

CHANGE OF PROPERTIES OF ACTIVE COKE ACCORDING TO REGENERATION

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Abstract

The active coke is widely used as adsorbent of SO_x and dioxin and catalyst for decomposition of NO_x in active coke process. The properties of active coke are changing with repetition of adsorption and catalytic reaction and regeneration cycles. In this study, properties and removal performance to pollutants of active cokes prepared from mixture of bituminous coals with other commercial active cokes were observed and considered with repetition of adsorption and regeneration.

Introduction

Sulfur oxides, nitrogen oxides and dioxins are important pollutants that contribute to the acid rain formation and health problems to the human. For the NO_x conversion to nitrogen and removal of sulfur oxide, selective catalytic reduction (SCR) deNO_x process and limestone deSO_x process have been developed, and for the removal of dioxin adsorption method with installing of activated carbon tower or injection of activated carbon powders or inorganic adsorbents into the bag filter has been developed. The active coke processes were developed for removal of SO_x, NO_x and dioxin simultaneously in the single process and have been operated successfully in many sites in Europe, Japan and Korea. The active coke, adsorbent of active coke process, supplies continuously from top of the adsorber bed and adsorbs SO_x and dioxin with catalytic reduction of NO_x in the adsorber tower which is operated with moving bed type and drawn off from adsorber. The discharged active coke is regenerated in the regenerator and recycled into the adsorber. The properties of active coke become changing with repetition of adsorption and regeneration. In this study, properties and removal performance to pollutants of active cokes prepared from mixture of bituminous coals with other commercial active cokes were observed and considered with repetition of adsorption and regeneration.

Experiment

The active coke was prepared from bituminous coals which volatile matter content is in the range of 20~25%. The several bituminous coals were milled and mixed in the proper ratio together with coal tar pitch binder, kneaded, formed, carbonized and activated in sequence. An active coke which BET surface area is 251m²/g and has similar hardness with metallurgical coke was selected for this experiment. For comparing two commercial active cokes produced by Shanxi Xinhua and Calgon were also considered together. The BET surface area and additional pore properties were determined by Micromeritics ASAP2020M model automatic physical adsorption analyzer using nitrogen gas at 77K.

The catalytic activities of active cokes for NO_x conversion were measured by passing simulated NO gas through a glass column packed with samples. Each sample was evacuated in a vacuum oven at 150°C for 1 hour before packing. The feed gas consisted of 400ppm NO and O₂ 5% and balance N₂ supplied into 10g of sample in the column with space velocity 1650h⁻¹. The each gas flow was metered by each mass flow controller and all gases were mixed with passing through the static mixer and then transferred to the reaction column. The temperature of the reaction column was maintained to 100~150°C by miniature furnace. NO concentration of exhaust gas was measured with Thermo Environmental Instrument 41H chemiluminescence NO_x analyzer.

The SO₂ adsorption amount of active cokes was measured with TherMax 500 high pressure and high temperature thermogravimetric analyzer. For SO₂ adsorption, the feed gas consisted of 1000 ppm SO₂ and helium.

Result and Discussion

Figure 1 and figure 2 illustrates pore size distributions of active cokes. The BET specific surface area of the prepared active coke was 251m²/g and Xinhua and Calgon active cokes show 160 m²/g and 184 m²/g, respectively. Pore size distributions of all active cokes were mainly distributed in micropore range similarly. The DFT plots in figure 2 shows also almost of pores are distributed in micropore range. Figure 3 shows SO₂ adsorption with reducing temperature by degrees from 150°C to 100°C. Adsorption amounts of SO₂ on active cokes increased with increasing BET specific surface areas and remarkably increased with reducing adsorption temperature.

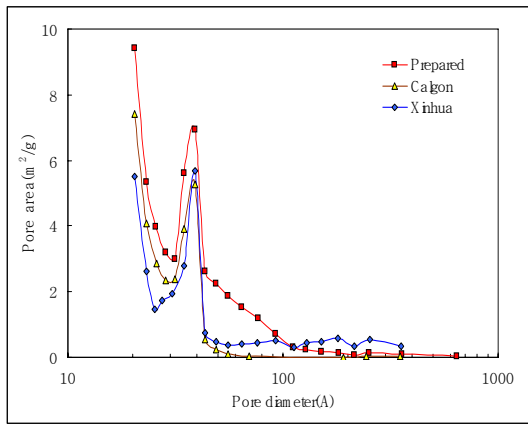


Figure 1 Pore size distribution measured by BJH plot of active cokes

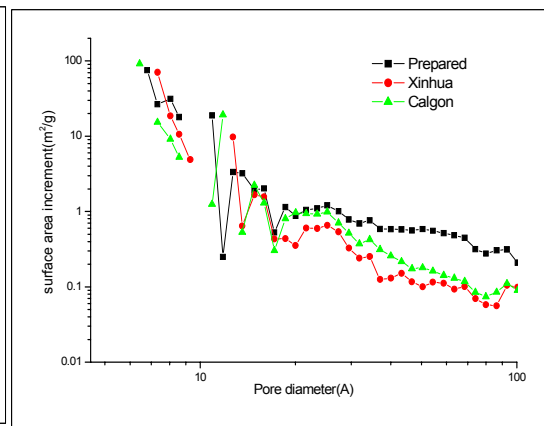


Figure 2 Pore size distribution measured by DFT plot of active cokes

This result will be made up for additional detail adsorption tests about repetition of regeneration and the relativity of regeneration treatment history and SO₂ adsorption with surface area. In the figure 4, it shows NO conversion at 150 °C of active coke with respect to repetition of regeneration at 250 °C in nitrogen atmosphere. The catalytic reactivities of active cokes become better with repetition of regeneration. It is presumed that reactivity is compositively affected with increase of specific surface area and changes of surface functional group. This will be made up with supplementary regeneration experiments and reported totally.

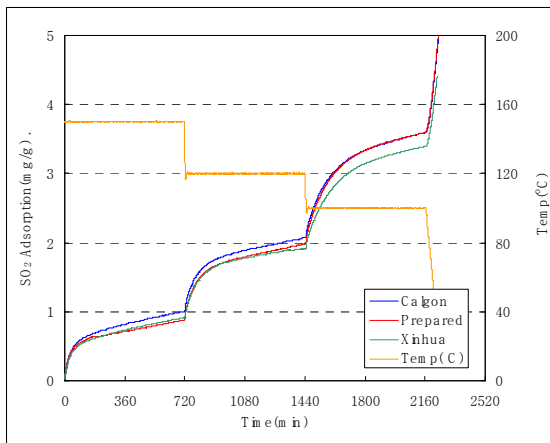


Figure 3 SO₂ adsorption of active cokes with respect to temperature

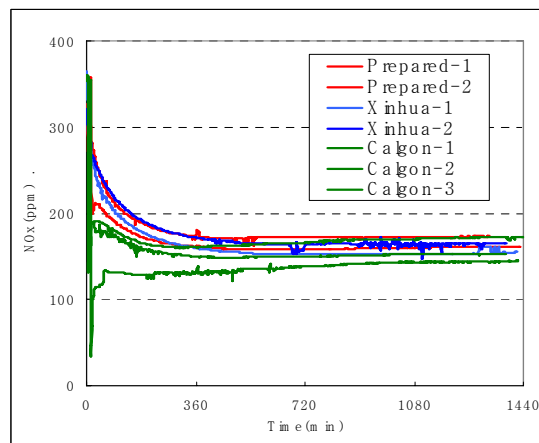


Figure 4 NO conversion of active coke with respect to repetition (150 °C)

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