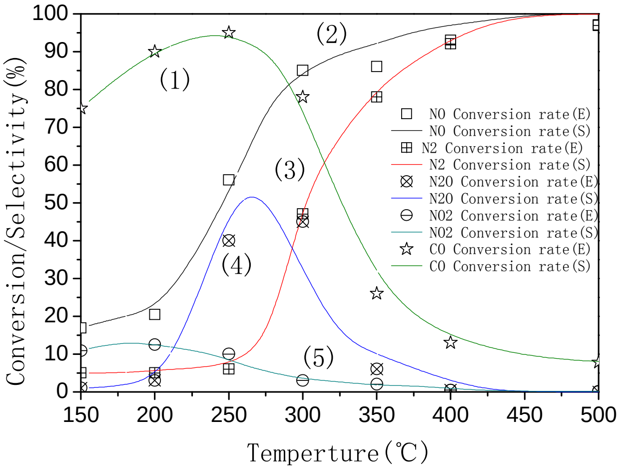

Fig.4 The relationship between temperature and simulation & experimental results

(1)Conversion of CO (2) Conversion of NO (3) Conversion of N_2 *(4) Conversion of* N_2O *(5) Conversion of* NO_2

The figure 4 shows the relationship between temperature and simulation & experimental results. From the simulation and experimental results we can see that the reduction reaction has obvious selectivity with the change of temperature.

The oxidation reaction of CO was the dominant reaction when the reaction temperature is lower than 200℃ and a few of NO was oxidized to NO_2 with the catalytic action of catalyst. The oxidization conversion rate of CO is over 80% and the reduction conversion rate of NO is about 10%. The oxidation reaction of CO continues to occur when the reaction temperature exceeds 200℃ and the maximum oxidization conversion rate of CO is about 90% when the reaction temperature is about 200℃. Then the oxidization conversion rate of CO decreased rapidly and CO involved in the reduction reaction as the mainly reducing agent.

CONCLUSION

Using blast furnace gas as a reducing agent to reduce the NO of sinter band flue gas is a novel denitration process. It doesn't need build an ammonia station and it is safety than SCR or SNCR process. Blast furnace gas and is much cheaper than ammonia as an associated gas. The economy performance and practicality are better than SCR or

SNCR process. That means this process has a good prospect to be widely used.

In this paper, the process of NO reduction by CO over Cu/Al_2O_3 is investigated. It indicates that NO can be reduced by CO under low concentration conditions of sinter band flue gas at appropriate temperature, and the resultants are N_2O and N_2. With the increase concentration of CO or O_2, the NO conversion is inhibited gradually. The increase of CO concentration prompts the reaction activity.

In this paper, the apparent activation energy of elementary reactions is estimated by UBI-QEP method. The PSR model of CHEMKIN is used to simulate the reduction reaction dynamics mechanism of sinter band flue gas with the [11]random method. The reduction reaction of NO of sinter band flue gas by CO was studied through analyzing the experimental data and simulation data. And this paper gives the reaction network diagram according to the distribution of the reaction products.

The adsorption reaction of NO on the surface of catalyst is the control step of the reduction reaction which the NO was adsorbed as NO* or $(NO)_2$*. There is no reduction reaction occurs when the reaction temperature is lower than 200℃ and the oxidation reaction of CO is the dominant reaction. NO is reduced to N_2O and N_2 when the reaction temperature is between 200～320℃. The proportion of N_2O is more than 50% when the temperature is about 200～280℃ and the rest reduction product is N_2. NO is reduced to N_2 when the reaction temperature is over 320℃. And the conversion rate of NO is more than 90%. The reducing agent CO is oxidized to CO_2.

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