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Iron-catalyzed nitrogen removal as N_2 from PAN-derived activated carbon

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ABSTRACT

Polyacrylonitrile-derived activated carbon as a model of coal char has been heated in high-purity He at 10 °C/min up to 1000 °C with a flow-type fixed bed quartz reactor, and the catalysis of N_2 formation by precipitated iron has been investigated by use of XPS, TEM and XRD methods. Fine iron particles with the average size of 15 nm increase remarkably the formation rate between 600 and 1000 °C, and N_2 yield up to 1000 °C reaches about 65% at 1.9 mass% Fe. The XPS and XRD measurements after heat treatment exhibit that nitrogen functionality does not change significantly, but carbon crystallization occurs through the dissolution of iron nanoparticles into the carbon substrate. The *in situ* XRD analyses during heating reveal the formation of austenite that is solid solution of Fe and N (and/or C). Interestingly, the catalysis of N_2 formation by iron and the formation of austenite occur at almost the same temperature range of 600–1000 °C. It is thus likely that nanoscale iron particles move in the carbon matrix and react with heterocyclic nitrogen in order to produce the solid solution, which is subsequently decomposed into N_2.

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1. Introduction

The nitrogen present in coal (coal-N) exists predominantly in thermally stable heterocyclic structures, such as pyridinic and pyrrolic forms [1,2]. When coal is burned with air in a combustion furnace in order to produce electricity, the pyrolysis first takes place: volatile components such as gas and tar are released, whereas mineral matter and fixed carbon, which is composed mainly of condensed aromatic structures, are retained as char. Subsequently, gas and tar are combusted with O_2 in air, and the carbon is then burned. In the similar way, coal-N is first pyrolyzed and transformed into volatile-N (tar-N, HCN and NH_3) and char-N. Because the partitioning of coal-N to gas, tar and char species in the pyrolysis step is one of the important factors determining NO_x and N_2O emissions in the subsequent combustion process [3–6], the pyrolytic behavior of coal-N has been examined extensively and reviewed by several workers [4,5,7–10]. Since char-N may make the major contribution to the formation of NO_x and N_2O [3,11], efficient nitrogen removal as N_2 from char-N at the pyrolysis stage might lead to significant reduction of these nitrogen oxides.

The present authors' group has been working on the fate of coal-N upon pyrolysis, in particular focusing on the formation of inert N_2 from many coals with different ranks [12–14], though most of the researchers have paid no attention to this topic. We have shown that char-N is the major source of N_2, and that nanoscale particles of metallic iron, which are formed from Fe^{3+} cations added to low rank coals [15,16] or naturally present in them [13,14], can catalyze the transformation of char-N to N_2 at 750–1000 °C. These findings are interesting from the above-mentioned viewpoints. Although it has also been suggested that the iron-catalyzed conversion of char-N to N_2 may occur via solid–solid interactions of iron nanoparticles with pyridinic and pyrrolic forms [16,17], no mechanistic studies have been made in more detail so far. In the present paper, therefore, the main objective is to clarify how iron–nitrogen interactions occur in the carbon matrix of char. For this purpose, polyacrylonitrile-derived activated carbon with heterocyclic nitrogen structures, denoted as PAN carbon, is used as a model of coal char, because it does not contain any metal impurities that may affect the main purpose of this work but includes the nitrogen amount sufficient for the detailed analysis and characterization. We first investigate the influence of nano-ordered iron catalyst on N_2 formation in the temperature-programmed heat treatment of PAN carbon, and then elucidate iron–nitrogen interactions at solid phase by means of XPS, TEM and XRD techniques.

2. Experimental

2.1. Carbon sample

PAN carbon was prepared in the following manner. Commercially available polyacrylonitrile, which was obtained from Polyscience, Inc., was first carbonized in a stream of He at 1000 °C

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for 30 min, and then activated in 20 vol% O_2/He at 500 °C for 100 min. The C, H, N and O contents in PAN carbon with size fraction of 44–74 μm were 79.3, 0.4, 6.8 and 13.5 mass%-dry, respectively. Since it has been reported that coal chars after pyrolysis at 500–900 °C contain C, H, N and O elements in the concentration range of about 75–95, 0.1–3.0, 0.5–2.5 and 2.0–20 mass%-daf, respectively [18], the present carbon sample may be regarded as N-enriched model char. The BET surface area of the PAN carbon analyzed by the N_2 adsorption method was 480 m^2/g, which was about 10 times larger than that (5 m^2/g) without any activation.

2.2. Iron addition

An aqueous solution of $FeCl_3$ was used as a catalyst precursor, because it is readily available as the main component of acid wastes from iron and steel pickling plants. A Cl-free iron catalyst in highly dispersed forms was precipitated onto the PAN carbon from $FeCl_3$ solution by using $Ca(OH)_2$. The procedure has been described in detail earlier [19] and is thus simply explained below. A mixture of the carbon and $FeCl_3$ solution was stirred at room temperature, and a sufficient amount of $Ca(OH)_2$ powder was then added to precipitate the iron as FeOOH onto the carbon surface according to the following equation:

$$2FeCl_3 + 3Ca(OH)_2 \rightarrow 2FeOOH + 3CaCl_2 + 2H_2O \qquad (1)$$

The resulting iron-loaded carbon was separated from the solution by filtration, then washed repeatedly with purified water in order to remove excess $Ca(OH)_2$, and finally dried in a flow of N_2 at 110 °C for 60 min. Fe loading was controlled by changing the initial concentration of $FeCl_3$ in water, and the actual loading in the dried sample, determined by the atomic absorption spectroscopy method after acid leaching [19], was 0.9 or 1.9 mass% as the metal. Further, Cl determination of each sample by a standard Eschka method (ISO 587-1981 (E)) exhibited that the iron was free from Cl contamination. The Cl ions in $FeCl_3$ solution could thus be removed completely as water-soluble $CaCl_2$ according to Eq. (1).

The Mössbauer and Fe 2p XPS measurements have revealed that Fe cations, which are precipitated onto the surface of an Australian brown coal by the same method as mentioned above, exist as fine particles of FeOOH [20]. The same Fe 2p XPS spectra were detectable for the present samples with Fe cations precipitated, and atomic Fe/C ratios determined by the XPS were larger than those obtained by the elemental analysis. These observations show that the present iron catalysts are also in the form of fine particles of FeOOH on the carbon surface. The N 1s XPS and elemental analyses exhibited that there was no significant difference between the surface and bulk N/C ratios (7.0×10^{-2} to 7.1×10^{-2}), which were almost unchanged before and after catalyst addition.

2.3. Heat treatment

All experiments were made in a temperature-programmed mode with a fixed bed quartz reactor. The details of the apparatus have been described earlier [12]. In the run, about 180 mg of the PAN carbon or iron-loaded carbon was first charged into a rectangular quartz cell on a quartz holder in the reactor, and special care was then taken in order to ensure that the whole reaction system was free from any leakage. After such prudent precautions, the reactor was heated at 10 °C/min up to 1000 °C in a stream of high-purity He (>99.9999%), soaked for 60 min, and then quenched to room temperature. The flow rate was controlled at 100 cm^3 (STP)/min, which corresponded to a linear velocity of 0.33 mm/s at atmospheric pressure.

2.4. Nitrogen analysis

The N_2 in the effluent from the reactor outlet was determined online at intervals of 5 min with a high-speed micro gas chromatograph (GC) (Microsensor Technology, Inc., M200). The effluent was also collected into an aluminum-laminated plastic bag, and the HCN and NH_3 in the bag were measured with a Fourier transform infrared spectrometer (FT-IR) (Bio-Rad, Inc., FTS40A) equipped with a long-path gas cell. The carbonaceous residue remaining in the cell after heat treatment was recovered as char, and the N in the char (char-N) was determined with a conventional nitrogen analyzer (Yanaco Analytical Instruments Corp., MT500HC/MTS1). Any tarry materials were not observed under the present conditions. In addition, no NO and N_2O were also detectable by the FT-IR method. These observations may be reasonable, because no significant amounts of volatile matters are released during heat treatment of PAN carbon samples. Yield of N_2, HCN, NH_3 or char-N was expressed in percent of total nitrogen in feed sample. Nitrogen mass balances for all runs fell within the reasonable range of 94–106%, which indicates that all of the analytical methods used for N determination are reliable.

2.5. XPS analyses and TEM observations

The X-ray photoelectron spectroscopy (XPS) measurements were carried out with a non-monochromatic Mg-Kα source operating at 240 W (Shimadzu Corp., ESCA750) in order to examine the chemical forms of the N and Fe on the surfaces of iron-bearing chars. The specimens were made into fine powders just before each XPS analysis and mounted onto a sample holder using Ag paste. Long acquisition times of several hours were used in order to obtain good resolution for the N 1s and Fe $2p_{3/2}$ spectra, and their binding energies were referred to the Ag $3d_{5/2}$ peak at 367.9 eV. Least-squares curve-fitting analyses of N 1s spectra were made using Gaussian peak shapes. Upon deconvolution, the binding energy of each peak and the full width at half-maximum (fwhm) value were fixed within ±0.1 eV, and only the amplitude was varied in order to obtain the optimum curve resolution [17].

Char samples after heat treatment at 600–1000 °C were further characterized with a high resolution transmission electron microscope (TEM) (JEOL, Ltd., JEM3010) at a resolution of 0.2 nm and at an accelerating voltage of 300 kV. The average size and size distribution of iron particles were estimated by counting 100 particles from representative TEM images of each sample. The analytical conditions have been described in detail previously [17].

2.6. XRD measurements

The powder X-ray diffraction (XRD) analyses of iron-bearing chars cooled to room temperature after heat treatment were conducted with an X-ray diffractometer (Shimadzu Corp., XRD6000) using Mn-filtered Fe-Kα radiation (30 kV, 40 mA) in order to identify crystalline forms of iron catalysts and evaluate carbon structures quantitatively. Changes in iron forms during heating were also examined by the *in situ* XRD technique, in which about 50 mg of the PAN carbon with 1.9 mass% Fe was heated up to 655–1025 °C under the same conditions as in the temperature-programmed heat treatment mentioned above. The C (0 0 2) signal after removal of the diffraction background was deconvoluted into amorphous (A-) (31.1°) and turbostratic (T-) (33.1°) carbon by the curve-fitting method using Gaussian peak shapes [21–23]. The reproducibility of the present deconvolution analysis fell within ±3% in every case.

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