

Regeneration Performance and Carbon Consumption of Semi-coke and Activated Coke for SO₂ and NO Removal

Yangyang Guo, Feng Qi, Song Ding, Yuran Li, Tingyu Zhu *

Abstract—To decrease the operating cost of flue gas purification technologies based on carbon-based materials, the adsorption and desorption performances of low-price semi-coke and activated coke were compared for SO₂ and NO removal in a simulated flue gas. The functional groups of two adsorbents before and after regeneration were determined by a Fourier transform infrared (FTIR) spectrometer, and were quantitatively tested using temperature programmed desorption (TPD) coupled with FTIR and acid-base titration. The results show that semi-coke has higher adsorption amounts (16.2% for SO₂ and 38.6% for NO) than activated coke because of its richer basic functional groups and lactone. After regeneration, the adsorption performances of semi-coke decrease because the active functional groups decreased and the micropores increased. Semi-coke has a better regeneration performance than activated coke. Semi-coke has a larger SO₂ recovery of 7.2% and a smaller carbon consumption of 12% than activated coke. Semi-coke carbon-based adsorbent could be regenerated at lower temperatures to depress the carbon consumption because the SO₂ recovery is only reduced a little.

Keywords—functional group; SO₂ recovery; adsorption; carbon consumption

Yangyang Guo (Author)
Institute of Process Engineering, Chinese Academy of Sciences
China

Feng Qi (Author)
Institute of Process Engineering, Chinese Academy of Sciences
China

Song Ding (Author)
Institute of Process Engineering, Chinese Academy of Sciences
Guizhou University
China

Yuran Li (Author)
Institute of Process Engineering, Chinese Academy of Sciences
China

Tingyu Zhu (Corresponding author)
Institute of Process Engineering, Chinese Academy of Sciences
China

I. Introduction

The combustion of coal and other fossil fuels emits many pollutants, such as SO₂ and NO_x. To decrease the amounts of these pollutants, many flue gas purification technologies have been developed. Flue gas purification technologies with carbon-based materials are considered as one of the best flue gas purification technologies (Tsuji and Shiraishi, 1997; Zhu et al., 2000; Li et al., 2012; Izquierdo et al., 2003; Guo et al., 2013; Hou et al., 2009). These technologies use activated coke, activated carbon or activated carbon fiber as the adsorbent for SO₂ and NO_x removal, since these materials possess an adsorption capacity for SO_x, NO_x, dioxins and other pollutants by physical-sorption and/or chemisorption, and a catalytic activity for NO_x reduction with NH₃. Moreover, no waste-water and secondary pollutants are produced, and SO₂ can be effectively recovered by the reactions of H₂SO₄ with carbon on the surface when adsorbents are heated (Guo et al., 2008; Zhang et al., 2012).

However, these flue gas purification technologies with carbon-based materials have two key problems, namely, a high operating cost and high heat consumption. For example, when activated coke (approximately 5000 Yuan/ton) is used as the adsorbent, the cost of activated coke is 50 ~ 70% of the total operating cost (Zhang and Xu, 2012). The regeneration temperature is usually 673K, requiring a large amount of heat. Therefore, the main study of the flue gas purification technologies with carbon-based materials is to find a low-price carbon-based material as the adsorbent for reducing the cost, improve the adsorption performances by modification, and lower the regeneration temperature for saving heat. Activated coke has been used in many plants, because its price is cheaper than that of activated carbon.

Semi-coke (approximately 1000 Yuan/ton) is prepared from non-caking coal or weakly caking coal, carbonized at 773 ~ 973K. Semi-coke possesses richer functional groups on the surface than activated coke which is treated by oxidization for increasing specific surface area. Although the preparation processes are different, semi-coke and activated coke have similar physical and chemical properties. It was reported that the low-price lignite semi-coke has an adsorption capacity for mercury (Zhang et al., 2012), the same as activated coke. Therefore, to explore the application prospect of semi-coke for SO₂ and NO removal, the comparison of adsorption and desorption performances is carried out between semi-coke and activated coke.

II. Experiments

Semi-coke from the Sanjiang Coal Chemical Plant (Shanxi, China) and activated coke from the Xinhua Chemical

Plant (Taiyuan, China) were used. Two materials were crushed, sieved, washed and then dried at 378K for 24 h after filtration.

An elemental analysis was performed on a Vario EL cube Analyzer, and the pore properties of adsorbents were determined at 77K through nitrogen adsorption (Quantachrome, Autosorb-iQ). Functional groups of adsorbents were characterized by a FTIR spectrometer (Thermo, Nicolet 6700). The functional groups, which contained oxygen, were analyzed by temperature programmed desorption (TPD) coupled with FTIR, and the basic functional groups were determined by acid-base titration.

The SO₂ recovery is the ratio of total SO₂ release amount during regeneration to total SO₂ adsorption amount during adsorption. Carbon consumption is the total C amount of CO and CO₂ during regeneration (mmol·g⁻¹).

During adsorption, the adsorbent was maintained for 90 min in the simulated flue gas, the temperature was 423K, the total flow was 300 ml·min⁻¹, and the gas hourly space velocity (GHSV) was approximately 5700 h⁻¹. After adsorption, the adsorbent was regenerated by heating. The regeneration temperature was from 423K to 673K at 5K·min⁻¹ and then was maintained at 673K for 40 min in N₂. The gas flow was 180 ml·min⁻¹ during regeneration. The adsorption experimental parameters for regenerated adsorbent were identical to the first adsorption experimental parameters. The concentrations of components in the inlet and outlet were measured online by a FTIR spectrometer (Bruker, Tensor27). The compositions of simulated flue gas are listed in Table 1.

TABLE 1 COMPOSITIONS OF THE SIMULATED FLUE GAS

SO ₂ / ppm	NO / ppm	NH ₃ / ppm	H ₂ O / %	O ₂ / %	N ₂
1000	500	500	5	5	balance

III. Experiments Results

A. Adsorption Performances

Figure 1 shows the breakthrough curves of two adsorbents. The SO₂, NO and NH₃ breakthrough concentrations of semi-coke were lower than those of activated coke. Through integration and calculation, the de-SO₂ and de-NO amounts of activated coke were 11.70 mg·g⁻¹ and 0.88 mg·g⁻¹, respectively, and the de-SO₂ and de-NO amounts of semi-coke were 13.60 mg·g⁻¹ and 1.22 mg·g⁻¹, respectively. The adsorption amounts of semi-coke were 16.2% higher for SO₂ and 38.6% higher for NO than those of activated coke. The result indicates that semi-coke has better adsorption performances for SO₂ and NO than activated coke.

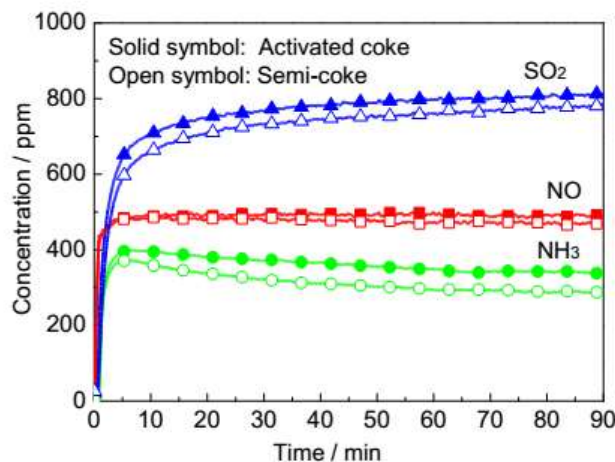


Figure 1. Breakthrough Curves of the Adsorbents

B. Re-Adsorption Performance after Regeneration

The breakthrough curves of adsorbents after regenerated are shown in Fig. 2. Through integration and calculation, the adsorption amounts of activated coke after regeneration are 12.07 mg·g⁻¹ for SO₂ and 0.88 mg·g⁻¹ for NO. The adsorption amounts of semi-coke after regeneration are 12.75 mg·g⁻¹ for SO₂ and 0.6 mg·g⁻¹ for NO. The de-SO₂ amount of semi-coke after regeneration is 5.6% higher than that of activated coke, but the de-NO amount of semi-coke after regeneration is 31.8% lower than that of activated coke. Compared the adsorption amounts of semi-coke before and after regeneration, the adsorption amounts of semi-coke after regeneration are 6.3% smaller for SO₂ and 50.8% smaller for NO than those of fresh semi-coke.

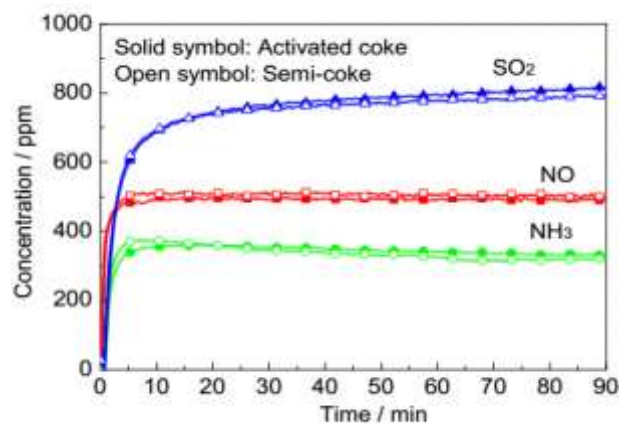


Figure 2. Breakthrough Curves of Adsorbents after Regeneration

C. Carbon Consumption

During thermal regeneration, H₂SO₄ and ammonium sulfates can react with carbon on the surface, releasing SO₂, NH₃, CO and CO₂ with the temperature rising. Through integrating the SO₂, CO and CO₂ concentration rising curves, the results are shown in Table 2. When 1 mol SO₂ is released, the

carbon consumption of semi-coke and activated coke are 0.8 mol and 0.91 mol, respectively. The carbon consumption of semi-coke is 12% smaller than that of activated coke.

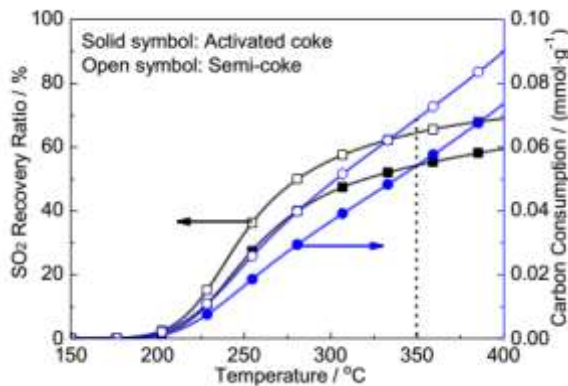


Figure 3. SO₂ Recovery and Carbon Consumption during regeneration

Figure 3 shows the SO₂ recovery ratios and the carbon consumptions of two adsorbents during regeneration at temperatures from 423K to 673K. The initial decomposition temperature is 473K. As the temperature rises, the SO₂ recovery ratios of two adsorbents firstly increase quickly and then slowly, and the carbon consumptions increase throughout the entire course. The SO₂ recovery ratios of semi-coke and active coke at 623K (64.6% and 54.4%, respectively) are 4.3% and 5.1% smaller than at 473K (68.9% and 59.5%, respectively). The carbon consumptions of semi-coke and active coke at 623K (0.069 mmol·g⁻¹ and 0.054 mmol·g⁻¹, respectively) are 23.3% and 27.0% smaller than at 673K (0.090 mmol·g⁻¹ and 0.074 mmol·g⁻¹, respectively). Therefore, to depressing the decomposition of active functional groups and reducing the carbon consumption, the adsorbents which adsorbed SO₂ could be regenerated at lower temperatures, and the SO₂ recovery would slightly decrease.

iv. Conclusions

Semi-coke shows better adsorption performances for SO₂ and NO than activated coke, because it possesses richer basic functional groups and lactone. After regeneration, the adsorption amounts of semi-coke decreased by 6.3% for SO₂ and 50.8% for NO, and the adsorption amounts of activated coke did not changed for SO₂ and NO. However, the adsorption amount of semi-coke is 5.6% higher for SO₂ than that of activated coke.

Semi-coke display a better regeneration performance than activated coke. After regeneration, the SO₂ recovery ratios of semi-coke and activated coke are 69.6% and 62.4%, respectively, and the carbon consumption of semi-coke is less than 12% of the carbon consumption of activated coke. When adsorbents are regenerated at a lower temperature, the carbon consumption will be depressed and the SO₂ recovery ratio will only slightly reduced.

Acknowledgments

The authors acknowledge the financial support from the National Natural Science Foundation of China (21207132) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB05050502).

References

- [1] K. Tsuji, I. Shiraishi, 1997. Combined desulfurization, denitrification and reduction of air toxics using activated coke: 1. Activity of activated coke. *Fuel*, 76(6):549-553.
- [2] Z. Zhu, Z. Liu, S. Liu, H. Niu, 2000. Adsorption and reduction of NO over activated coke at low temperature. *Fuel*, 79: 651-658.
- [3] P. Li, Q. Y. Liu, Z. Y. Liu, 2012. Behaviors of NH₄HSO₄ in SCR of NO by NH₃ over different cokes. *Chemical Engineering Journal*, 181-182:169-173.
- [4] M. T. Izquierdo, B. Rubio, C. Mayoral, J. M. Andres, 2003. Low cost coal-based carbons for combined SO₂ and NO removal from exhaust gas. *Fuel*, 82:147-151.
- [5] Y. Guo, Y. Li, T. Zhu, M. Ye, 2013. Effects of concentration and adsorption product on the adsorption of SO₂ and NO on activated carbon. *Energy & Fuels*, 27(1): 360-366.
- [6] Y. Hou, Z. Huang, S. Guo, 2009. Effect of SO₂ on V2O5/ACF catalysts for NO reduction with NH₃ at low temperature. *Catalysis Communications*, 10(11): 1538-1541.
- [7] Guo Y. X., Liu Z. Y., Liu Q. Y., Huang Z. G., 2008. Regeneration of a vanadium pentoxide supported activated coke catalyst-sorbent used in simultaneous sulfur dioxide and nitric oxide removal from gas: Effect of ammonia. *Catalysis Today*, 131:322-329.
- [8] L. Zhang, H. Jiang, C. Ma, D. Yong, 2012. Microwave regeneration characteristics of activated carbon for flue gas desulfurization. *Journal of Fuel Chemistry and Technology*, 40(11): 1366-1371
- [9] X. Zhang, D. Xu, 2012. The Preparation and Properties of Activated Semi-coke, and Mechanisms of Flue Gas Desulfurization. *Chemical Industry Press, Beijing*, pp. 10-11.
- [10] H. Zhang, J. Chen, P. Liang, L. Wang, 2012. Mercury oxidation and adsorption characteristics of potassium permanganate modified lignite semi-coke. *Journal of Environment Sciences*, 24(12): 2083-2090.