Application Research on Pd-Co-Ti Catalyst for Purifying CO in Flue Gas of Hot-blast Stove in Steel Rolling Mill

Jianyu Cai, Zehui Yu, Junda He and Jian Li*

Beijing University of Technology, Key Laboratory of Beijing on Regional Air Pollution Control, Beijing 100124, China
E-mail: ljian@bjut.edu.cn
**Corresponding Author*

Received 08 December 2021; Accepted 05 January 2022;
Publication 25 January 2022

Abstract

The Pd-Co-Ti catalyst was successfully prepared by the method of impregnation-precipitation-ball milling. The structure and redox properties of Pd-Co-Ti catalyst was investigated by N_2 desorption, X-ray powder diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and H_2-TPR. The results show that the Pd-Co-Ti catalyst has a large specific surface area and a rich pore structure, and there are Co_3O_4 and anatase TiO_2 crystals in the catalyst. The synergistic effect of Pd and Co improves the redox ability of Pd-Co-Ti catalyst. The catalyst is used to treat CO in the flue gas of rolling mills. It runs for 168 hours at a space velocity of 30,000 $cm^3/(g \cdot h)$ and a temperature of 280°C, and the CO removal rate is basically maintained at more than 90%. The ratio of inlet CO content and O_2 content affects the catalyst CO removal efficiency. When the ratio is greater than 0.5, the CO removal efficiency has a downward trend. The results of this study are of great significance to the practical application of CO oxidation technology.

Keywords: Pd-Co-Ti, catalyst, steel rolling mill, CO, application.

Strategic Planning for Energy and the Environment, Vol. 40_4, 455–470.
doi: 10.13052/spee1048-5236.4048

1 Introduction

The source of CO is very wide, and CO exist in the fields of chemical industry, power generation, electronics, transportation, aviation and so on [1–3]. CO is a toxic gas that can combine with hemoglobin, causing suffocation and even death of the human body, and a serious threat to human life and health [4, 5]. CO is both a gaseous pollutant and a resource. In this era of continuous consumption of resources, CO is a very important resource. Oxidizing CO to CO_2 and recovering the reaction heat is an effective way to reduce pollution, recover energy, and turn waste into treasure.

The CO content in the exhaust gas of the iron and steel industry is relatively high, and it is mainly directly emitted. However, it is difficult to achieve direct oxidation of CO in the exhaust gas under actual conditions of steel plants. The combination of CO catalytic oxidation method and heat exchange technology may be an ideal way for resource utilization of CO in exhaust gas. The heat exchange technology is relatively mature, but the application of CO catalytic oxidation technology in the iron and steel industry is still very few. CO catalytic oxidation technology is one of the effective methods to remove CO [6]. Catalyst is the key to CO catalytic oxidation technology. At present, the main factors restricting the application of CO catalytic oxidation technology are: (1) The stability of the catalyst needs to be improved. (2) The price of the catalyst is relatively high. CO catalysts are mainly divided into precious metal catalysts [7–10] and non-precious metal catalysts [11–14].

In order to promote the application of CO oxidation technology, research is mainly focused on improving the activity of CO catalysts, reducing the amounts of precious metals, and improving the tolerance of the catalysts to components such as SO_2, H_2O or CO_2 and so on. Jiang [15] believed that the competitive adsorption of SO_2 and H_2O with CO on the catalyst surface affects the CO oxidation performance of the catalyst. Studies have shown that the dual-carbon vacancy graphene supported Pt single atom catalyst can reduce the adsorption of SO_2 and H_2O and enhance the adsorption of CO. Therefore, the catalyst exhibits good sulfur and water resistance. Thormählen [16] prepared a catalyst using a cobalt-rich cobalt-aluminate spinel as the active material, and found that CO_2, C_3H_6, NO, H_2, H_2O or SO_2 had inhibitory effect on catalyst activity, and the inhibitory effect of SO_2 and H_2O is higher than other components. Taira [17] studied the effects of different surfaces, crystals and pore structures on the CO oxidation performance of Pt/TiO_2 catalysts. It was found that the catalyst with a high ratio of larger pores has better sulfur and water resistance. Shi [18] studied the effect of W addition on the CO oxidation performance of the Co-Ce catalyst, and found that the introduction of W increased the specific surface area of the catalyst and inhibited the accumulation of sulfate on the surface of the catalyst, thereby improving the sulfur resistance of the catalyst. Zhu [19] found that the Pt/TiO_2 catalyst prepared by FeO_x calcined at 400°C had good resistance to H_2O and CO_2. The presence of γ-Fe_2O_3 in the catalyst improved the reduction ability of the catalyst, a large number of hydroxyl groups were generated when H_2O is present, and the rapid reaction between CO and surface hydroxyl groups improved the reaction activity. Li [20] used the CeO_2-TiO_2 catalyst to oxidize Hg in the flue gas. The study found that the doping of Co improved the SO_2 resistance of the catalyst. The interaction between Co and Ce promoted the dispersion of CeO_2, increased oxygen vacancies, improved oxygen storage capacity, and inhibited the poison of SO_2 to Ce^{4+}.

This study explored the CO catalytic performance and stability of Co-doped Pd/TiO_2 catalyst in the actual flue gas of a steel plant. It provides an important basis for the application of CO oxidation technology in practical engineering.

2 Experimental

2.1 Catalyst Preparation

The Pd-Co-Ti catalyst was prepared by a combination of precipitation method, impregnation method and ball milling method. The specific preparation method is as follows: (1) Weigh 40 g of cobalt acetate (China National Pharmaceutical Group Corporation, Beijing, China) and dissolve it in a 50% ethanol solution (China National Pharmaceutical Group Corporation, Beijing, China), and stir the resulting solution in water at 60°C for 10 minutes. (2) Weigh 1.8 g of stannous chloride (China National Pharmaceutical Group Corporation, Beijing, China) and 0.1g of ammonium molybdate (China National Pharmaceutical Group Corporation, Beijing, China), respectively, and prepare them into solutions. (3) The prepared solution was slowly added dropwise to the cobalt acetate solution, and stirring was continued for 10 minutes. (4) Add ammonia water dropwise to the mixed solution until the pH reaches about 14. (5) After the suspension continued to be stirred for 30 minutes, it was transferred to a blast drying oven and dried overnight at 102°C. (6) After the mixture is fully dried, it is transferred to a muffle furnace, calcined at 450°C for 1 hour, and cooled to obtain raw material I. (7) Weigh 0.2 g of palladium chloride (China National Pharmaceutical Group Corporation, Beijing, China) and 0.1 g cerium nitrate (China National Pharmaceutical Group Corporation, Beijing, China) to prepare a mixed solution, stir in a 40°C water bath for 10 minutes, then weigh 15 g of TiO_2 (China National Pharmaceutical Group Corporation, Beijing, China), slowly add it to the mixed solution, and continue to stir for 30 minutes. (8) Place the resulting mixture in a blast drying oven and dry overnight at 102°C. (9) The obtained powder was calcined at 350°C for 2 hours, and then cooled to obtain raw material II. (10) The raw material I and the raw material II are mixed in a ratio of 1:1. In order to ensure uniform mixing, the ball milling method is used for mixing, and finally the Pd-Co-Ti catalyst is obtained.

2.2 Catalyst Characterization

The surface areas of the catalysts were determined by the BET method with a Autosorb – iQ (USA). XRD patterns were recorded with an Ultima IV instrument (Japan) operated at 40 kV and 40 mA using nickel-filtered Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). The morphology of the catalysts was observed by a JEM-00F SEM instrument (Japan) operating at 20 kV. The samples were coated with gold for 30 s before measurement. TEM was also used to observe catalyst morphology (JEM 2100F, Japan). Temperature programmed reduction (H_2-TPR) was performed with Micromeritics AutoChem II Chemisorption Analyzer (USA). The H_2-TPR experimental steps were as follows: 100 mg of sample (40–60 mesh) were pretreated at 300°C in air for 30 min, cooled to room temperature, and purged with He for 30 min. After pretreatment, the H_2-TPR test was performed with a 10% H_2–He mixture and a 10°C/min heating rate using a thermal conductivity detector to measure hydrogen consumption. The surface chemical states of the Pd-Co-Ti catalyst was investigated by XPS (Thermo Scientific K-Alpha, America) using an Al $K\alpha$ X-ray source (1486.7 eV) at 15 kV and 25 W with the binding energy calibrated by C1s at 284.8 eV.

2.3 Evaluation of Catalytic Performance

The catalyst CO oxidation performance evaluation was carried out in a rolling mill. The flue gas is extracted from the chimney of the rolling mill and tested

Table 1 Main components and contents in the flue gas

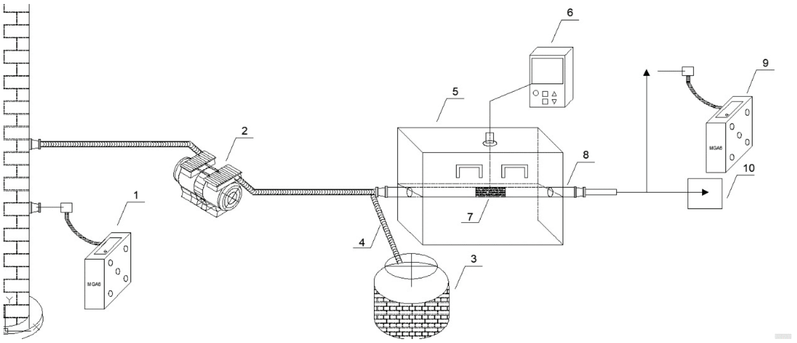
Components	Contents (%)
CO	1.5∼3.7
O_2	3∼10
CO_2	12∼24
NO_x	$\leq 5\times 10^{-3}$
H_2O	10∼20
N_2	42.285∼73.5
Other components	$\leq 10\times 10^{-3}$

in a continuous flow fixed-bed quartz reactor. The main components and contents in the flue gas are shown in Table 1.

The schematic diagram of the test device is shown in Figure 1. The mass of the catalyst was 3 g, and the total gas flow rate was 1500 cm^3/min. Import and export flue gas components are monitored by an MRU infrared flue gas analyzer (MGA6 Plus, Germany). At 280°C, the catalytic performance of the catalyst in the actual flue gas was tested continuously for 168 h. The CO removal efficiency is calculated by the following formula:

$$\eta = \frac{C_{in} \times Q_{in} - C_{out} \times Q_{out}}{C_{in} \times Q_{in}} \times 100\% \tag{1}$$

where C_{in} is the inlet CO concentration of the catalyst, Q_{in} is the inlet flue gas volume of the catalyst, C_{out} is the outlet CO concentration of the catalyst, and Q_{out} is the outlet flue gas volume of the catalyst.



1- MGA6 Plus; 2-air pump; 3-Voltage regulating transformer; 4-Accompanying tropical; 5-Tubular heating furnace; 6-Temperature Controller; 7-Catalyst; 8-Quartz reaction tube; 9- MGA6 Plus; 10-Exhaust gas treatment device

Figure 1 Schematic diagram of test device.

3 Results and Discussion

3.1 Catalyst Characterization

3.1.1 BET

The physical property of Pd-Co-Ti catalyst was tested by N_2 adsorption. The BET surface area, pore volume, and pore size of the Pd-Co-Ti catalyst are 60 m^2/g, 0.306 cm^3/g, and 20.3 nm respectively. Figure 2(a) is the N_2 adsorption and desorption isotherm of Pd-Co-Ti catalyst. Catalyst showed type IV adsorption and desorption curves, and an H3 lag loop appeared under the relative pressure (P/P_0) from 0.6 to 1.0, which indicating the existence of a mesoporous structure in Pd-Co-Ti catalyst. Figure 2(b) is the pore size distribution diagram of Pd-Co-Ti catalyst. As shown in Figure 2(b), most of the pore diameters are between 10 nm and 40 nm. Large BET surface area and rich pore structure facilitate the diffusion of reactants and reaction products.

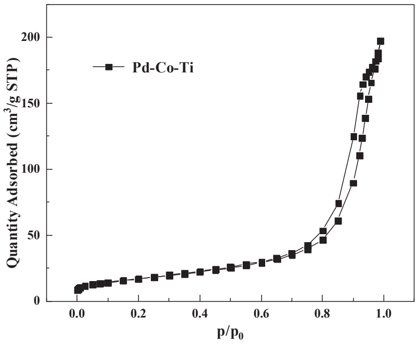


Figure 2(a) N_2 adsorption and desorption isotherm of Pd-Co-Ti catalyst.

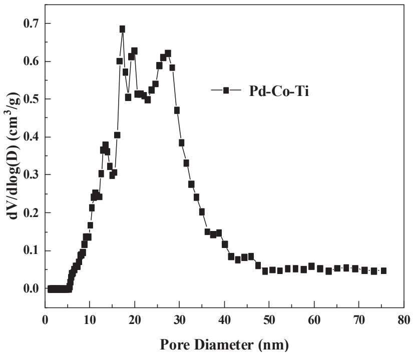


Figure 2(b) Pore size distribution diagram of Pd-Co-Ti catalyst.

3.1.2 XRD

The crystal structure of the Pd-Co-Ti catalyst was investigated by XRD, and the XRD patterns of Pd-Co-Ti catalyst was shown in Figure 3. In the test results, only diffraction peaks of Co_3O_4 and anatase TiO_2 were observed, but no diffraction peaks of Pd species were observed. This may be due to the small loading of Pd, which is below the lower detection limit of the instrument, or the Pd is highly dispersed on the carrier.

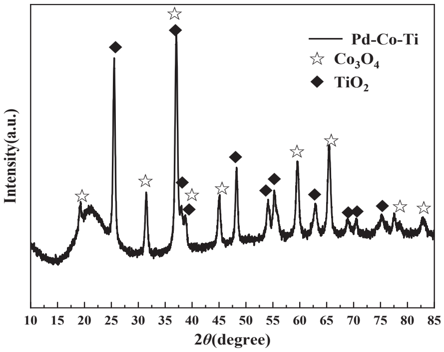


Figure 3 XRD patterns of Pd/TiO_2 catalysts.

3.1.3 TEM

The TEM image of the Pd-Co-Ti catalyst is shown in Figure 4. The lattice spacing observed in Figure 5(a) is 0.24 nm, 0.26 nm and 3.5 nm, which are consistent with the lattice spacing of the Co_3O_4 (311) plane, PdO (101) plane and TiO_2 (101) plane, respectively. The results fully proved that Pd was successfully supported on the surface of the catalyst.

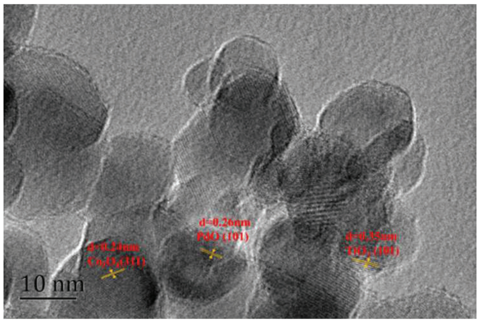


Figure 4 TEM images of Pd-Co-Ti catalyst.

3.1.4 H_2-TPR

H_2-TPR tests were done on Pd-Co-Ti catalyst and Co_3O_4 respectively, and the test results are shown in Figure 5. Pure Co_3O_4 showed two reduction peaks at 270°C and 400°C, which were attributed to the reduction peaks of Co^{3+} being reduced to Co^{2+} and Co^{2+} being reduced to Co^0, respectively. In the Pd-Co-Ti catalyst, the two reduction peaks of Co_3O_4 both shifted to the low temperature direction. Among them, the reduction peak of Co^{3+} reduced to Co^{2+} decreased by 110°C, the reduction peak of Co^{2+} reduced to Co^0 decreased by 75°C, and the reduction peak appeared at 120°C The reduction peak attributable to the PdO. The H_2-TPR results show that there is a synergistic effect between Pd and Co_3O_4, which improves the oxidation-reduction capacity of the catalyst, and Pd-Co-Ti has better CO oxidation activity.

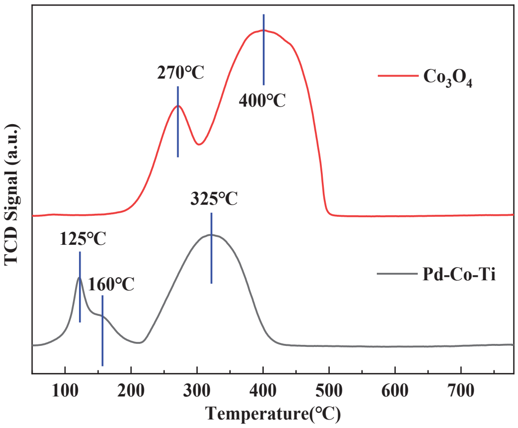


Figure 5 H_2-TPR profiles of Pd-Co-Ti catalyst.

3.1.5 XPS

In order to verify the successful loading of Pd and determine the existence of Pd, the Pd-Co-Ti catalyst was tested by XPS. XPS spectra of the Pd 3*d* core level region in the Pd-Co-Ti catalyst is shown in Figure 6, and doublet peaks were observed the spectra, which can be attributed to the PdO peak at 337.2 eV and 342.4 eV. The results are sufficient to prove that Pd was successfully supported on the surface of the catalyst and mainly exists in the form of PdO.

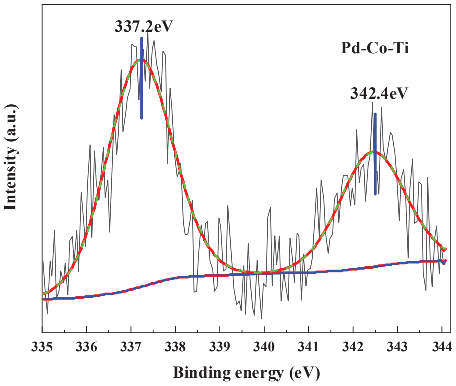


Figure 6 XPS profiles of core level spectra of Pd 3*d* for Pd-Co-Ti catalyst.

3.2 Catalytic Performance

The test results of the Pd-Co-Ti catalyst under actual flue gas conditions are shown in Figure 7. During the 168-hour test period, the inlet CO concentration and O_2 content fluctuated greatly, and the CO removal efficiency was mostly stable above 90%, with some fluctuations during the period. In the first 20 hours, the CO removal efficiency stabilized at around 99%, and then fluctuated. As shown in the green box in Figure 7, large fluctuations occurred from 80∼100 h and 116∼134 h of the test. It is worth mentioning that the CO removal efficiency is greatly affected by the inlet CO concentration and O_2 content. The four large fluctuations in CO removal efficiency all occurred when the inlet CO concentration increased and the O_2 content decreased. In order to further explore the influence of the inlet CO concentration and O_2 content on the CO removal efficiency, Figure 8 is the change curve of the ratio of the inlet CO content and O_2 content over time, and compared with the CO removal efficiency. It is found that the ratio of inlet CO content and O_2 content affects the CO removal efficiency. When the ratio is greater than 0.5, the CO removal efficiency has a downward trend. Within 120∼130h, the ratio is much higher than 0.5, and the CO removal rate at this time drops to around 80%. According to the chemical equation of CO oxidation, the stoichiometric ratio of CO and O_2 is 2:1, which is far greater than 0.5, indicating that when the ratio of inlet CO content to O_2 content is greater than 0.5, the O_2 content is still sufficient. But at this time, the CO removal efficiency measured in the field test decreased. The reason may be that CO is more easily adsorbed on the active sites. Only when the O_2 content is sufficient and the O_2 content is higher than twice the CO content, the catalyst can exert excellent activity.

This parameter is of great significance for the practical application of CO catalysts. When the ratio of inlet CO content to O_2 content is higher than 0.5, air can be added to the flue gas to reduce the CO load and increase the O_2 content, so as to ensure that the CO removal efficiency reaches require.

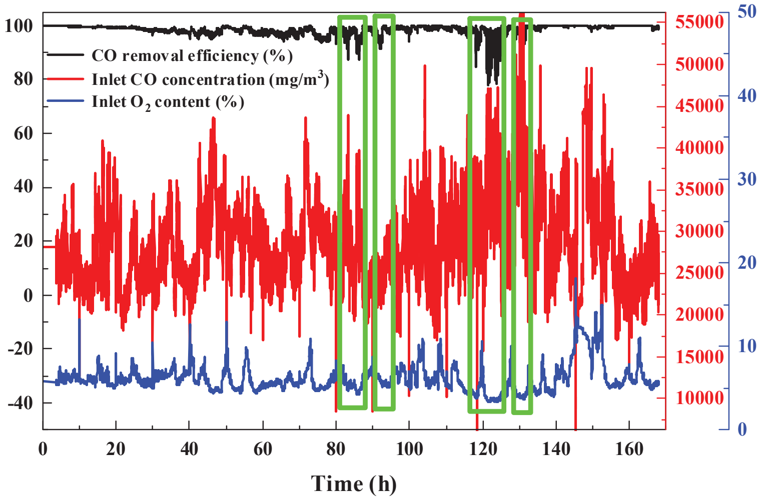


Figure 7 Activity of Pd-Co-Ti catalyst for the catalytic oxidation of CO.

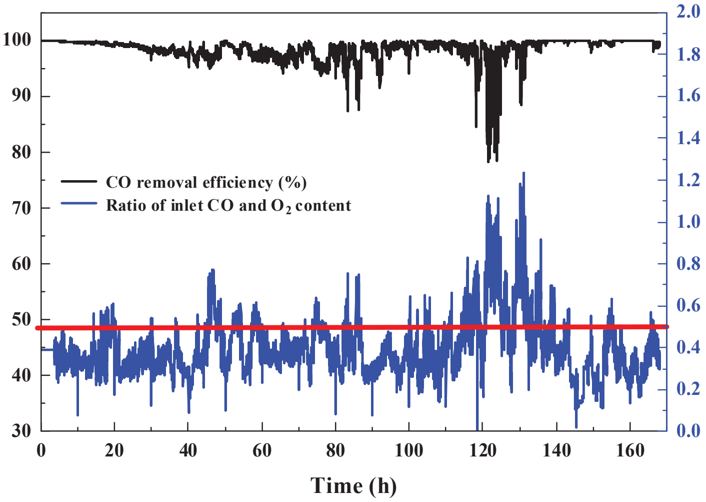


Figure 8 Time-varying curve of CO removal efficiency and the ratio of inlet CO concentration and O_2 concentration.

4 Conclusion

In this study, a Pd-Co-Ti catalyst was prepared by the method of impregnation-precipitation-ball milling. The catalyst has a large specific surface area and a rich pore structure. The synergistic effect of Pd and Co increases the oxidation-reduction capacity of the catalyst. The Pd-Co-Ti catalyst was used to treat CO in the flue gas of a rolling mill. During the 168 hours test period, the catalyst showed good catalytic performance and stability, and the CO removal efficiency was mostly maintained above 90% at a space velocity of 30,000 $cm^3/(g{\cdot}h)$ and a temperature of 280°C. The CO removal efficiency is greatly affected by the ratio of the inlet CO content and the O_2 content. When the ratio is higher than 0.5, the CO removal efficiency shows a downward trend. When the ratio decreases, the CO removal efficiency will increase. This conclusion has very important guiding significance for the practical application of CO catalysts.

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Biographies

Jianyu Cai is a Ph.D. student at the Beijing University of Technology since 2017. He attended the Hebei University of Agriculture, China where he received his bachelor of science in Environmental Science in 2015. He has been engaged in air pollution control engineering research for a long time, including CO catalytic oxidation technology, low temperature SCR denitration technology, acid mist, SO2, NOx and other pollutants adsorption technology, etc.

Zehui Yu is a postgraduate student at the Beijing University of Technology since 2019. He attended the Inner Mongolia University of Science and Technology, China where he received his bachelor of engineering in Mining Major in 2018. He is mainly engaged in air pollution control engineering research, including catalysis, catalyst coating, etc.

Junda He is a Ph.D. student at the Beijing University of Technology since 2020. He attended the Northeast Electric Power University, China where he received his bachelor of engineering in Applied Chemistry in 2016. He then went on to get a master of engineering in Beijing University of Technology, China in 2020. He is mainly engaged in air pollution control engineering research, including CO catalytic oxidation, low temperature SCR denitration technology, Chemical, etc.

Jian Li is a professor and doctoral supervisor at Beijing University of Technology. He attended the Xi'an Institute of Metallurgy and Architecture, China where he received his bachelor degree in engineering in environmental engineering in 1986.He then went on to get a master of engineering in Xi'an Institute of Metallurgy and Architecture, China in 1991. He taught at Xi'an Mining Institute from 1991 to 1996. He received his Ph.D. from Xi'an University of Architecture and Technology in 1999. In 2004, he went to Canada University of Waterloo for further study as a visiting scholar sent by the state. Professor Li has been engaged in air pollution control engineering research for a long time. Professor Li's research mainly includes particle control technology, acid mist control, volatile organic compounds (VOCs) and odor control technology, NO_x pollution control, integrated desulfurization, denitrification and dust removal technology, CO catalytic technology and NH3 oxidation technology, etc.