# Distribution and Catalytic Activity of Eutectic Salts in Steam Gasification of Coal

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The reactivity of coal char in steam is enhanced by the addition of binary and ternary eutectic alkali salts due to their reduced melting points. The catalytic steam gasification of Illinois No. 6 coal was carried out using binary ($Na_2CO_3$–$K_2CO_3$) and ternary ($Li_2CO_3$–$Na_2CO_3$–$K_2CO_3$) eutectic salt mixtures in a fixed bed reactor at different catalyst loadings. For the same catalyst loading, the ternary catalyst showed higher carbon conversions compared to the binary catalyst. The physical distribution of both catalyst systems on the coal char surface was examined using a scanning electron microscope (SEM). Both catalysts showed uniform dispersion on the ungasified coal matrix indicating homogeneous physical mixing. An attempt has been made to establish a qualitative correlation between the type of catalyst, its distribution, and effect on the overall carbon conversions. Gasified chars were highly porous in nature and coalesce in the case of the binary catalyst whereas the ternary catalyst showed highly porous and crystalline morphology. X-ray diffraction spectra showed the formation of potassium polysulfides ($K_xS_y$) in the gasified chars of the eutectic catalyst systems.

## Introduction

The reactivity of coal char toward steam is known to be enhanced by the presence of alkali and alkaline earth metal salts or oxides.[1–2] Among alkali metal salts that have been thoroughly investigated, $K_2CO_3$ appears to show the highest catalytic activity.[3] Gasification rates of coal char in steam can be further increased by the addition of binary and ternary eutectic alkali salts due to their reduced melting points compared to the gasification temperature.[4]

In our earlier work, the catalytic effect of the binary ($Na_2CO_3$–$K_2CO_3$) and ternary eutectic salts ($Li_2CO_3$–$Na_2CO_3$–$K_2CO_3$) on the steam gasification of Illinois No. 6 was investigated in a high-pressure high-temperature fixed bed reactor system.[5] The catalyst addition techniques of single salts and eutectic salt mixtures had little effect on the overall gasification rates.[3,5] Kinetic studies have been carried out to describe the dependence of the catalyzed steam gasification on temperature, pressure, catalyst loading, and steam flow rates.[5] A Langmuir–Hinshelwood type of rate expression was found to explain the kinetics of the steam gasification reaction.[5]

In the present study, physical distribution of the binary and ternary catalyst in the coal matrix is evaluated using a scanning electron microscope (SEM). The two eutectic catalysts at different initial loadings were observed before and after the steam gasification. Gasified chars were also structurally characterized by the X-ray diffraction technique. An attempt was made to establish a correlation between the type of catalyst, its distribution, and effect on the overall carbon conversions.

## Experimental Procedures

**Sample Preparation.** Illinois No. 6 coal obtained from the Penn State Coal Sample Bank was used for catalytic coal gasification. Bench scale experimentation was carried out using the binary and ternary eutectic salt mixtures. The composition, eutectic temperature, and the eutectic phase of these salt mixtures are listed in Table 1. Sample preparation for steam gasification of coal involves several steps viz. catalyst addition, devolatilization/pyrolysis, and sieving.[5]

**Catalyst Addition Technique.** The catalyst was physically mixed in amounts of 5 wt %, 10 wt %, and 15 wt % of the raw coal. The amount of catalyst loading was chosen on the basis of experience of the earlier researchers.[1,3] Addition of potassium based single salts above 15 wt % of the raw coal has shown no significant effect on the overall gasification rates.[1,3] After catalyst addition, the resulting coal sample was devolatilized.

**Devolatilization/Pyrolysis.** This step was carried out under nitrogen at 1023 K in a Barnstead Thermolyne-Model F48015 muffle furnace at atmospheric pressure to remove the moisture and volatile contents from the coal sample.

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(1) Liu, Z. L.; Zhu, H. L. *Fuel* **1986**, *65*, 1334–1338.
(2) Verra, M.; Bell, A. T. *Fuel* **1978**, *57*, 194–197.
(3) Hirsch, R. L.; Gallagher, J. E., Jr.; Lessard, R. R.; Wesselhoft, R. D. *Science* **1982**, *215*, 121–127.
(4) McKee, D. W.; Clifford, L. S.; Kosky, P. G.; Edward, J. L. *Fuel* **1985**, *64*, 805–809.
(5) Godavarty, A. M.S. Thesis. Catalytic Coal Gasification using Eutectic Salt Mixtures. University of Tennessee Space Institute, August, 1999.

**Table 1. Composition and Eutectic Temperatures of the Eutectic Salt Mixtures**

| eutectic salt composition (mol %) | eutectic temp (K) | physical state at eutectic point | nomenclature |
|---|---|---|---|
| 43.5%$Li_2CO_3$−31.5% $Na_2CO_3$−25% $K_2CO_3$ | 673 | liquid | LNK |
| 29% $Na_2CO_3$−71% $K_2CO_3$ | 416 | solid solution | NK |

**Table 2. Experimental Conditions for Steam Gasification Runs Using the LNK and NK Eutectic Catalysts**

| run | temp (K) | pressure (MPa) | catalyst loading (wt %) | steam/water flow rate (mL/s) |
|---|---|---|---|---|
| 1 | 1005 | 0.44 | 5 | 13.8 |
| 2 | 1005 | 0.44 | 10 | 13.8 |
| 3 | 1005 | 0.44 | 15 | 13.8 |
| 4 | 1005 | 0.44 | 5 | 13.8 |
| 5 | 1005 | 0.44 | 10 | 13.8 |
| 6 | 1005 | 0.44 | 15 | 13.8 |
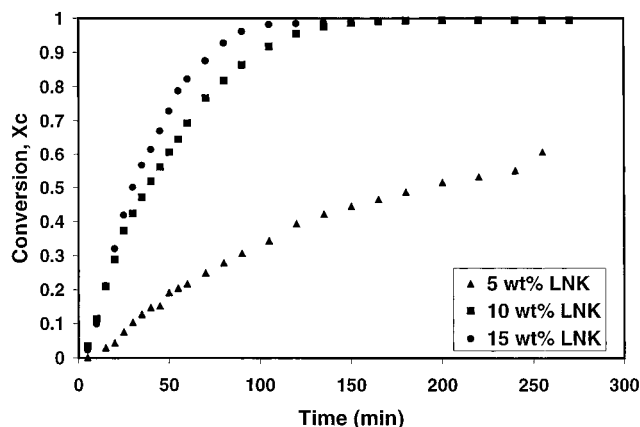


**Figure 1.** Carbon conversions for the LNK catalyst system at different catalyst loadings.



**Figure 2.** Carbon conversions for the NK catalyst system at different catalyst loadings.

**Table 3. M/C Molar Ratios for LNK and NK Systems at Different Catalyst Loading**

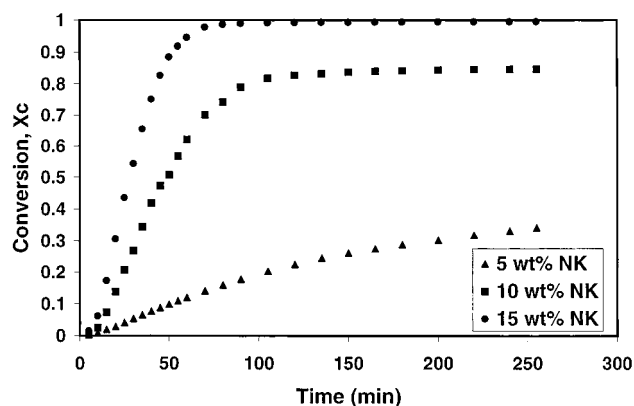| catalyst system | catalyst loading (wt %) | metal/ carbon (mol/mol) |
|---|---|---|
| LNK | 5 | 0.0164 |
| LNK | 10 | 0.0341 |
| LNK | 15 | 0.0560 |
| NK | 5 | 0.0151 |
| NK | 10 | 0.0267 |
| NK | 15 | 0.0497 |

**Sieving.** The pyrolyzed char was crushed and sieved to obtain the feed for the gasification study. The average particle size of the feed was between −30 mesh and +100 mesh.

**Steam Gasification.** The catalytic steam gasification experiments were carried out in a high-pressure, high-temperature fixed-bed gasifier system. The gasifier was typically operated with a downdraft gas flow regime and in a differential fixed bed mode. A set of six experiments on steam gasification were performed for 4 h each using the LNK and NK catalysts. The operating conditions for these experimental runs are tabulated in Table 2. Runs 1−3 were carried out using the ternary salt mixture (LNK), whereas runs 4−6 were performed using the binary salt mixture (NK) as the catalyzing agent.

**Chemical and Structural Characterization.** The physical distribution and morphology of both catalyst systems on the coal matrix, before and after the steam gasification, were observed using a ISI Super III-A scanning electron microscope (SEM). EDS and X-ray mapping were performed to characterize the elemental distribution in a semiquantitative manner. Structural characterization for phase identification was carried out on a Philips Norelco X-ray diffractometer with Cu Kα radiation (1.54 Å) operating at 40 kV and 20 mA.

## Results and Discussion

**Effect of Catalyst Loading.** Figure 1 shows the reactivity of the LNK catalyst system at different loadings. In the 5 wt % loaded LNK sample, the carbon conversion was only 60% after 4 h of gasification. On doubling the catalyst loading the reaction was almost 99% complete in less than 150 min. At 15 wt % loading, the reaction went to completion, but the rate of reaction was not significantly different from that at 10 wt %

loading. A similar trend of conversion behavior was observed in the NK catalyst system as illustrated in Figure 2. At 5 wt % loading, the reaction was only 35% complete at the end of 4 h of gasification process. When the loading was doubled, the system reached 85% completion, whereas at 15 wt % loading, the reaction was about 95% complete in the first 1 h of experimentation. Such an increase in the conversion levels with an increase in the catalyst loadings is attributed to the amount of available catalyst in terms of M/C molar ratio and the distribution of the catalyst in the coal matrix.

**Amount of Catalyst (metal/carbon molar ratio).** The increase in catalyst loading increases the number of cations (alkali metals), i.e., metal/carbon or M/C ratio, available for the catalytic activity.[6] The M/C ratio for the LNK and NK catalyst systems at different weight percent loading is tabulated in Table 3. At lower catalyst loading of 5 wt %, the number of cations are possibly less than the available active sites on the coal matrix. As the loading is increased from 5 to 10 wt % for the LNK system, the M/C ratio is doubled, which possibly tends to fill all the available active sites of coal, thus enhancing the gasification process. However, at the same loading of 10 wt % of the NK catalyst, there was a relatively less increase in the M/C ratio in comparison to the LNK system. This resulted in a lower conversion level in the NK system in contrast to the complete conversion in the LNK catalyzed system (Figures 1 and 2).
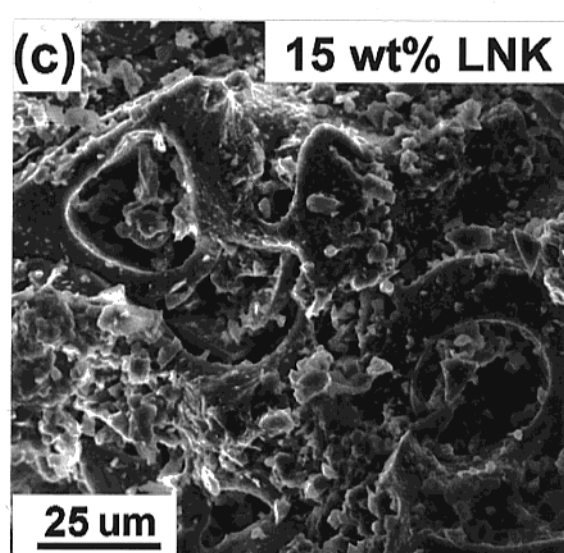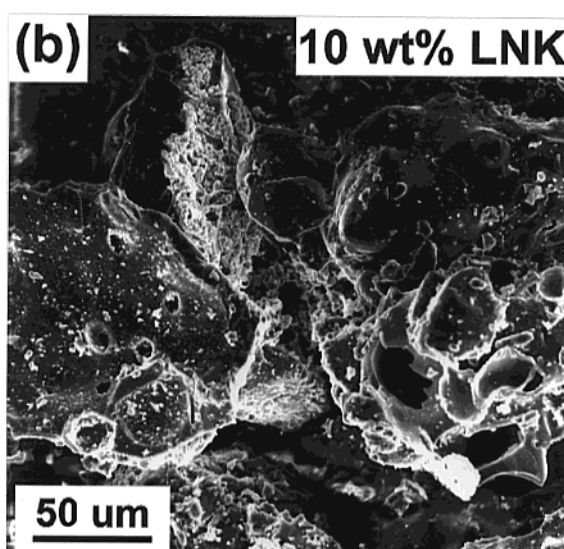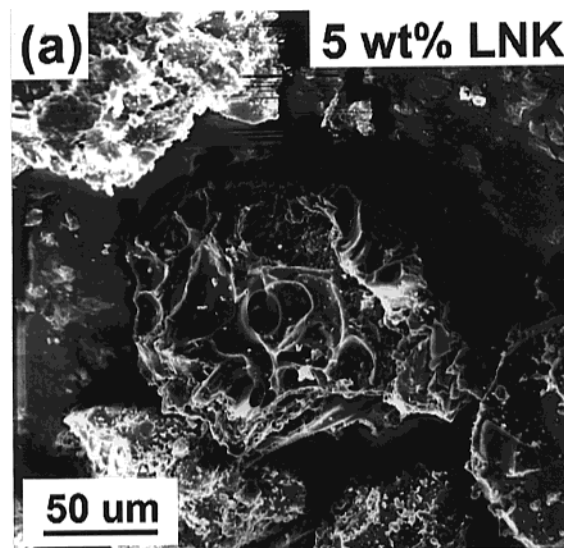
(6) Schumacher, W.; Mühlen, J. H.; Heek, K. H. V.; Jüntgen H. *Fuel* **1986**, *65*, 1360−1363.
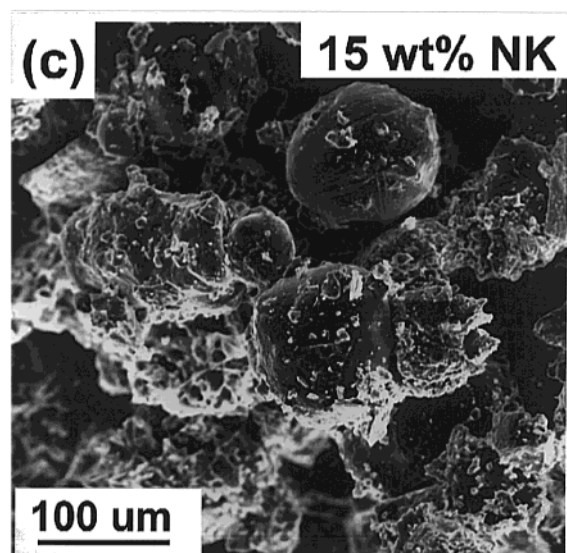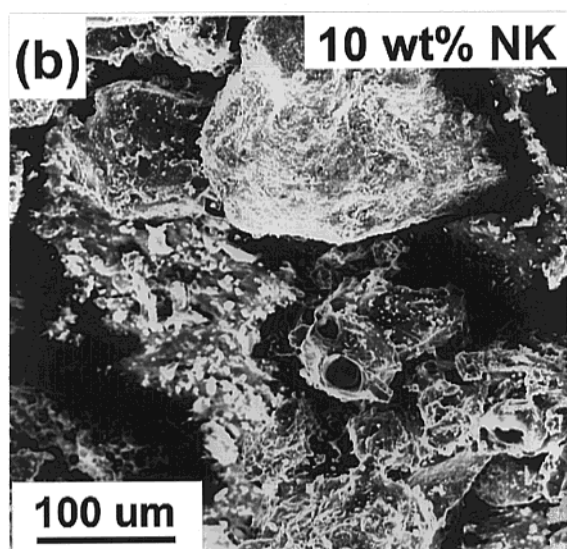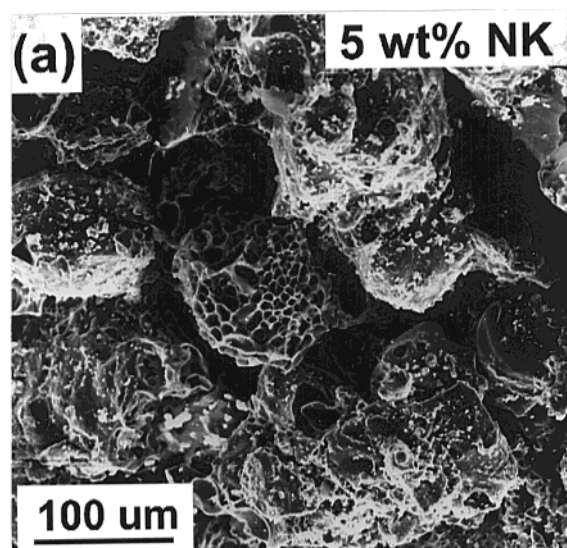
**Figure 3.** Low-magnification SEM micrographs showing NK catalyst on coal particles at (a) 5 wt % loading, (b) 10 wt % loading, and (c) 15 wt % loading.

In general, for similar catalyst loadings, the ternary system (LNK) had a relatively larger number of cations available (i.e., M/C ratio) than the binary system (NK).



**Figure 4.** Low-magnification SEM micrographs showing LNK catalyst on coal particles at (a) 5 wt % loading, (b) 10 wt % loading, and (c) 15 wt % loading.

This accounts for the fact that conversion level at same wt % catalyst loading is greater for the LNK catalyst in comparison to the NK catalyst. Moreover, at low
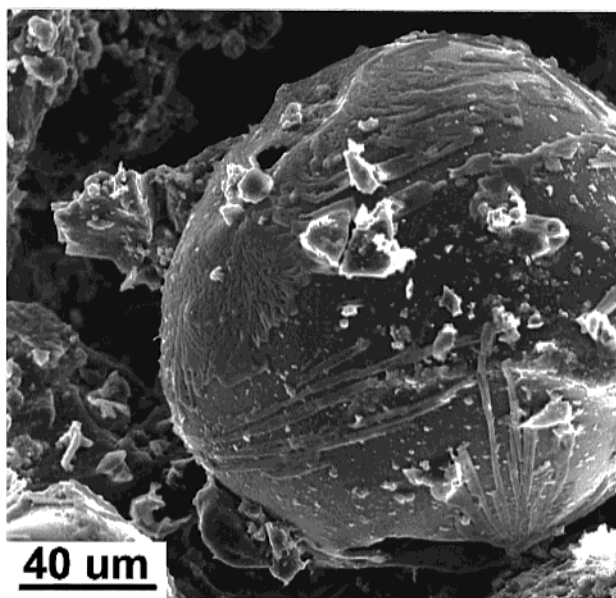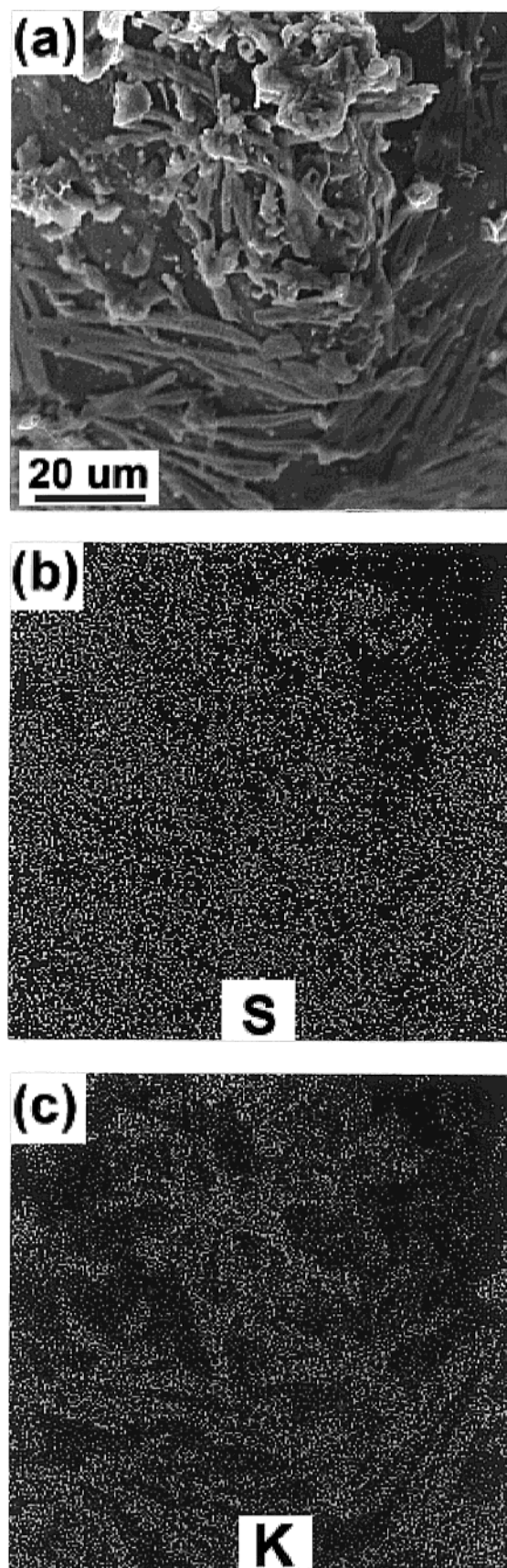
**Figure 5.** SEM micrograph of the coal particle saturated with 15 wt % NK catalyst.

catalyst loadings, some of the catalyst probably would deactivate by the reaction of the catalyst with the mineral matter during coal gasification, and thereby showing very low carbon conversions and overall gasification rates.[1,7]

**Catalyst Distribution on Coal Matrix before Gasification.** In the microscopic studies of the catalyst distribution on the coal matrix, observations were consistent with the concept of the amount of catalyst (i.e., M/C ratio) described above. Figure 3 shows the low magnification SEM micrographs of the NK catalyst on coal particles at different catalyst loadings. At 5 wt % loading (Figure 3a), the coal sample is highly porous in nature, whereas the porosity decreases with higher catalyst loadings (Figure 3b,c). A similar phenomenon is also observed in the LNK catalyst, which is illustrated in Figure 4 for different catalyst loadings. The addition of eutectic catalysts to the raw coal causes some possible interaction between the alkali metals in the eutectic catalyst with the surface functional groups on the carbon during pyrolysis.[8] Such surface interaction is responsible for the pores on the coal surface being covered in these samples. With an increase in the catalyst loading in the system, the coal matrix was largely covered with the catalyst, thus decreasing the visible porosity on the surface (Figures 3 and 4).

As the NK catalyst loading is increased from 5 to 15 wt %, the surface of the coal sample becomes physically saturated with the alkali metal cations (Figure 5). This explains the increase in conversion levels with the rise in the catalyst loading. Figure 6a shows the magnified view of the coal surface covered with a 15 wt % of the NK catalyst. Corresponding X-ray maps showing the elemental distribution for S and K are illustrated in Figure 6, parts b and c. The distribution of sulfur is indicative of coal particles in the sample. A large number of acicular/needle-shaped particles of the NK

(7) Formella, K.; Leonhard, P.; Sulimma, A.; Heek, K. H. V.; Jüntgen, H. *Fuel* **1986**, *65*, 1470−1472.
(8) Tetsuya, H.; Kozo, N.; Masashi, A.; Yoshiyuki, N. *Appl. Catal.* **1991**, *67*, 189−202.
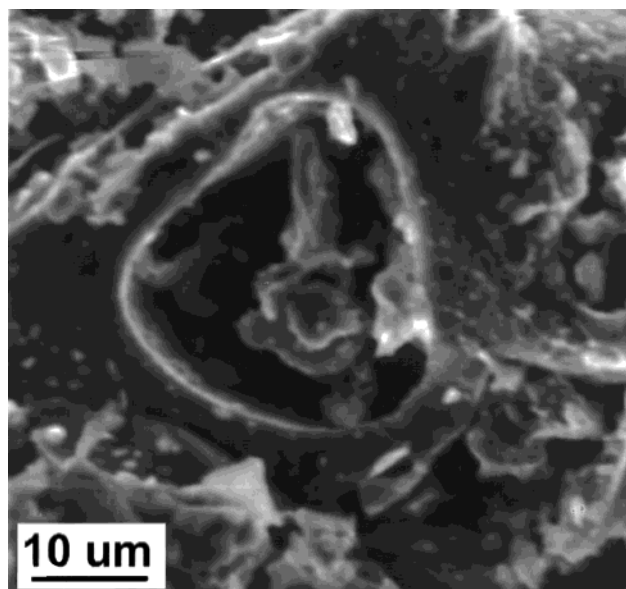


**Figure 6.** (a)-High magnification SEM micrograph of the coal particle saturated with 15 wt % NK catalyst and corresponding X-ray elemental map for (b) S and (c) K.

catalyst provides greater surface area, enhancing the gasification step (Figure 6c). The elemental distribution
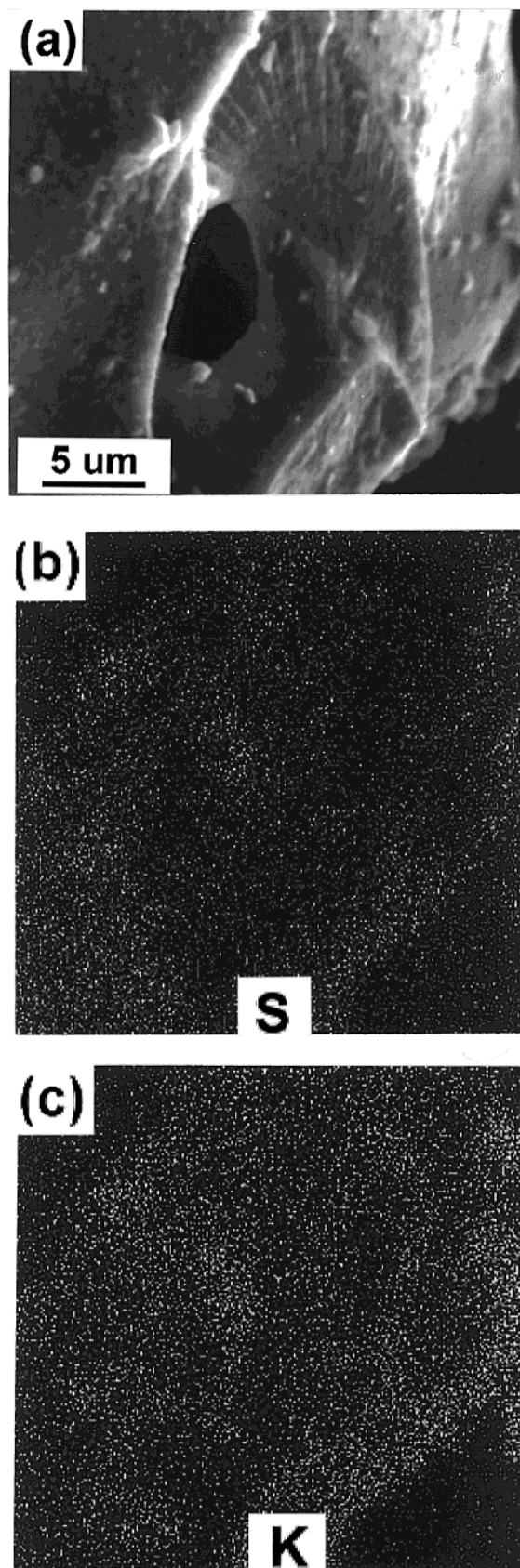
**Figure 7.** SEM micrograph of the coal particle saturated with 15 wt % LNK catalyst.

of lightweight elements (e.g., Na and Li) could not be observed due to limitations of energy dispersive spectrometer (EDS), attached to the scanning electron microscope.

In the case of the LNK system, the coal sample was observed to be porous, unlike the NK system, for a 15 wt % loading (Figure 7). This is attributed to the liquid nature of the LNK eutectic during the devolatilization process. It is postulated that the LNK catalyst in the liquid state at the gasification temperature infiltrates the pores of the coal particle. Such a phenomenon is corroborated from Figure 8a that shows a high magnification view of a pore within a coal particle. Corresponding X-ray maps showing the elemental distribution for S and K in Figure 8, parts b and c reveal the presence of the catalyst within the pore.

EDS analysis for all the coal samples at several locations indicated uniform distribution of the catalyst, suggesting its uniform physical mixing. This fact is confirmed from the elemental X-ray mapping of K shown in Figures 6b and 8b. $K_2CO_3$ was presumed to melt to form a liquid film at gasification temperature.[9] In NK eutectic catalyst, $K_2CO_3$ being the dominant salt, the melting of $K_2CO_3$ could cause a uniform dispersion of the catalyst. The ternary LNK catalyst exists in the liquid state at gasification temperatures, enhancing the catalytic mobility and favoring better dispersion of the catalyst particles uniformly in the coal matrix. This further improves the carbon conversions during gasification.

**Catalyst Distribution on Coal Matrix after Gasification.** At 15 wt % loading, the reaction was almost complete in both catalyst systems. Hence the gasified chars were analyzed to observe the distribution of the catalyst at this loading. Figure 9 shows the highly porous structure of the gasified char having NK catalyst. The gasified char particles have coalesced indicating some liquid formation during the gasification process.

(9) Wood, B. J.; Fleming, R. H.; Wise, H. *Fuel* **1984**, *63*, 1600.
(10) Johnson, J. L.; German R. M. *Metall. Mater. Trans.* **1996**, *27B (6)*, 901−909.
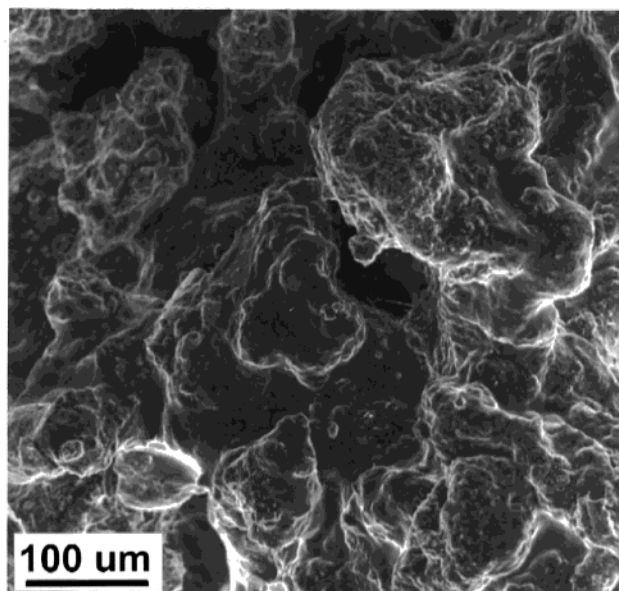


**Figure 8.** (a) High-magnification SEM micrograph of the coal particle saturated with 15 wt % LNK catalyst and corresponding X-ray elemental map for (b) S and (c) K.
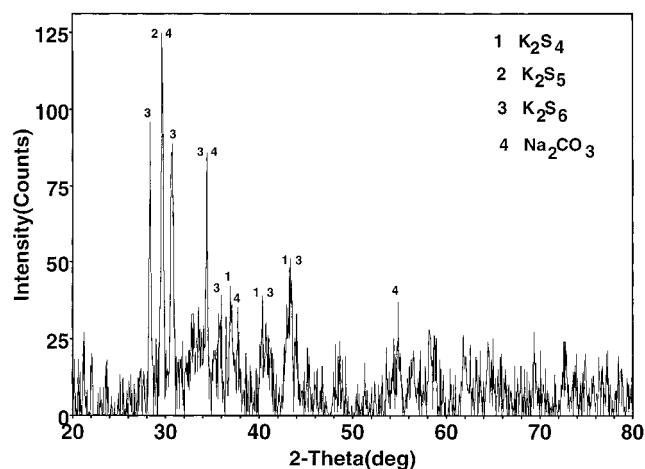
The process is very similar to liquid-phase sintering where a low melting point liquid infiltrates the powder particles and tends to coalesce.[10] X-ray diffraction

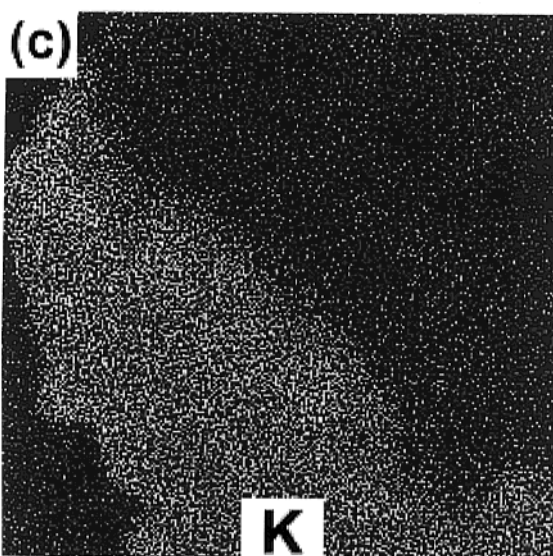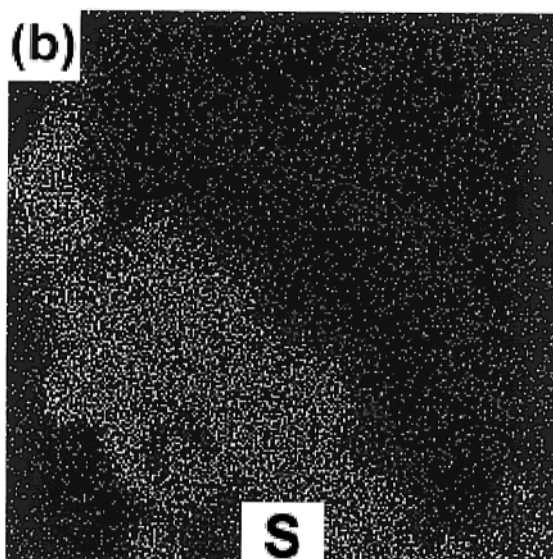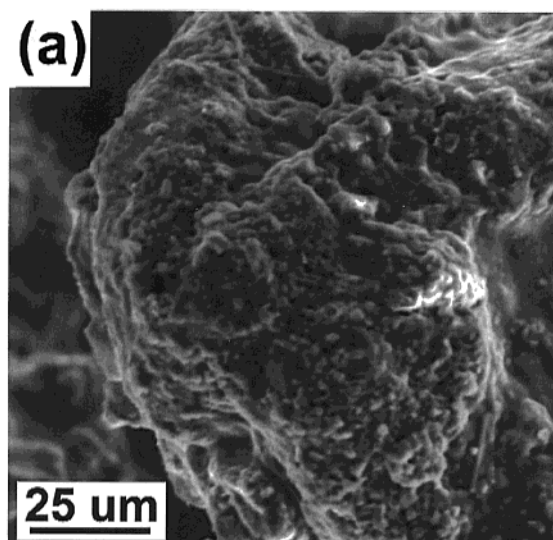**Figure 9.** SEM micrograph of the gasified char having 15 wt % NK catalyst.



**Figure 10.** X-ray diffraction spectrum of the gasified char with 15 wt % NK catalyst.

spectrum of the gasified char having NK catalystillustrated in Figure 10 indicates the formation of potassium polysulfides ($K_xS_y$) such as $K_2S_4$, $K_2S_5$, and $K_2S_6$. Due to low melting points (<533 K), these polysulfides ($K_xS_y$) could form a liquid phase during gasification, which is distinctly observed in Figure 9.[11−12] Na salt of the NK catalyst exists in its carbonate form even in the gasified char. On the contrary, $K_2CO_3$ reacts with sulfur in coal to form polysulfides ($K_xS_y$). This can be attributed to the greatest activity of $K_2CO_3$ compared to $Na_2CO_3$.[3] X-ray diffraction studies in the past have also shown the disappearance of $K_2CO_3$ as it interacts with coal.[3] However, the mechanism of the formation of potassium polysulfides is not completely understood at this stage. A high magnification view of the same sample is shown in Figure 11 along with the elemental distribution maps of S and K. The highly porous structure indicates that most of the carbon in the sample was gasified to carbonaceous compounds such as CO, $CH_4$, and $CO_2$.[5]

(11) David, R. L. *CRC Handbook of Chemistry and Physics*, 74th ed.; CRC Press: Boca Raton, FL, 1993; pp 4-36 to 4-113.
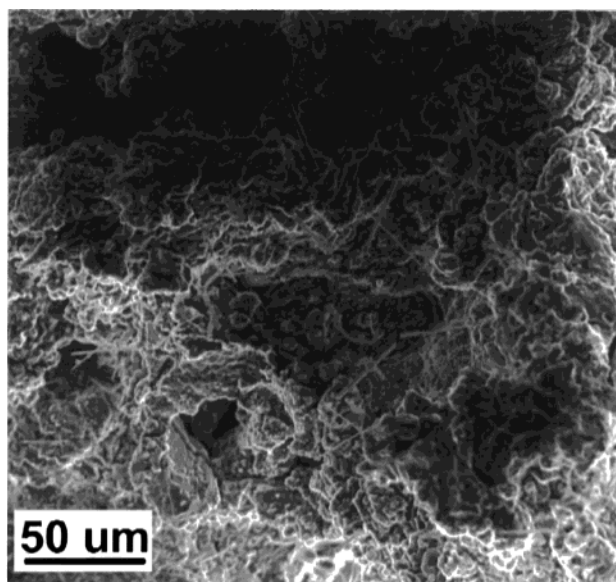
(12) *ASM Handbook Binary Alloy Phase Diagrams*, Vol. 3; ASM International: Materials Park, OH, 1992; pp 2−270.



**Figure 11.** (a) High-magnification SEM micrograph of the gasified char with 15 wt % NK catalyst and corresponding X-ray elemental map for (b) S and (c) K.

This complete gasification of the char is also confirmed from the conversion curves shown in Figure 2.
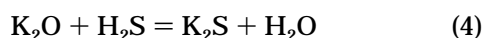
**Figure 12.** SEM micrograph of the gasified char having 15 wt % LNK catalyst.
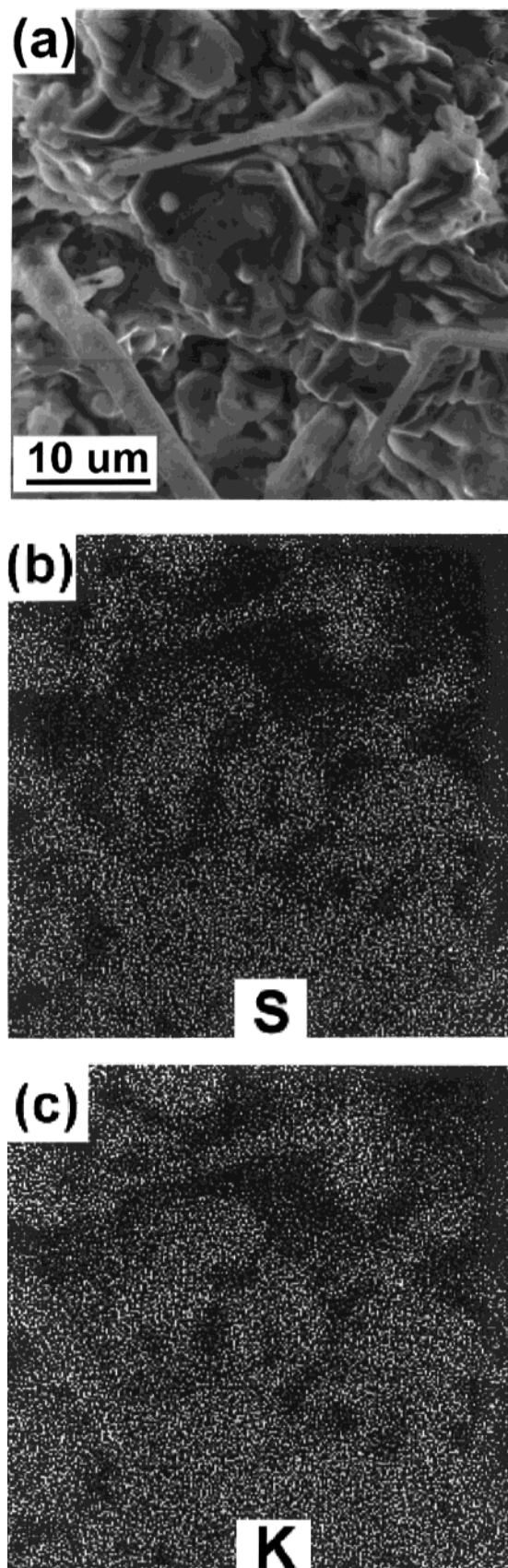
The gasified char containing the LNK catalyst shows a highly porous and crystalline structure (Figure 12). The greater porosity is indicative of almost complete carbon conversions in the sample, which was also confirmed from the experimental results shown in Figure 1. A magnified view of the crystalline structure in this sample is observed in Figure 13 along with the corresponding elemental distribution maps for S and K. The atomic ratio of K/S obtained by the EDS analysis is 2:1, insinuating the possible formation of $K_2S$. X-ray diffraction spectrum of the gasified char having the LNK catalyst in Figure 14 corroborates the formation of cubic $K_2S$. The melting point of $K_2S$ is 1254 K, which is greater than the gasification temperature, 1005 K.[11−12] Hence, after its formation, $K_2S$ possibly exists in a solid crystalline state during and after gasification. However, most of the $Na^+$ and $Li^+$ cations exist in their carbonate form even after the gasification process, as observed from the X-ray analysis. This is attributed to a relatively higher molar fraction of $Na_2CO_3$ and $Li_2CO_3$ in the initial eutectic compositions of LNK (Table 1). The tendency of the K salt in LNK catalyst to form $K_2S$ indicates that the catalyst also acts as a desulfurizing agent.[13] The plausible mechanism for the K salt in LNK during steam gasification is given by eqs 1−4.[13,14]

$$K_2CO_3 + 2C = 2K + 3CO \qquad (1)$$

$$2K + CO_2 = K_2O + CO \qquad (2)$$
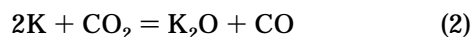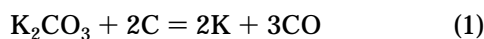
$K_2O$ has a tendency to react with the $CO_2$ and $H_2S$, formed during the gasification process, to obtain $K_2CO_3$ and $K_2S$.

$$K_2O + CO_2 = K_2CO_3 \qquad (3)$$

$$K_2O + H_2S = K_2S + H_2O \qquad (4)$$

The presence of major $K_2S$ peaks in the X-ray diffraction spectrum indicates that formation of $K_2S$ is the domi-

(13) Tomita, A. *Nenryo Kyokai-shi* **1979**, *58* (5), 332−342.
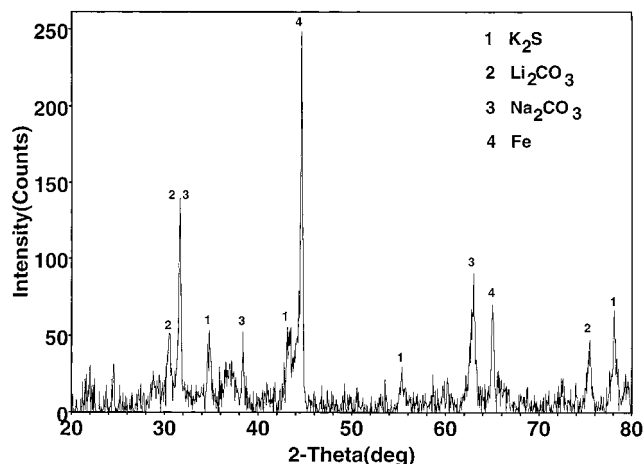(14) McKee, D. W. *Carbon* **1982**, *20* (1), 59−66.



**Figure 13.** (a) High-magnification SEM micrograph of the gasified char with 15 wt % LNK catalyst and corresponding X-ray elemental map for (b) S and (c) K.

nant reaction among reactions shown in eqs 3 and 4. The free energy of formation of $K_2S$ for eq 4 is −230

**Figure 14.** X-ray diffraction spectrum of the gasified char with 15 wt % LNK catalyst.

kJ/mol, which proves the thermodynamic feasibility of the reaction.[15] Additionally, $K_2S$ is also known to catalyze the steam gasification of coal.[3] Fe peaks were also detected in this sample representing the mineral content of the coal. However, these peaks were absent in the gasified chars with 15 wt % NK catalyst. This could be due to a large amount of potassium polysulfides present on the coal surface, which may shield the reflections obtained from the minerals present in the coal. Further analysis need to be carried out to understand the reaction mechanisms for the formation of potassium polysulfides ($K_xS_y$) during the steam gasification of coal using eutectic catalyst systems.

(15) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14* (1), 1272−1425.

## Conclusions

(1) Complete carbon conversions were observed with 10 wt % loading of the LNK catalyst, whereas 15 wt % of NK catalyst was required to achieve the same results.

(2) For the same wt % catalyst loading, the LNK system has a higher M/C ratio in comparison with the NK system.

(3) The porosity of the coal sample before gasification decreases with the increase in the catalyst loading for both catalyst systems. However, higher porosity was observed in the LNK-based sample due to the possible infiltration of the liquid catalyst into the coal matrix.

(4) Uniform distribution of the catalyst was observed in both systems, indicating their homogeneous mixing during sample preparation. The mobility of the liquid ternary catalyst is higher, favoring a higher level of carbon conversions compared to the binary catalyst system.

(5) The gasified chars of the NK system were highly porous after gasification and showed the formation of potassium polysulfides ($K_2S_4$, $K_2S_5$, and $K_2S_6$). The reaction mechanism of the formation of $K_xS_y$ is poorly understood at present.

(6) The gasified chars of the LNK system were highly porous and crystalline in nature. The crystalline nature of these samples is attributed to the formation of $K_2S$. A mechanism for the $K_2S$ formation has been proposed.

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