SCR REACTIVITY OF ACTIVATED CARBON FROM FLUIDIZED BED PYROLYSIS

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Introduction

Use of activated carbon for simultaneous removal of both SO_x, and NO_x and for removal of NOx following a flue gas desulfurization plant has been recognized as an effective means for reduction of air toxics in flue gas because this process is reliable, efficient and environmental-friendly a process which produces useful byproducts instead of waste [1]. However, the catalytic activity of activated carbon for denitrification(selective catalytic reduction: SCR) is not sufficiently high compared to that of desulfurization. In order for the activated carbon process to be more effective for the combined SO_2 and NO_x removal, the catalytic activity of activated carbon should be improved.

Activated carbons used in this study showed varied physical and chemical properties such as surface area, surface oxygen functional groups, oxygen to carbon mole ratio and content of volatile matter, depending on the pyrolysis conditions under which they are obtained. It is also follows from our experiments that their catalytic activities are dependent on pyrolysis conditions. Thus it is important to find relationships between the properties of activated carbon and catalytic activities of them in order to establish pyrolysis conditions for producing suitable activated carbons to be used as SCR catalyst.

Experimental

A fluidized bed whose inside diameter and length were 0.1 m and 0.6 m, respectively was employed to prepare activated carbon from a lignite. Steam, oxygen and nitrogen could be supplied to the reactor at any desired flow rate and composition. The pyrolysis temperature was adjusted by controlling the external surface temperature of the fluidized bed reactor using a PID-type temperature controller.

Catalytic activity of the activated were evaluated with a fixed bed integral reactor. The reactor was made of Pyrex® tube with 3.8cm inside diameter and 35cm length. Ammonia, nitric oxide, oxygen and nitrogen were fed to the reactor through mass flow controllers. Ammonia gas in the effluent gas was removed by 4% boric acid trap before it was pumped to the NO_x analyzer(NDIR, Horiba Ltd.). The measured NO concentration was stored with a data acquisition system consisting of an analog/digital interface connected to a personal computer. Conversion of NO was defined as follows: (1-output NO concentration/input NO concentration)x100%. Standard reaction conditions were as follows: reaction temperature 150°C, NO and NH_3 concentration 1,000 ppm, oxygen concentration 3%, space velocity 400 hr^{-1}. In the range of our experimental conditions, formation of N_2O over carbon catalyst was not observed using a quadrupole mass spectrometer (Quadstar 420, Balzers).

Surface oxygen functional groups are known to decompose as CO_2 and CO at high temperature in inert atmosphere. Hence, the quantities that are destroyed can be represented indirectly by the temperature-programmed desorption(TPD) analysis. An attempt was made to identify the CO_2 and CO from surface functional groups of the activated carbons by gas chromatography using a Porapak Q column at 40°C. Surface area measurement of the activated carbon was carried out with carbon dioxide adsorption at 25°C in a conventional volumetric apparatus.

Results and Discussion

Initially dependency of catalytic activity on O/C ratio and volatiale matter content was examined with activated carbon samples obtained under different pyrolysis conditions. But, it was insufficient to elucidate the effect of preparation conditions on catalytic activities of the activated carbons. The catalytic properties of carbon catalyst for denitrification do not always depend on their BET surface area.

Considering the TPD profiles of the activated carbon samples oxygen-containing groups might play a significant role in the activity behavior. The catalytic

active sites of carbon catalysts for SCR reaction are mainly surface oxides, which are bonded to carbon surface [2]. Therefore, we tried to explain the difference in catalytic activities with the result of surface area and the amount of surface functional groups .

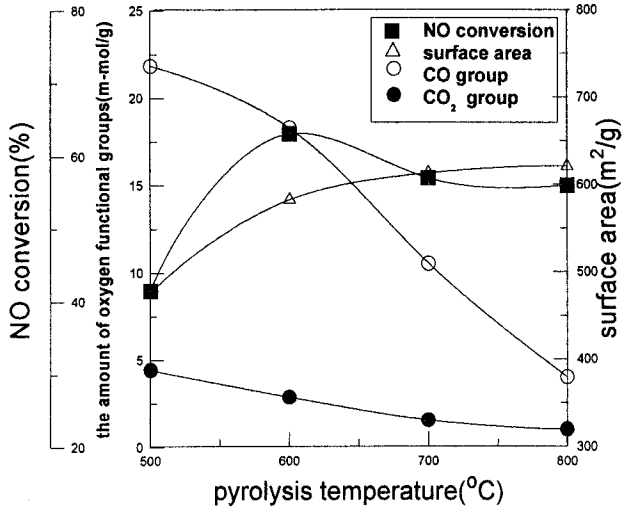

Figure 1. Effect of pyrolysis temperature on surface area, oxygen functional groups measured as CO and CO_2 and catalytic activities of activated carbon prepared. Pyrolysis gas, N_2 containing 3.2% O_2, SCR reaction temperature 150°C, NO and NH_3 concentration 1000 ppm, oxygen concentration 3.2%, space velocity 420 hr^{-1}.

As shown in Figure 1. Catalytic activity of activated carbon(NO conversion) which was obtained from 500°C of pyrolysis temperature was lower than those from higher temperature, even though it had higher amount of oxygen functional groups. This implies the existence of other parameters which are important in deciding catalytic activities of activated carbons. As can be seen in the figure, surface area of activated carbon increases rapidly with pyrolysis temperature between 500 and 600°C, but very slowly at higher temperatures. Therefore we can construe that effect of pyrolysis temperature on NO conversion be a combination of the surface area and the amount of oxygen functional groups of activated carbons prepared. The observed maximum catalytic activity at pyrolysis temperature of 600°C is the result of their combination [3, 4].

This result described above is that there is an optimal density of oxygen functional groups. Surface functional groups are act as active site for oxidative adsorption of NO, but too high a surface density of oxygen functional groups interferes with the adsorption as a result of the repulsive interaction of NO_2 present in the adsorbed multilayer. Figure 2 shows the relationship between the NO conversion and the density of oxygen functional groups. The density of oxygen functional groups described in Figure 2 meant that the total sum of mole of CO_2 and CO evolved was divided by the surface area of activated carbon sample. As shown in Figure 2, the maximum catalytic activity was observed for activated carbon sample prepared at the intermediate value of density of oxygen functional groups which was strongly affected by the pyrolysis temperature.

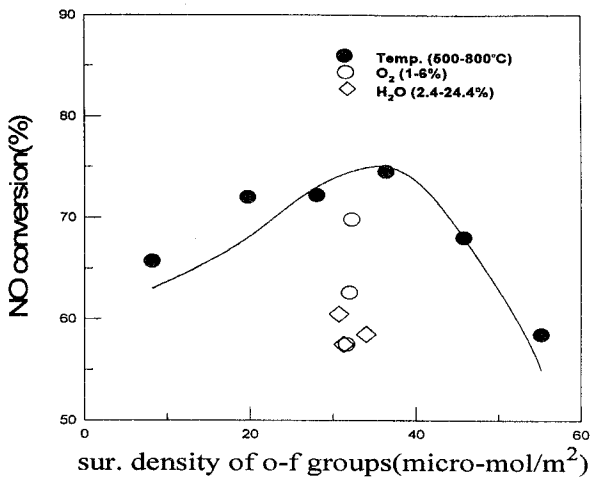

Figure 2. Relationship between the NO conversion and the density of oxygen-functional groups of activated carbons prepared under various kinds of pyrolysis conditions.

Conclusions

Pyrolysis temperature appears to be a primary variable in affecting SCR reactivity of activated carbon derived from lignite pyrolysis. The surface area and the amount of oxygen functional groups have an important effect on the catalytic activity of activated carbon. The dependency came from proper amount of oxygen functional groups per unit surface area of the activated carbon.

Reference

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