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Enhancement of N₂ Formation from the Nitrogen in Carbon and Coal by Calcium

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The effects of Ca catalysts on nitrogen release during heat treatment of polyacrylonitrile-derived carbon and pyrolysis of low rank coals have been studied with a fixed bed quartz reactor in a stream of high purity He. In the temperature-programmed treatment at 10 °C/min of the carbon with 3 wt % Ca, the Ca promotes N₂ formation at 850–1000 °C and the catalytic effect is larger at a higher temperature. When a low rank coal, after demineralization and subsequent addition of 3 wt % Ca, is pyrolyzed in the same manner as above, the Ca enhances the rate of N₂ formation at 850–1100 °C at largest by a factor of 15. In the fast heating pyrolysis at 400 °C/min of the demineralized samples, the Ca at loading of 1–3 wt % also increases N₂ yields at 1200–1350 °C irrespective of type of coal. These observations and nitrogen distribution indicate that the N₂ increased by Ca addition arises mainly from solid-phase reactions of heterocyclic nitrogen forms. The X-ray diffraction measurements after heat treatment and pyrolysis reveal that catalyst particles are too fine on the carbon to be detected and as small as 45–65 nm in size on the chars. The catalysis of N₂ formation at solid phase by the Ca is discussed in terms of the mobility of CaO particles, their agglomeration, and sulfur poisoning.

Introduction

Alkali, alkaline earth, and transition metal cations exist inherently and significantly in coal as mineral matters. Some of these species change the distribution of volatile products during coal pyrolysis.¹ It is thus expectable that such minerals affect the release of S- or N-containing products in this process. In fact, the Ca²⁺ ions naturally present in coal can capture the sulfur evolved during pyrolysis. We have recently shown that small amounts of Fe-containing minerals, probably as ion-exchanged forms, change dramatically the fate of the nitrogen in coal (coal-N) and catalyze conversion of coal-N to N₂.^{2,3}

Since Ca²⁺ ions are usually present most abundantly in coal among metal cations described above, the present paper focuses on clarifying the effect of Ca species on nitrogen release upon pyrolysis, in particular, N₂ formation. Efficient conversion of coal-N to N₂ during pyrolysis can reduce the emissions of nitrogen oxide pollutants during subsequent combustion. Although a number of studies on the emissions of NO_x and N₂O have been carried out,^{4–6} N₂ formation in the precombustion

Table 1. Analyses of Carbon and Coal Samples Used

sample code	ultimate analysis, wt % (daf)					ash, wt % (db)
	C	H	N	S	O	
PA carbon	79.3	0.4	6.8	0	13.5	0
ZN coal	69.9	4.8	1.7	0.4	23.2	4.1
AD coal	70.8	5.0	1.2	0.1	22.9	1.5

process has attracted almost no attention, except for our pioneering work.^{7–10} In this paper, pure carbon without any minerals is first selected as a sample to avoid their influences on nitrogen release, and low rank coals after demineralization are then used in place of the carbon from a practical point of view. Ca catalysts are incorporated into these samples in ion-exchanged forms, because the Ca²⁺ ions in low rank coals are mainly exchanged with the protons in oxygen-containing functional groups.

Experimental Section

Carbon and Coal Samples. Pure carbon without any minerals was prepared by carbonizing powdery polyacrylonitrile (PAN), from Polyscience Inc., in He at 1000 °C for 30 min, followed by activation in 20 vol % O₂–He at 500 °C. The activated carbon derived from PAN is denoted as PA carbon throughout the present paper. The elemental analysis is shown in Table 1. The carbon and nitrogen contents were 79.3 and 6.8 wt % (db), respectively.

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Two low rank coals, Zalainuoer and Adaro coals from China and Indonesia, respectively, were used in this study. The elemental and proximate analyses are provided in Table 1, where Zalainuoer and Adaro coals are designated as ZN and AD, respectively. ZN and AD coals were demineralized with 18% HCl solution at 60 °C before use, and the ash contents decreased to 0.8 and 0.4 wt % (db), respectively. The suffix 'dem' is added to the code ZN or AD to denote the demineralized coal.

Calcium Addition. PA carbon, ZN-dem or AD-dem coal was first mixed with a saturated aqueous solution of Ca(OH)₂ in a rotary evaporator at ambient temperature. Then, the resulting sample was dried under vacuum at 60 °C. The method of Ca addition using the saturated solution of Ca(OH)₂ makes it possible to exchange the Ca²⁺ ions with oxygen-containing functional groups in low rank coals.¹¹ The Ca loading in the dried sample was 3 wt %, unless otherwise stated.

Heat Treatment and Pyrolysis. All runs were carried out with a fixed bed quartz reactor under flowing high purity He (>99.9999%). In a temperature-programmed heat treatment, about 180 mg of the PA carbon was first charged into a graphite cell on a graphite holder in the reactor. After precautions against leakage, the reactor was heated at 10 °C/min up to 1000 °C and soaked for 60 min. The details of the apparatus and procedure have been described elsewhere.²

Coal samples were pyrolyzed in two different manners, such as temperature-programmed and fast heating modes. In the former case, about 0.5 g of the sample was heated in the same way as above. In the latter case, the sample was heated at 400 °C/min up to 1200–1350 °C.

Nitrogen Analysis and Catalyst Characterization. The N₂ evolved during temperature-programmed heat treatment and pyrolysis was determined on line at 5 min intervals with a high-speed micro gas chromatograph (GC). In the fast heating pyrolysis, the effluent after removal of tarry materials and water was collected into an aluminum-laminated plastic bag. The N₂ in the bag was detected by the GC, and the NH₃ and HCN in the bag were analyzed with a Fourier transform infrared spectrometer equipped with a long-path gas cell. When the pyrolysis run was repeated for a given sample, the reproducibility was within ±2%, ±2%, and ±0.5% for N₂, NH₃, and HCN, respectively. The nitrogen in the tar or char recovered after heat treatment or pyrolysis, denoted as tar-N or char-N, respectively, was determined with a conventional nitrogen analyzer. Any tarry materials were not observed during heat treatment of the PA carbon. The reproducibility of char-N was ±1%.

Chemical form and dispersion state of Ca catalysts in the chars after heat treatment or pyrolysis were analyzed by the X-ray diffraction (XRD) method using Ni-filtered Cu K α radiation. The average crystalline size of CaO was determined by the Debye–Shörrer method.

Results

Profiles for N₂ Formation. Figure 1 shows the rate of N₂ formation during temperature-programmed heat treatment of PA carbon without and with 3 wt % Ca. In the absence of the Ca, N₂ started to evolve at about 600 °C, and the rate increased with increasing temperature, but it decreased during holding the sample at a constant temperature of 1000 °C. When the Ca was added to the carbon, the catalytic effect on N₂ formation appeared at about 850 °C, and the rate increased more rapidly with increasing temperature than without the catalyst. The rate enhancement by Ca addition became largest at 1000 °C. When the sample was held at 1000

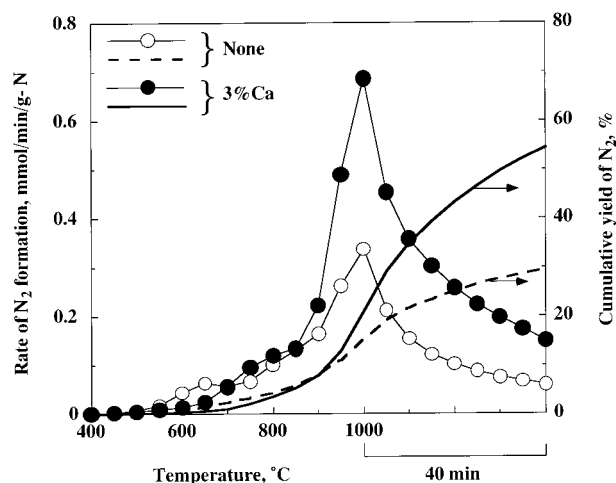


Figure 1. Rate of N₂ formation and cumulative yield of N₂ in the temperature-programmed heat treatment of PA carbon without and with 3 wt % Ca.

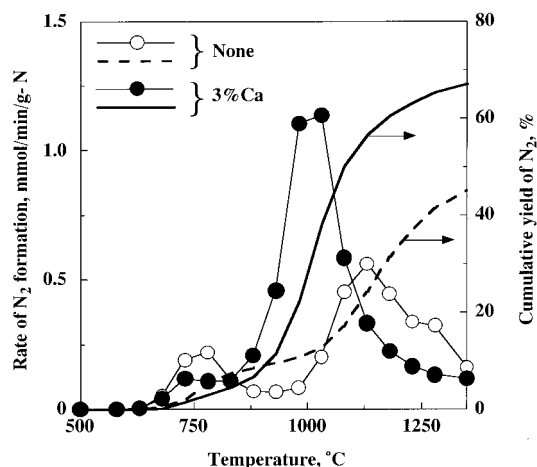


Figure 2. Rate of N₂ formation and cumulative yield of N₂ in the temperature-programmed pyrolysis of ZN-dem samples without and with 3 wt % Ca.

°C, the rate decreased with increasing soaking time as observed without the Ca catalyst, but the rate was much higher in the presence of the Ca.

Cumulative yield of N₂ can be calculated by integrating each curve shown in Figure 1. The results are also provided in Figure 1. The effect of Ca addition on the yield was small at 1000 °C, but it was much larger after 40 min soaking at this temperature; the yield after 40 min soaking was 30 and 55% without and with 3 wt % Ca, respectively.

Figure 2 shows the temperature-programmed profiles for N₂ formation from ZN-dem samples without and with 3 wt % Ca. In the absence of the catalyst, N₂ started to evolve at about 625 °C and had a small rate at around 750 °C. The rate of N₂ formation rapidly increased beyond 1000 °C, but it decreased with increasing temperature via the maximal value at 1125 °C. The Ca catalyst promoted N₂ formation predominantly at the temperature range of 850–1100 °C. The catalytic effect was largest at 950–1000 °C, and the rate of N₂ formation with 3 wt % Ca in this region was about 15 times that without the Ca. After 1100 °C, the rate was rather lower in the presence of the catalyst.

As is seen in Figure 2, there was no significant difference in cumulative yield of N₂ at ≤900 °C in the

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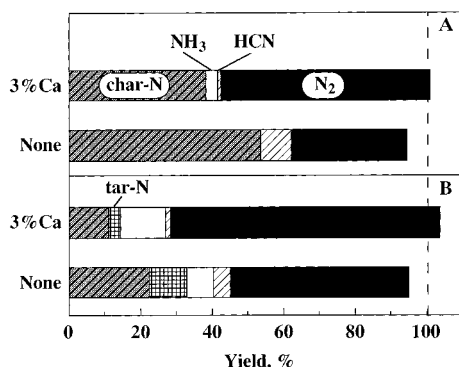


Figure 3. Nitrogen distribution for heat treatment of PA carbon (A) and pyrolysis of ZN-dem (B) samples.

absence and presence of the Ca. The difference was clear at 1000 °C, largest at 1050–1100 °C, but rather smaller beyond 1200 °C because of lower rate of N₂ formation with the Ca catalyst. N₂ yields at 1350 °C were 46 and 67% without and with 3 wt % Ca, respectively.

Nitrogen Distribution. Figure 3 shows nitrogen distribution after heat treatment at 1000 °C and after pyrolysis at 1350 °C. Since N₂ yield was calculated by using the amount of N₂ collected in the gas bag, the values given in Figure 3 were slightly different from cumulative yields of N₂ estimated from Figures 1 and 2. Nitrogen mass balance fell within the reasonable range 95–104% in every case.

In the heat treatment of PA carbon without the Ca, as shown in Figure 3A, N₂ was the dominant product, and some HCN was observed, but any NH₃ and tar-N were not detected. It is well-known that HCN is formed from PAN-derived carbons at lower temperatures than N₂.^{12,13} No formation of NH₃ and tar-N was reasonable, because no significant amounts of volatile matters were released from PA carbon. When the Ca was added to the carbon, N₂ yield increased remarkably as indicated in Figure 1. NH₃ was also formed. In contrast, char-N decreased considerably, and HCN also decreased.

As is seen in Figure 3B, product yield at 1350 °C upon pyrolysis of ZN-dem without Ca catalyst increased in the sequence of HCN < NH₃ < tar-N < N₂. The addition of 3 wt % Ca to ZN-dem enhanced yields of N₂ and NH₃, whereas it decreased HCN, tar-N, and char-N. The Ca changed yields of N₂ and char-N most significantly.

Every data point in Figure 3 is normalized on the basis of nitrogen balance of 100% to investigate the effect of Ca catalyst quantitatively, and the change in a normalized yield by catalyst addition is provided in Figure 4. With PA carbon, the change in yield of N₂ or char-N, denoted as $\Delta(N_2)$ or $\Delta(char-N)$, was +24% or –19%, respectively. In other words, the absolute value of $\Delta(N_2)$ corresponded to 80% of that of $\Delta(char-N)$, which means that the N₂ formed by catalyst addition originates mainly from char-N and/or precursors. As is seen in Figure 4, $\Delta(HCN)$ and $\Delta(NH_3)$ were –8.4% and +3.2%, respectively. These observations reveal that the HCN decreased by Ca addition is converted to not only NH₃ but N₂. Since it has been suggested in coal pyrolysis that HCN may react with the hydrogen in char to form NH₃,¹⁴ the Ca may catalyze this process.

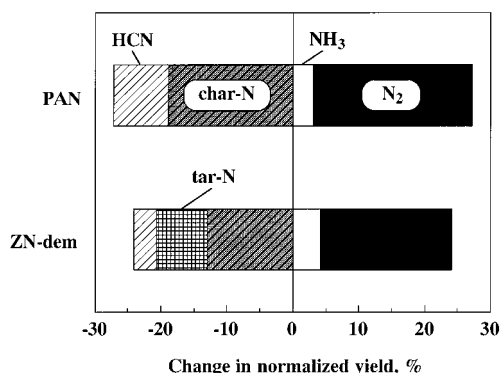


Figure 4. Changes in normalized yields by catalyst addition.

Table 2. Effects of Ca Loading, Heating Rate, and Temperature on N₂ Yield during Pyrolysis of Low Rank Coals after Demineralization

coal sample	Ca loading (wt %)	heating rate (°C/min)	temperature (°C)	N ₂ yield (%)
ZN-dem	0	10	1350	47
ZN-dem	3	10	1350	73
ZN-dem	0	400	1350	47
ZN-dem	3	400	1350	67
AD-dem	0	400	1200	34
AD-dem	1	400	1200	54
AD-dem	0	400	1350	47
AD-dem	3	400	1350	65

Figure 4 also shows the effect of the Ca catalyst on the normalized yield with ZN-dem. The change in the yield increased in the sequence of HCN ~ NH₃ < tar-N < char-N < N₂, and $\Delta(N_2)$ and $\Delta(char-N)$ were +19% and –13%, respectively. The absolute value of the former corresponded to 65% of that of the latter. This means that the contribution of char-N to the N₂ formed in the presence of the Ca is lower with ZN-dem than with PA-carbon. It is likely that some of the N₂ arises from secondary decomposition reactions of tar-N.¹⁰

Factors for N₂ Formation from Coals. Influences of some factors on N₂ yield for coal samples with Ca catalysts were examined from a practical point of view. The results are summarized in Table 2, where the average value of the two runs is provided. The presence of 3 wt % Ca enhanced N₂ formation by a factor of 1.6 in the temperature-programmed pyrolysis of ZN-dem at 1350 °C. In the fast heating pyrolysis, that is, upon increase in heating rate from 10 °C/min to 400 °C/min, N₂ yield at 1350 °C increased from 47% without Ca catalyst to 67% at 3 wt % Ca. The enhancement factor was 1.4, which was slightly lower than that in the temperature-programmed mode.

When AD-dem was pyrolyzed at 400 °C/min in place of ZN-dem, the Ca at a low loading of 1 wt % worked efficiently as the catalyst for N₂ formation and enhanced N₂ yield at 1200 °C by a factor of 1.6. The catalytic effect of 3 wt % Ca for AD-dem was almost the same as for ZN-dem, as shown in Table 2. These observations point out that Ca catalysts at the loading of 1–3 wt % are active for N₂ formation at 1200–1350 °C irrespective of heating rate and coal type.

Catalyst State. Figure 5 shows XRD profiles of Ca-bearing chars after heat treatment at 1000 °C and after pyrolysis at 1350 °C. No XRD lines attributable to any

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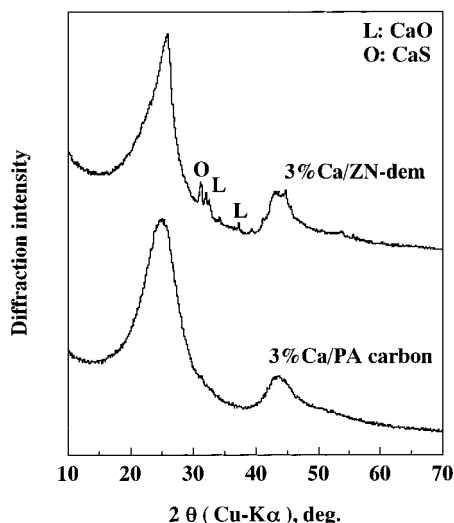


Figure 5. XRD profiles for Ca-bearing chars after heat treatment and pyrolysis.

Table 3. Calcium Species and Average Crystalline Size of CaO after Pyrolysis of Demineralized Low Rank Coals at 1350 °C

sample ^a	heating rate (°C/min)	temperature (°C)	calcium species ^b	average size of CaO crystallites (nm)
ZN-dem	no pyrolysis		none	
ZN-dem	10	1350	CaO (w), CaS (w)	n.d. ^c
ZN-dem	400	1350	CaO (w), CaS (w)	65
AD-dem	400	1350	CaO (s), CaS (w)	44

^a With 3 wt % Ca. ^b Identified by XRD; w, weak; m, medium; s, strong. ^c Not determined.

Ca species are detectable in the char derived from PA carbon, indicating that catalyst particles were too small to be detected by XRD. On the other hand, very small XRD peaks of CaO (lime) and CaS (oldhamite) appeared in the pyrolyzed char from ZN-dem. The same species were also observed after pyrolysis at 1000 °C, though the intensities were slightly lower. The in situ XRD measurements of Ca²⁺ ions-exchanged coals have shown the complete transformation of the species into CaO at 750 °C.¹⁵ These observations suggest that the Ca catalyst on the char from PA carbon also exists as CaO.

The XRD results for ZN-dem and AD-dem samples with 3 wt % Ca are summarized in Table 3. Any XRD signals of Ca species could not be detected on the Ca-loaded ZN-dem. This is not surprising, because the Ca added by this method is present in ion-exchanged forms, in other words, as an atomically dispersed state. When this sample was heated at 10 °C/min up to 1350 °C, CaO and CaS appeared (Figure 5). Table 3 shows the presence of the same Ca species after the fast heating pyrolysis at 1350 °C of ZN-dem and AD-dem samples with 3 wt % Ca. The average crystalline sizes of CaO in both chars were 45–65 nm. The formation of CaS in the demineralized chars shows the reaction of CaO particles with H₂S evolved during pyrolysis and/or organic sulfur in the char matrix.

Discussion

Formation of N₂ at Solid Phase. Since any significant amounts of tar-N as well as volatile matters could not be detected during heat treatment of PA carbon samples (Figure 3A), the heterocyclic nitrogen included in them must be retained in the solid matrix throughout the treatment. It is thus evident that N₂ formation from the carbon proceeds through solid-phase reactions of heterocyclic nitrogen forms. This point can also be supported by the fact that the absolute value of Δ(N₂) increased by Ca addition corresponded to most of that of Δ(char-N) decreased (Figure 4), though part of the N₂ is formed probably through secondary reactions of HCN evolved from the carbon. In other words, the Ca catalyst promoted N₂ formation predominantly at solid phase.

As is seen in Figure 2, the Ca also catalyzed N₂ formation from ZN-dem at 850–1100 °C. Since the release of volatile matter from low rank coals is almost complete until 850 °C,¹ the Ca shows the catalytic effect mainly on conversion of char-N and/or precursors to N₂ as observed with PA carbon. The comparison of nitrogen distribution on a normalized base without and with 3 wt % Ca indicates lower contribution of char-N to the N₂ increased by catalyst addition with ZN-dem than with PA-carbon, because some of N₂ originates from tar-N in the former case (Figure 4). When heating rate was increased from 10 °C/min to 400 °C/min, Ca catalysts at loading of 1–3 wt % exhibited almost the same effects on N₂ formation from the demineralized coals (Table 2).

Catalysis of N₂ Formation by Ca. The XRD measurements of Ca-bearing chars after pyrolysis at 1350 °C revealed the presence of CaO irrespective of heating rate and coal type (Table 3). Although no species attributable to Ca compounds were detectable by XRD after heat treatment of PA carbon at 1000 °C because of high degree of catalyst dispersion (Figure 5), it is possible that the Ca exists as CaO at ≥850 °C where N₂ formation proceeds, as mentioned above. These observations suggest that the bulk form of the active Ca catalyst is CaO on PA carbon as well as ZN-dem and AD-dem samples.

Since the Ca catalyzes N₂ formation dominantly at solid phase as discussed above, the mobility of CaO particles would be one of the key factors determining the catalytic activity. It is well-known that surface atoms of metals or metal oxides become mobile above the Tanmman temperature that is one-half of their melting points expressed in Kelvin. The temperature for CaO is 1422 K, that is, 1149 °C. Thus, the enhancing effect on N₂ formation may appear around this temperature. As shown in Figures 1 and 2, however, the Ca on PA carbon and ZN-dem started to catalyze N₂ formation at around 850 °C, which was lower by 300 °C than the Tanmann temperature. Some reasons for this difference would be considered. First, the N₂ observed at a lower temperature arises from secondary reactions of either the HCN evolved from the carbon or the tar-N released from the demineralized coal, as discussed above. The mobility of CaO particles is not important for such reactions over the solid catalyst. Second, surface atoms of fine particles of CaO become mobile at lower temperatures than the Tanmann tem-

perature (1149 °C) of the bulk oxide. This may be supported by the largest enhancement of N₂ formation observed at around 1000 °C with ZN-dem (Figure 2). It is thus likely that the mobility of fine particles of CaO determines N₂ formation in this temperature region.

As is seen in Figure 2, the rate of N₂ formation decreased at higher temperatures of ≥ 1000 °C, despite the increased catalyst mobility with increasing temperature. This may be caused by agglomeration of CaO particles, because it results in the lowering in the catalytic activity. Table 3 reveals the existence of CaS after pyrolysis of ZN-dem and AD-dem at 1350 °C. Fine particles of CaO readily captures H₂S evolved during coal pyrolysis even at low temperatures of 650–700 °C.¹¹ The CaO may also react with organic sulfur at solid phase to form CaS, which may decrease the activity of the Ca catalyst. The deactivation with organic sulfur may be another reason for the decreased rate of N₂ formation observed at ≥ 1000 °C.

It has been proposed in our previous study^{9,16} that precipitated iron on low rank coals catalyzes conversion of char-N to N₂ through formation of iron nitrides by solid–solid reactions of heterocyclic nitrogen and fine particles of metallic iron. In the present study, Ca nitrides, such as CaCN₂ and Ca₃N₂, may also be formed as the intermediates in the process of N₂ formation, though any XRD signals of these species could not be detected. Since very fine particles with the size of <5 nm¹⁷ and less crystallized species cannot be detected by the XRD technique, all of the Ca in the chars may not be provided necessarily in Table 3. To clarify the mechanism of Ca-catalyzed N₂ formation in detail will be the subject of future study.

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Conclusion

To make clear the effect of Ca catalyst on nitrogen release, Ca²⁺ ions are incorporated into either activated carbon prepared from PAN or low rank coals after demineralization by using an saturated aqueous solution of Ca(OH)₂, the resulting sample is heat-treated or pyrolyzed with a fixed bed reactor. In the temperature-programmed treatment or pyrolysis at 10 °C/min of the carbon or the demineralized coal with 3 wt % Ca, the Ca enhances the rate of N₂ formation at temperatures of ≥ 850 °C in both cases, and the catalytic effect is larger for the latter sample, the enhancement factor being 15 at highest. The Ca also catalyzes secondary reactions of HCN and tar-N. When the demineralized coals are heated at 400 °C/min up to 1200–1350 °C, Ca catalysts at loading of 1–3 wt % also increase N₂ yields by factors of 1.4–1.6 irrespective of type of coal. The X-ray diffraction measurements reveal that catalyst particles after heat treatment are too fine to be detected and the sizes of CaO particles on pyrolyzed chars are as small as 45–65 nm. The results obtained here strongly suggest that the highly dispersed CaO promotes N₂ formation predominantly through solid-phase reactions of heterocyclic nitrogen in the carbon and coals.

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