[Review Paper]

Selective Conversion of Fuel-bound Nitrogen to N_2 with Iron Nanoparticles

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The highlight of this review article is a novel method to remove fuel-bound nitrogen as N_2 during coal pyrolysis in an inert atmosphere.

When a Cl-free iron catalyst is precipitated on Australian brown coal from $FeCl_3$ solution using $Ca(OH)_2$, N_2 yield increases with increasing pyrolysis temperature and reaches 50% at $900^\circ C$, whereas it is $< 5\%$ without the iron. A low loading (1 wt% Fe) is sufficient for the remarkable formation of N_2 , and the use of H_2 instead of inert He is unnecessary. The iron catalyst decreases the partitioning to not only volatile nitrogen (tar, HCN, and NH_3) but also char nitrogen. A smaller catalytic effect of the precipitated iron is observed with bituminous coal. The iron catalyst after pyrolysis exists as fine particles with a smaller size of 20–30 nm for the brown coal char, Fe_3C and graphitized carbon being also present. It is likely that N_2 originates mainly from solid phase reactions involving the formation and subsequent decomposition of iron nitrides.

In the pyrolysis of different coals at $1000^\circ C$, N_2 yields for low-rank coals from China and Germany reach 50–60% despite the absence of catalyst. Demineralization with HCl washing removes mainly Fe and Ca elements from these coals and drastically decreases N_2 yield with a corresponding increase in nitrogen retention in the chars. The Ca ion-exchanged with the demineralized coals is inactive for N_2 formation. Iron nanoparticles, derived from Fe-containing minerals, catalyze predominantly solid phase reactions to extract N_2 from char and/or precursors.

1. Introduction

The nitrogen present in fossil fuels, such as coal and heavy oil, that is, fuel-bound nitrogen (fuel-N), exists mostly as heteroatoms within aromatic rings, and is the source of nitrogen oxide pollutants emitted during combustion. The nitrogen content of coal on a dry, ash-free basis mainly ranges from 0.5 to 2 wt%, which is several orders of magnitude greater than that of heavy oil. Technologies for the control of emissions of nitrogen oxide pollutants are thus more important in coal combustion processes.

When coal is burnt, NO_x and N_2O are emitted. In conventional pulverized coal-fired plants, 75–95% of the NO_x consist of fuel- NO_x , which originates from fuel-N, the remainder being thermal NO_x from air^{1)–3)}. As is well-known, NO_x has been implicated in acid rain and photochemical smog formation. Various technologies, such as combustion modifications and flue gas treatment, have thus been developed to comply with regulations concerning NO_x emissions from coal combustion^{1)–3)}.

On the other hand, N_2O emissions from conventional combustion are low^{4),5)}. It has been suggested, however, that some NO_x abatement and control technologies increase the N_2O emissions. Further, fluidized bed combustion of coal, which has improved environmental performance and can be operated at a lower tempera-

ture than in pulverized coal-fired boilers, emits considerably higher concentration of N_2O ^{4),5)}. N_2O is known to be involved in both the greenhouse effect and the ozone layer depletion, but it appears that any technologies for the control of N_2O have not yet been developed.

When coal is fed into a combustion chamber, the pyrolysis (devolatilization) first takes place, and subsequently volatiles released from coal and remaining solid residues (called “char”) react with O_2 . A simplified scheme of NO_x and N_2O emissions from coal is thus illustrated in **Fig. 1**, where coal-N, tar-N, and char-N mean the nitrogen present in coal, tar, and char, respectively, and volatile-N comprises tar-N, HCN, and NH_3 . Upon pyrolysis, part of coal-N is initially released as tar-N and the remainder is retained as char-

Fig. 1 A Simplified Scheme of NO_x and N_2O Emissions in a Coal Combustion Process

Table 1 Ultimate and Proximate Analyses of Coals Used

Coal (code)	Ultimate analysis [wt% (daf)]					Proximate analysis [wt% (db)]		
	C	H	N	S	O ^{a)}	Ash	VM ^{b)}	FC ^{c)}
Rhein Braun (RB)	64.4	4.8	0.74	0.3	29.8	4.7	54.4	40.9
Loy Yang (LY)	65.9	4.7	0.60	0.3	28.5	0.5	51.0	48.5
Zalainuoer (ZN)	72.0	5.0	1.7	0.4	21.0	4.1	42.5	53.4
Blair Athol (BA)	78.6	4.4	2.0	0.3	14.7	7.5	28.7	63.8

a) Determined by difference. b) Volatile matter. c) Fixed carbon.

N, tar-N being subsequently decomposed into HCN and NH₃^(6)~8).

If coal-N can be converted efficiently to N₂ in the pyrolysis stage, the NO_x and N₂O emissions can be greatly reduced during subsequent combustion. This conversion must be more effective in fluidized bed combustion, since the NO_x and N₂O emitted in this process arise from coal-N alone. Such a precombustion method of nitrogen removal would be one of the most essential ways to meet more stringent regulations in the near future. No successful approaches, however, have yet been reported. This review article describes a novel method to convert coal-N to N₂ with iron nano-particles.

2. Experimental

2.1. Coal and Polymer Samples

Many coals with different ranks were used. Among them, Rhein Braun coal from Germany, Loy Yang coal from Australia, Zalainuoer coal from China, and Blair Athol coal from Australia were mainly used, and these are denoted as RB, LY, ZN, and BA throughout the present paper, respectively. All of the samples were dried in a laboratory air, ground, and sieved to obtain coal particles in the range of 150-250 μm. The proximate and ultimate analyses of the four coals are shown in Table 1.

Polyacrylonitrile (PAN) with the average molecular weight of 150,000, from Polysciences Inc., was also used instead of coal samples, since PAN has a much higher nitrogen content of 26.4 wt% and provides N-containing heterocyclic ring structures similar to coal-N upon pyrolysis.

2.2. Addition of Catalyst

Since FeCl₃ is readily available as a major component in acid wastes from a steel pickling plant, an aqueous solution of FeCl₃ was used as a catalyst precursor. A Cl-free iron catalyst in highly dispersed forms was precipitated on coal from FeCl₃ solution by using Ca(OH)₂^(9),10). The procedure has been described in detail elsewhere¹⁰⁾ and thus it is simply explained below. After a predetermined amount of Ca(OH)₂ powder with a constant molar ratio of Ca(OH)₂/FeCl₃ was first added to a mixture of coal particles and FeCl₃

solution, the resulting iron-bearing coal was separated by filtration, then washed repeatedly with deionized water, and finally dried at 110°C in a flow of N₂.

Cl determination of the dried sample by a standard Eschka method revealed that the iron precipitated on coal was free from Cl contamination¹⁰⁾. The Cl ions in FeCl₃ solution could be removed completely as water-soluble CaCl₂. Excess Ca(OH)₂ on the iron-bearing coal was also removed almost completely by repeated water-washing after filtration, but a slight amount of Ca, ≤0.5 wt%, was retained.

In another method for addition of catalyst, a nanophase iron oxide catalyst with an average particle size of 3 nm, from Mach I, Inc.¹¹⁾, was added to BA coal by mixing in ethanol at ambient temperature. When PAN was used instead of coal, fine particles of Fe metal with a mean particle size of 20 nm, from Vacuum Metallurgical Co., were also added by soaking with PAN in acetone under ultrasonic wave irradiation¹²⁾.

2.3. Pyrolysis Runs

Pyrolysis runs of coal samples were carried out with a quartz-made fluidized or fixed bed reactor. The former reactor with the bed zone of 2.5 cm i.d. and 35 cm long was heated with a transparent, electric furnace, which made it possible to watch the fluidization state of coal particles. About 5 g of the iron-bearing coal was first fluidized in atmospheric He, then heated at 600-700 K/min up to 750-1000°C, and finally soaked for 10 min. Any fluidizing agents such as sand were not used to avoid their possible influence on nitrogen release upon pyrolysis. The procedure has been described in more detail elsewhere^{13),14)}.

With the fixed bed pyrolysis, a rectangular graphite cell (6 mm wide, 46 mm long, 8 mm deep) including about 0.5 g of coal particles was placed in the center of the reactor (4 cm i.d., 37 cm long), which was heated at 400 K/min in a stream of high-purity He (>99.9999%) with an electric furnace with infrared image lamps attached and soaked for 2 min at a constant temperature. Special care was taken to ensure that the entire system was free from any leakage before every run. The details of the reactor and procedure have been described in the previous papers^{15),16)}.

The pyrolysis of PAN with and without fine metal

particles was carried out with a thermobalance, and 40 mg of the sample was heated at 10 K/min in a flow of high-purity He at atmospheric pressure.

2. 4. Analysis of Nitrogen

Pyrolysis products from coal samples were separated into gas, tar (including oil fraction), and char^{14),16)}. The concentration of N₂ in the gas collected in a plastic bag was analyzed by gas chromatography with a thermal conductivity detector. The amount of N₂ evolved was determined by the difference in N₂ concentration before and after pyrolysis. HCN and NH₃ were analyzed by two different methods. One included dissolution of HCN and NH₃ evolved into deionized water and subsequent determination of dissolved CN⁻ and NH₄⁺ ions with a specific ion electrode¹⁴⁾. In another method, the concentration of HCN or NH₃ in the gas collected was analyzed by the Gastec standard detector tube¹⁶⁾. To ensure the accuracy of this method, these gases were also analyzed by a Fourier transform infrared spectrometer equipped with a long path gas cell, and it was confirmed that the concentrations determined by both methods fell within experimental errors.

The nitrogen in the tar or char recovered, denoted as tar-N or char-N respectively, was determined with a conventional, combustion-type elemental analyzer.

The amount of N₂ evolved from PAN samples was analyzed by on-line gas chromatography, and the nitrogen in the carbon after pyrolysis was determined in the same manner as above.

2. 5. Characterization

Mössbauer spectra were measured at room temperature with a constant acceleration spectrometer¹⁷⁾, and isomer shift (IS) and quadrupole splitting (QS) were used as Mössbauer parameters. X-Ray diffraction (XRD) measurements were made with Mn-filtered Fe K α radiation. Some samples were also characterized by the Fe 2p_{3/2} or N 1s X-ray photoelectron spectroscopy (XPS) using Mg K α radiation. The specimen was ground and mounted on a sample holder using Ag paste. A long acquisition time of several hours was used to ensure good resolution, and the binding energy was referred to the Ag 3d peak at 367.9 eV. The dispersion and chemical composition of iron catalysts and inherent minerals in the chars after pyrolysis at 900-1000°C were also analyzed with a high resolution transmission electron microscopy (TEM) with an energy-dispersive X-ray analyzer (EDX) attached.

3. Results and Discussion

3. 1. Formation of N₂ from PAN

Rate of formation of N₂ as a function of temperature is illustrated in **Fig. 2**, where the rate is expressed on the basis of the initial weight of PAN, and Fe(prec) and Fe(fine) mean precipitated iron and fine iron particles, respectively. In the absence of the iron, N₂ started to

Fig. 2 Rate of Formation of N₂ during Temperature Programmed Pyrolysis of Polyacrylonitrile

evolve significantly beyond 700°C as reported in several studies^{18),19)}, and the rate around 1000°C was as low as <0.05 mmol/g-PAN/min¹²⁾. On the other hand, the addition of fine iron at a loading of 7.9 wt% not only lowered the onset temperature of N₂ formation by $\approx$ 200°C but also increased the rate between 600°C and 900°C remarkably. When the iron was precipitated onto PAN from FeCl₃ solution, the rate increased further in the temperature region of 700-800°C, which lead to a two-fold increase in the maximum rate, compared with that for fine iron²⁰⁾.

Table 2 shows the effect of iron addition on N₂ yield which is defined as conversion of the nitrogen present in PAN (denoted as PAN-N) to N₂. The yield was $\approx$ 5% for PAN alone and almost unchanged by the addition of coarse particles of iron metal. On the other hand, the presence of fine particles and precipitated iron increased N₂ yield drastically as can be expected from **Fig. 2**, and the yield for the latter iron reached 42%²⁰⁾. The precipitated iron was thus more active for conversion reactions of PAN-N to N₂.

Elemental analysis of carbons formed by pyrolysis is also summarized in **Table 2**. The nitrogen content was as large as 12 wt% for PAN alone, whereas it decreased to 4.3 wt% or 3.5 wt% for fine or precipitated iron, respectively. It is evident that a higher yield of N₂ results in lower nitrogen retention in the carbon. **Table 2** also indicates that the carbon with a lower N/C ratio is more aromatized. This agrees with the XRD results that crystallized carbon is observed only in the presence of these iron.

When PAN is pyrolyzed and then carbonized, cyclization and dehydrogenation reactions first take

Table 2 N₂ Yield during Temperature Programmed Pyrolysis of Polyacrylonitrile up to 1000°C and Elemental Analysis of Carbons Formed

Addition of iron		Content [wt% (daf)]					Atomic ratio	
Type of iron	Loading ^{a)} [wt%]	N ₂ yield [N-%]	C	H	N	O ^{b)}	H/C	N/C
—	0	4.7	79.1	0.3	12.1	8.5	0.05	0.13
Metal powder ^{c)}	6.6	5.1	—	—	—	—	—	—
Fine particles ^{d)}	7.9	33	93.6	0.3	4.3	1.8	0.04	0.039
Precipitated iron	8.9	42	95.2	0.2	3.5	0.2	0.02	0.031

a) Determined from ash content after burning. b) Determined by difference. c) Size fraction 44-74 μm. d) Average particle size of 20 nm.

place, which leads to the formation of the ladder polymers including heterocyclic nitrogen, and they subsequently undergo condensation and aromatization reactions to form carbon with graphite-like structures^{18),19)}.

In these processes NH₃, HCN, and N₂ are evolved from PAN, and the former two are released at lower temperatures than N₂. The N₂ observed at ≤600°C in the presence of fine or precipitated iron would thus be formed by secondary decomposition reactions of NH₃ and HCN with these iron. It has been accepted that N₂ formation from PAN alone proceeds at ≥700°C through condensation reactions of the ladder polymers^{18),19)}. The remarkable enhancement of the formation rate by iron catalysts observed in this work, therefore, points out that the iron markedly promotes solid-phase reactions to extract N₂ from the polymers, which results in the formation of a more aromatized carbon with a lower nitrogen content (Table 2).

Since fuel-N has almost the same heterocyclic ring structures as those derived from PAN, it is expected from the above-mentioned observations that the iron precipitated onto coal from FeCl₃ solution can also catalyze more effectively conversion of fuel-N to N₂ upon pyrolysis than the physically mixed fine particles of iron metal. The following section thus focuses on N₂ formation during pyrolysis of coals with precipitated iron.

3.2. Nitrogen Release during Pyrolysis of Coals with Precipitated Iron

3.2.1. Catalytic Effect on Distribution of HCN, NH₃, and N₂

Table 3 shows the distribution of gas phase N during pyrolysis of LY coal at 900°C¹⁴⁾. Without the catalyst, NH₃ was the predominant product followed by HCN, whereas N₂ was the minor species. It has been suggested that NH₃ originates from secondary reactions of HCN^{21)~23)} and that a larger extent of secondary reactions between volatiles and char results in higher conversion to NH₃⁸⁾. The dominant formation of NH₃ shown in Table 3 thus suggests the significance of the secondary decomposition of volatile-N under the present conditions.

As shown in Table 3, the addition of a small amount of the iron, 0.7 wt%, to LY coal changed the distribu-

Table 3 Distribution of HCN, NH₃, and N₂ Evolved during Pyrolysis of LY Coal at 900°C

Iron loading [wt%]	Amount evolved [μmol/g-coal (daf)]			
	HCN	NH ₃	N ₂	Total
0	28 (25) ^{a)}	76 (67) ^{a)}	9.0 (8) ^{a)}	113
0.73	10 (6)	50 (28)	118 (66)	178
2.8	6.1 (3)	62 (32)	125 (65)	193

a) Proportion in mol%.

tion of HCN, NH₃, and N₂ drastically; N₂ was the dominant product, and the amount was 13 times that without the catalyst, the proportion of N₂ reaching 66 mol%. In contrast, the presence of the iron decreased the amounts of HCN and NH₃. The remarkable increase in N₂ by catalyst addition led to the increased total amount of HCN, NH₃, and N₂. When iron loading was increased further to 2.8 wt%, the nitrogen distribution did not change significantly.

3.2.2. Factors Influencing N₂ Formation

Figure 3 shows the effect of pyrolysis temperature on formation of N₂ from LY coal²⁴⁾. Without the iron, N₂ yield at a heating rate of 700 K/min increased slightly with increasing temperature, but it was <5% even at 900°C. In contrast, the yield in the presence of the catalyst increased remarkably with temperature, and it reached 15% and 50% at 750°C and 900°C, respectively. When heating rate was decreased to 30 K/min, N₂ yield at 900°C increased slightly. Thus, formation of N₂ from LY coal with precipitated iron depended strongly on temperature.

Figure 4 summarizes the effects of iron loading, co-existence of Ca, fluidizing gas, and coal type on N₂ formation at 900°C^{13),14),24)}. In the pyrolysis of LY coal in He, the iron at a low loading of 0.7 wt% promoted N₂ formation dramatically, and N₂ yield reached 50%. However, it seemed to level off beyond ≈1 wt% Fe. The catalytic effect at lower loadings of <0.7 wt% Fe should be the subject of future work. When Ca(OH)₂ was co-loaded onto LY coal, N₂ yield at 4.5 wt% Fe was almost unchanged. In other words, the Ca did not affect the catalysis of N₂ formation by the iron. This observation is interesting from a view-point of *in situ*

Fig. 3 Effects of Iron Catalyst and Pyrolysis Temperature on N_2 Yield during Pyrolysis of Loy Yang Coal

Fig. 4 Effects of Iron Loading, Pyrolysis Conditions, and Type of Coal on N_2 Yield at 900°C

desulfurization during coal pyrolysis, since the CaO derived from $Ca(OH)_2$ added to coal can efficiently capture the sulfur evolved²⁵⁾.

Figure 4 also reveals that the use of H_2 instead of He as a fluidizing gas shows no further improvement on N_2 yields at loadings of 6–8 wt% Fe. This is noteworthy from a practical point of view, since expensive H_2 is unnecessary for the iron-catalyzed removal of nitrogen from coal. In contrast to the present finding, it is well known that pressurized H_2 is essentially needed for hydrodenitrogenation reactions of heavy oils and

Fig. 5 Fate of Fuel Nitrogen during Pyrolysis of Loy Yang and Blair Athol Coals at 900°C

coal-derived liquids with Mo-based catalysts.

As shown in Fig. 4, the catalytic effect of the precipitated iron on N_2 formation depended on type of coal. A slight amount of the catalyst, 0.2 wt% Fe, promoted formation of N_2 from BA coal, but further improvement on N_2 yield was very small, even when iron loading exceeded 0.5 wt%. The smaller catalytic effect observed for BA coal can be ascribed to lower dispersion of the iron, as will be discussed later.

3. 2. 3. Fate of Fuel Nitrogen

Fate of fuel nitrogen in LY or BA coal during pyrolysis at 900°C is illustrated in Fig. 5, where each yield of N_2 , NH_3 , HCN, tar-N, or char-N is provided¹⁴⁾. Nitrogen mass balance fell within the reasonable range 100–108% in every case. For LY coal without the iron, about 50% of fuel-N was retained in the char, while tar-N and NH_3 were the main products. When 0.7 wt% Fe was added, the nitrogen distribution changed dramatically. N_2 was the dominant product, whereas the partitioning to all other nitrogen such as NH_3 , HCN, tar-N, and char-N decreased. The catalyst at 2.8 wt% showed almost the same trend, though N_2 yield increased slightly with a corresponding decrease in char-N yield.

When BA coal was pyrolyzed in the absence of the iron, as shown in Fig. 5, a similar distribution to that for LY coal without the catalyst was observed; about 65% of fuel-N was retained as char-N, and tar-N and NH_3 were mainly released. Small amounts (0.2–1 wt%) of the iron precipitated onto BA coal increased N_2 yield, whereas it decreased all other nitrogen components. This trend was the same as with LY coal. There were, however, the major differences in yields of

N₂ and char-N between both coals, and the catalytic effect of the iron on the nitrogen distribution was much larger for LY coal.

3. 2. 4. Nitrogen Functionality in Char

As shown in Fig. 5, iron catalysts decreased char-N yields at 900°C irrespective of coal type, and the extent of the decrease was larger with LY coal. The effect of the iron on nitrogen functionality in LY char was thus examined by XPS. It has been accepted that XPS is the most successful technique to study the functionality of nitrogen in coal and char^{26)~28)}. When the atomic ratios of N/C determined by both N 1s XPS measurements and elemental analysis were compared for several samples with and without the iron, there was the excellent surface:bulk correlation.

The proportion of nitrogen functional groups in LY char pyrolyzed at 900°C is shown in Table 4, where a least-square curve fitting method using Gaussian peak shapes is used for peak resolution, and pyridinic, pyrrolic, and quaternary nitrogen forms are resolved at 398.7, 400.3, and 401.4 (± 0.1) eV, respectively²⁹⁾. Without the iron, pyrrolic nitrogen was the dominant species followed by pyridinic form, as reported in the previous studies^{27),28)}. The presence of the catalyst decreased the proportion of pyrrolic and pyridinic forms, whereas it increased quaternary nitrogen.

When char samples were subjected to Ar ion sputtering with the rate of several nm/min, the proportion of quaternary nitrogen did not change for the original char, but on the contrary it decreased remarkably for the iron-bearing char (Table 4). Since it has been suggested that quaternary nitrogen species are pyridinic

forms associated with hydroxyl oxygen²⁷⁾, it is likely that the quaternary nitrogen observed in the presence of the iron before Ar sputtering is formed by interactions between pyridinic forms and surface hydroxyl groups on the iron catalyst. This is supported by the result that pyridinic nitrogen was the predominant species after Ar sputtering (Table 4).

Table 4 also shows that the ratio of pyrrolic to pyridinic nitrogen is smaller in the presence of the iron and this phenomenon is more remarkable by Ar sputtering. These observations suggest that the catalyst promotes preferential conversion of pyrrolic form to N₂.

3. 2. 5. Catalyst State and Char Structure

Table 5 summarizes the species identified by XRD before and after pyrolysis of iron-loaded coals^{13),14)}. No diffraction lines attributable to iron species were detectable on LY coal with 2.8 wt% Fe. The Fe XPS spectra of this sample and bulk compounds of FeOOH and α -Fe₂O₃ showed the peaks at 711.1, 711.0, and 710.6 eV, respectively, suggesting that the present catalyst exists in the form of FeOOH. When the Mössbauer spectra were measured, however, the present iron had a doublet, which differed from the spectrum of bulk compound of FeOOH. The Mössbauer parameters, such as isomer shift and quadrupole splitting, for the precipitated iron were in good agreement with those for fine particles of FeOOH dispersed on an Australian brown coal^{9),17)}. These observations indicate that the iron precipitated onto LY coal exists in highly dispersed form of FeOOH.

When LY coal with the iron was pyrolyzed at 600°C and 750°C (Table 5), FeOOH was reduced to metallic iron (α -Fe), but some remained partly oxidized (Fe₃O₄ and Fe_{1-x}O). On the other hand, the pyrolysis at 900°C led to complete reduction to α -Fe irrespective of iron loading. Since large amounts of reducing gases such as H₂, CO, and hydrocarbons were evolved upon pyrolysis, FeOOH could readily be reduced by these gases, even when inert He was used as a fluidizing gas. Notably, the XRD signals of cementite (Fe₃C) and graphitized carbon appeared after pyrolysis of LY coal with 0.7-6.8 wt% Fe (Table 5), whereas LY char with-

Table 4 Change in Nitrogen Functionality in Char during Pyrolysis of LY Coal at 900°C

Iron loading [wt%]	Functional groups [mol/%]			Pyrrolic/ pyridinic
	Pyrrolic	Pyridinic	Quaternary	
0	59 (47) ^{a)}	37 (49) ^{a)}	4 (4) ^{a)}	1.6 (0.96) ^{a)}
2.8	48 (35)	34 (63)	18 (2)	1.4 (0.56)

a) After Ar sputtering.

Table 5 Species Identified by XRD and Particle Size of Iron Catalysts

Coal	Iron loading [wt%]	Temperature [°C]	Species identified by XRD ^{a)}	Particle size ^{b)} [nm]
LY	2.8	— ^{c)}	not detectable	n.a. ^{d)}
LY	6.0	600 ^{e)}	Fe ₃ O ₄ (w), α -Fe (s)	n.a.
LY	6.8	750	Fe _{1-x} O (w), α -Fe (s)	n.a.
LY	0.73	900	Fe ₃ C (w), α -Fe (w), G ^{f)} (s)	20-30
LY	2.8	900	Fe ₃ C (m), α -Fe (w), G ^{f)} (s)	30-50
LY	6.8	900	Fe ₃ C (m), α -Fe (s), G ^{f)} (s)	40-60
BA	1.2	900	Fe-C ^{g)} (w), α -Fe (vw)	70-100

a) XRD intensities designated as vw (very weak), w (weak), m (medium), and s (strong). b) Determined by TEM. c) Before pyrolysis.

d) Not analyzed. e) in H₂. f) Graphitized carbon. g) Austenite.

Fig. 6 Micrograph after Pyrolysis at 900°C of Loy Yang Coal with 0.7 wt% Fe

out the iron was amorphous. In the pyrolysis of BA coal with 1.2 wt% Fe at 900°C, however, Fe₃C was not formed and the char remained amorphous (Table 5).

The TEM micrograph after pyrolysis of LY coal with 0.7 wt% at 900°C is presented in Fig. 6. The average size of iron particles was as small as 20-30 nm. The XRD results (Table 5) suggest that both α -Fe and Fe₃C may be included in the observed particles. The TEM observations also revealed the presence of lamella structures attributed to graphitized carbon in the vicinity of catalyst particles. As summarized in Table 5, the increase in iron loading on LY coal to 6.8 wt% slightly increased the average size, indicating a larger degree of catalyst agglomeration at a higher loading. The size of iron particles was dependent on coal type and larger for BA char in spite of a lower loading.

The formation of smaller nanoparticles on LY char is probably attributed to higher dispersion of the precipitated iron. The amount of CO₂ evolved from LY coal increased linearly with increasing iron loading¹³. Since CO₂ is formed through decomposition reactions of COOH groups present in coal³⁰, the linear increase in CO₂ yield with catalyst loading shows that most of Fe³⁺ ions interact strongly with free COOH groups unassociated with metal cations, which means the atomic dispersion of the iron. The iron would be less finely dispersed on BA coal with a smaller content of COOH groups.

3. 2. 6. Routes of Formation of N₂ and Mechanism of Solid-phase Conversion to N₂ with Iron

As can be expected in Fig. 5, the changes in the amounts of N₂, volatile-N (comprising HCN, NH₃, and tar-N), and char-N by catalyst addition indicate that the iron added to LY coal always increases N₂, whereas it decreases volatile-N and char-N, and the increased amount of N₂ is nearly equal to the sum of the decreased amounts of volatile-N and char-N. Similar trend was observed with BA coal. These observations point out that not only volatile-N but char-N is the

source of N₂.

In one route of formation, N₂ originates from secondary decomposition reactions of volatile-N. This route is well understandable, since it has been accepted that some catalysts added to coal promote the secondary decomposition of volatiles evolved upon pyrolysis. Iron-containing materials are catalytically active for NH₃ decomposition³¹, and fine particles of iron metal supported on carbon catalyze selective conversion of N-containing heterocyclic compounds to N₂³². Since catalyst dispersion plays a crucial role in such gas-solid reaction, N₂ formation can occur to a larger extent with smaller catalyst particles on LY char (Fig. 5).

Another route of formation is via solid phase reactions, which extract N₂ from char-N and/or precursors. In order to verify this point, nitrogen-enriched carbons derived from PAN were first mixed with fine particles of iron metal having the size of 20 nm and then heated in an inert atmosphere³³. In fact, the iron catalyzed conversion reactions of the nitrogen in the carbon to N₂. As shown in Table 5, not only Fe₃C but also graphitized carbon was formed on the chars from LY coal with iron catalysts. Since the metal-catalyzed graphitization of amorphous carbon such as LY char proceeds through a cycle mechanism involving carbon dissolution into metal particles and subsequent decomposition of metal carbides³⁴, the following reaction scheme can be suggested for the formation of Fe₃C and graphitized carbon¹⁴:

It is likely that the reaction between α -Fe and char-N also takes place in this process¹⁴.

Metallic iron first reacts with pyrrolic and pyridinic nitrogen forms in the char substrate to form interstitial iron nitrides, which are subsequently decomposed to α -Fe and N₂, because the nitrides are thermally unstable under the present conditions. As shown in Fig. 2, nanoparticles of metallic iron promoted formation of N₂ from condensed heterocyclic ring structures, formed during carbonization of PAN.

Table 5 showed the formation of iron particles having smaller size on LY char than on BA char. Since a more finely dispersed metal has higher reactivity and larger mobility, the iron in LY char can more readily not only react with char-N but also migrate in the char matrix, and consequently solid-solid reactions can proceed at a higher rate to a larger extent, which leads to higher N₂ yield and lower char-N yield for LY coal (Figs. 4 and 5).

Fig. 7 Yields of N_2 and Char-N as a Function of Carbon Content in Coal during Pyrolysis of Different Coals at 1000°C

Fig. 8 Effects of Temperature, Demineralization of Coal, and Addition of Catalyst on Distribution of Nitrogen at 1000°C for Zalainuour Coal

3.3. Catalytic Role of Inherent Minerals in N_2 Formation during Coal Pyrolysis

3.3.1. Formation and Source of N_2 from Different Coals

Figure 7 shows yields of N_2 and char-N at 1000°C for varying carbon content (%C) in coal¹⁶. N_2 yield depended strongly on coal type, in particular for low-rank coals with %C of ≤ 72 wt%. Surprisingly, a German RB coal exhibited the highest yield as large as 61%, followed by a Chinese ZN coal which provided N_2 yield of 48%. Although many studies on nitrogen release during coal pyrolysis have been carried out^{6)~8)}, most researchers have paid almost no attention to N_2 formation, and such remarkable formation of N_2 in the absence of catalyst is thus the first finding. As is seen in Fig. 7, RB coal showed the lowest yield of char-N, and it tended that char-N yield increased with increasing %C in the range of ≥ 74 wt%, in contrast with the decrease in N_2 yield in this region.

The temperature dependence of distribution of nitrogen for ZN coal is illustrated in Fig. 8, where R and D denote the raw and demineralized coal, respectively³⁵. Nitrogen balance fell within the reasonable range of 97–102%. With the raw coal, at 600°C , tar-N and NH_3 were the main products, and only a slight amount of N_2 was formed. On the other hand, N_2 was the dominant species at 800°C , where the release of volatile-N was almost complete. N_2 yield increased linearly with increasing temperature, but contrarily char-N yield decreased with temperature.

In order to elucidate possible sources of N_2 , yield of volatile-N or char-N as function of yield of N_2 is plotted for all of coal samples examined in Fig. 9, where

Fig. 9 Relationship between Yield of N_2 and Yield of Volatile-N or Char-N during Pyrolysis of Different Coals at 1000°C (Reprinted with permission from reference No. 16, Copyright (1997) American Chemical Society)

volatile-N comprises HCN, NH_3 , and tar-N¹⁶. Volatile-N decreased slightly as N_2 increased, which shows that some of the N_2 originates from volatile-N, but its contribution to N_2 formation is minor. On the other hand, char-N yield remarkably decreased almost linearly with increasing N_2 yield. In other words, there was a strong, reverse correlation between char-N and N_2 . This observation indicates that char-N (and/or

Table 6 Changes in Ash Content, Metal Composition, and Yields of N₂ and Char-N by Demineralization

Coal	Ash [wt%]	Metal content in coal [wt%]					Yield ^{a)} [N-%]	
		Mg	Al	Si	Ca	Fe	N ₂	Char-N
ZN-raw	4.1	0.08	0.21	0.34	0.96	0.26	48	37
ZN-dem ^{b)}	0.8	0.03	0.12	0.27	0.11	0.10	13	68
RB-raw	4.7	0.35	0.07	0.56	1.01	0.56	61	22
RB-dem ^{b)}	1.5	0.14	0.04	0.55	0.28	0.24	32	47

a) Pyrolysis at 1000°C. b) Demineralized coal.

precursors) is the major source of N₂. This can be supported by the result that N₂ formation takes place predominantly after almost complete release of volatile-N (Fig. 8).

3.3.2. Effects of Demineralization of Coal and Addition of Catalyst on N₂ Formation

It is well known that some minerals inherently present in coal, mainly metal cations as the ion-exchangeable forms in low-rank coals, can influence its pyrolytic reactions. This section thus clarifies the effect of demineralization on formation of N₂ from ZN and RB coals which showed high N₂ yields.

These coals were first demineralized with 5 N HCl at 50°C and then pyrolyzed in the same manner as above. The results are summarized in Table 6 and Fig. 8^{15),16),35)}. As expected, the ash contents in ZN and RB coals were greatly decreased by demineralization. The composition of the main five elements present in these coals also changed considerably. Removal of Ca, as the dominant species in both coals, was the highest, followed by Fe. As shown in Table 6 and Fig. 8, demineralization changed distribution of nitrogen drastically irrespective of type of coal; N₂ increased, whereas char-N increased. Table 6 also indicates that the decreases in N₂ yield by demineralization, 35% and 29% for ZN and RB coals, are roughly equal to the increases in char-N yield, 31% and 25% for the corresponding coals. These results agreed with the reverse correlation of char-N with N₂ (Fig. 9). It is evident that some minerals in these coals control N₂ formation upon pyrolysis.

Since Ca element was mainly removed by HCl washing (Table 6), it may have the catalytic effect on formation of N₂ from ZN and RB coals. The demineralized ZN coal was thus exchanged with the Ca cations in a saturated solution of Ca(OH)₂³⁵⁾, and the resulting sample, denoted as D/Ca in Fig. 8, was subjected to pyrolysis runs. The calcium at a loading of 3 wt% had no significant effect on N₂ yield (Fig. 8). In other words, it was almost inactive for N₂ formation under the present conditions. When the nanophase iron oxide was added to the demineralized ZN coal, however, the iron at a low loading of 1 wt% promoted N₂ formation and doubled N₂ yield (Fig. 8), though it was less than the yield for the raw coal. The beneficial

Fig. 10 Micrograph after Pyrolysis at 1000°C of Rhein Braun Coal

effect of the iron could readily be expected from the above-mentioned results. The nanophase iron catalyst added to the demineralized RB coal had almost the same effect on N₂ formation as above. These observations strongly suggest that Fe-containing minerals naturally present in ZN and RB coals account for the remarkable formation of N₂.

The TEM-EDX analysis after pyrolysis of RB coal at 1000°C revealed that iron particles were finely dispersed in the char and the size was as small as 10-20 nm. A typical micrograph is shown in Fig. 10³⁶⁾. Lamella structures attributable to graphitized carbon also existed in the char matrix, as observed after pyrolysis of LY coal with precipitated iron (Fig. 6). When the RB demineralized coal with the nanophase iron was pyrolyzed at 1000°C, however, graphitized carbon was not formed, and the size of iron particles was much larger. Thus, the iron derived from Fe-containing minerals provided more highly dispersed iron than the nanophase catalyst physically mixed with the demineralized coals, and in turn showed higher catalytic activity for N₂ formation. It is known that the iron naturally present in low-rank coals exists in the ion-exchangeable forms, which initially provide essentially atomic dispersion³⁷⁾, as with the iron precipitated onto LY coal.

There is no doubt, therefore, that iron nanoparticles, which are formed from Fe-containing minerals present in ZN and RB coals, can promote N₂ formation through

the same routes as discussed with iron catalysts on LY coal. N₂ formation after almost complete release of volatile-N (Fig. 8) and a strong, reverse correlation between N₂ and char-N (Fig. 9) indicate that the mineral derived iron catalyzes predominantly solid phase reactions to extract N₂ from char-N and/or precursors.

4. Conclusions

Nitrogen release from several coals with and without catalyst during pyrolysis under atmospheric pressure has been studied with a quartz reactor, and summary of conclusions follows:

- 1) A Cl-free iron precipitated onto an Australian brown or bituminous coal from FeCl₃ solution promotes conversion of fuel-N to N₂ at low loadings of 0.2-0.7 wt% Fe. The catalytic effect is much higher for the brown coal, and N₂ yield at 900°C reaches 50%, which is greater by 15 times that without the iron.
- 2) In contrast, the iron decreases yields of volatile-N (comprising tar-N, HCN, and NH₃) and char-N. The analysis of nitrogen mass balance points out that N₂ originates from solid phase reactions of char-N and/or precursors as well as from secondary decomposition reactions of volatile-N.
- 3) Not only α -Fe and Fe₃C, but also graphitized carbon existed in the chars derived from iron-loaded brown coals, and the size of iron particles is smaller than that on the bituminous coal char. It is proposed in the route of formation of N₂ from char-N that nanoparticles of metallic iron react with char-N to form interstitial iron nitrides, which subsequently decompose to N₂.
- 4) Low-rank coals from China and Germany show exceptionally high N₂ yields of 50-60% at 1000°C, even without any catalysts. N₂ starts to evolve after almost complete release of volatile-N, and there is a strong, reverse correlation between N₂ and char-N. These observations show that char-N and/or precursors are the main source of N₂.
- 5) Demineralization with HCl washing dramatically suppresses formation of N₂ from these low-rank coals by removing mainly Fe- and Ca-containing minerals. A nanophase iron catalyst added to the demineralized coals promotes N₂ formation, but the addition of Ca(OH)₂ has almost no effect on it. Upon pyrolysis, Fe-containing minerals in the ion-exchangeable forms are transformed into finely dispersed iron, which catalyzes efficient conversion of char-N to N₂ in solid phase.
- 6) Thus, iron nanoparticles, derived not only from externally added catalysts, but from inherently present minerals, play crucial roles in the selective conversion of fuel-bound nitrogen to N₂. Since the presence of oxygen-containing functional groups is essentially needed for the formation of the iron, iron-

catalyzed conversion reactions to N₂ would proceed efficiently in the pyrolysis of low-rank coals.

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要 旨

鉄ナノ微粒子によるフュエル窒素の N₂ への選択的転換

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石炭中のフュエル窒素を燃焼前の熱分解過程で無害な N₂ として除去することを目的として、石炭熱分解時の N₂ 生成に及ぼす鉄触媒、反応条件、炭種、鉱物質の影響を検討した。

塩化鉄水溶液を用いて塩素フリーの鉄触媒を豪州褐炭上に沈殿担持したところ、N₂ 収率（窒素基準）は熱分解温度の上昇とともに増加し 900℃ では 50% に達した。これは無触媒時の 15 倍に相当する。一方、N₂ 以外の HCN, NH₃, タールやチャーに移行する窒素の量はいずれも減少した。このような著しい N₂ の生成反応は 1 wt% 程度の鉄の存在下で進行し、H₂ は全く不要であることが明らかとなった。触媒の効果は歴青炭では小さくなったが、これは触媒の分散性に起因した。褐炭チャー上では、20~30 nm の微粒子が存在し、金属鉄以外に炭化鉄や結晶性炭素が観測されたことから、金属鉄微粒子がチャー中のピロール環やピリジン環構造と反応して窒化鉄が生成しその分解

により N₂ が発生する固相反応経路が、N₂ 生成のメインルートであると結論した。

中国やドイツ産の低炭化度石炭の熱分解では、無触媒下でも、N₂ 収率は 1000℃ で 50~60% に昇った。揮発分窒素の脱離後に N₂ が発生し、N₂ の増加はチャー中窒素を減少させるので、チャーが N₂ の主なソースである。これらの石炭を塩酸で洗浄すると、Ca や Fe を含む鉱物質が主に除去され、N₂ 収率は著しく低下した。しかし、脱鉱物質炭に Ca イオンを添加しても、N₂ 収率は変わらなかった。熱分解チャー中には、10~20 nm の鉄微粒子とともに結晶性炭素が存在することから、イオン交換状態で存在する鉄含有鉱物質が熱分解時にナノ微粒子に転化し、沈殿担持した鉄触媒と同様に固相脱 N₂ 反応を促進すると推論した。

Keywords

Brown coal, Fuel-bound nitrogen, Heterogeneous catalysis, Iron nanoparticle, Molecular nitrogen, Pyrolysis