

Short Communication

Catalytic coal gasification: use of calcium versus potassium*

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A comparative study is made of the relative catalytic effects of potassium and calcium on the gasification in air and 3.1 kPa steam of North Dakota lignitic chars prepared under slow and rapid pyrolysis conditions. It is indicated that potassium achieves relatively high catalytic activity by chemical interaction with the carbonaceous support, no matter how it is added to the lignite or its char. Deactivation of the catalytic potassium is brought about by interaction with inherent aluminosilicates. However, deactivation of calcium is related to its sintering via crystallite growth.

(Keywords: coal; gasification; catalysis)

Catalytic gasification is one of the most promising (and challenging) alternatives for improving the energy efficiency and economics of coal conversion processes. Among the potential catalysts, K and Ca are presently the most interesting. The former, when added to bituminous coal by impregnation, has been shown to be very effective in the Exxon process¹. The latter is the most important *in situ* catalyst, present in abundance in the mineral matter of many low-rank coals². The objective of the investigation reported here was to study the relative merits (or liabilities) of these two catalysts in coal char gasification. This work is a part of a more extensive study on char gasification reactivity, reported elsewhere³⁻⁶.

EXPERIMENTAL

A well-characterized lignite from North Dakota was used in this study⁷. The 60 × 100 mesh fraction (mean particle size ≈ 170 μm) was washed with HCl and HF in order to remove essentially all the inherent inorganic constituents. Subsequently, H⁺ on the carboxyl groups was replaced by K⁺ or Ca⁺⁺, through ion exchange using the corresponding acetates. The raw (as received), demineralized (Dem) and cation-exchanged lignite (Dem + Ca and Dem + K) were devolatilized in a stream of N₂ (99.99% purity) at 1275 K and residence (soak) times between 0.3 s and 1 h. Slow pyrolysis (10 K min⁻¹) was performed in a conventional horizontal-tube furnace. Rapid pyrolysis (≈ 10⁴ K s⁻¹) was conducted in an entrained-flow reactor. The intrinsic, chemically-controlled gasification reactivity of the resulting chars was determined by isothermal thermogravimetric analysis (TGA) in 0.1 MPa air (20 kPa O₂), at temperatures between 525 and 675 K, and in 3.1 kPa H₂O, at temperatures between 825 and 925 K. Further details of the experimental procedure were reported previously^{3-6,8}.

RESULTS AND DISCUSSION

The raw lignite contains 0.43 mmol Ca⁺⁺ g⁻¹ (dmmf) and 4.85 × 10⁻³ mmol K⁺ g⁻¹ (dmmf), i.e. two orders of magnitude less of the latter cation⁹. However, the ion exchange on the demineralized lignite resulted in similar loadings of the two cations: 0.74 and 0.38 mmol g⁻¹ (dmmf) for Ca⁺⁺ and K⁺, respectively. Figure 1 shows the reactivities in 0.1 MPa air of the raw, demineralized, Dem+Ca- and Dem+K-chars prepared by slow pyrolysis at 1275 K with 1 h soak time. It is seen that both K and Ca are very effective catalysts. The same high activity

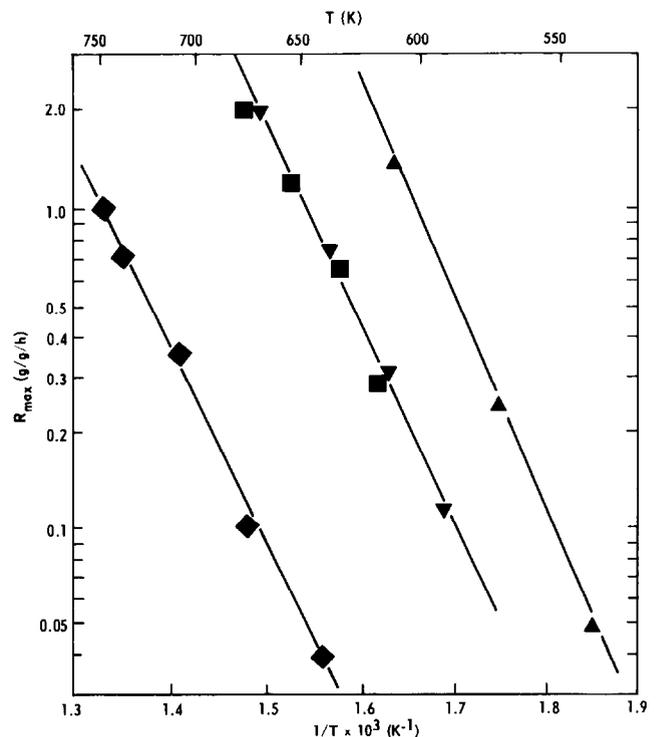


Figure 1 Effect of coal pretreatment on char reactivity in 0.1 MPa air. Pyrolysis conditions: 1275 K, 1 h: ◆, Dem; ○, Raw; ■, Dem+Ca; ▲, Dem+K

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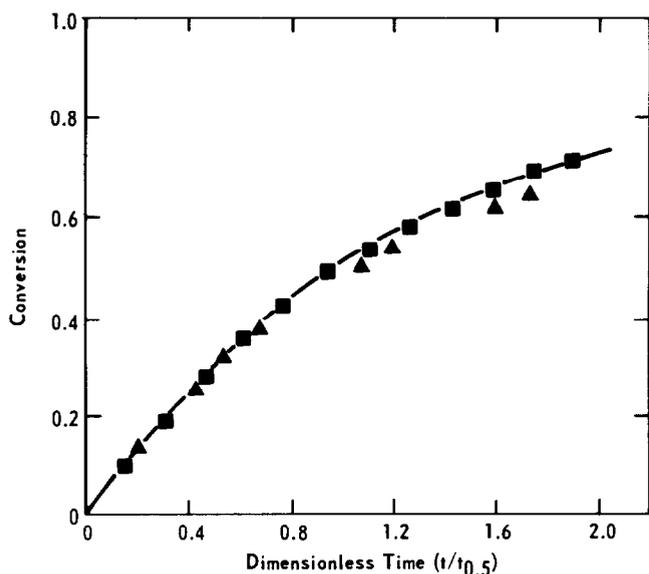


Figure 2 Normalized TGA plots for R-0.3 s (1275 K) raw and Dem+K-char in 0.1 MPa air: \blacktriangle , raw ($T=565$ K), $t_{0.5}=75$ min; \blacksquare , Dem+K ($T=550$ K), $t_{0.5}=63$ min

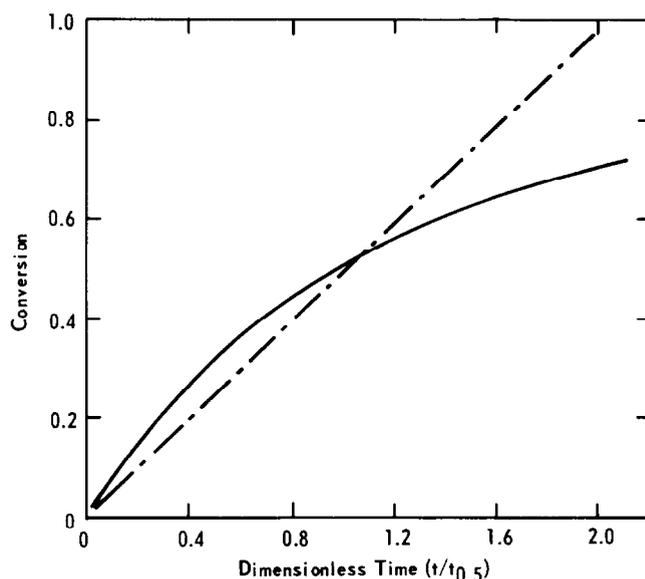


Figure 3 Normalized TGA plots for R-0.3 s (1275 K) raw and Dem+K-char in 3.1 kPa H_2O : —, raw ($T=925$ K), $t_{0.5}=76$ min; - - -, Dem+K ($T=900$ K), $t_{0.5}=52$ min

relative to the demineralized char is exhibited by both catalysts in 3.1 kPa H_2O .

Potassium and calcium behave quite similarly in 0.1 MPa air at low temperatures. An increase in the severity of coal pyrolysis (heat treatment) causes a decrease in char reactivity. In Ca-catalysis the air reactivity at 550 K, for example, decreases by a factor of ≈ 10 for pyrolysis residence times of between 0.3 s and 5 min at 1275 K. In K-catalysis the deactivation is about fifteen-fold. *Figure 2* shows the normalized TGA plots for the reactions of raw and Dem+K-chars in 0.1 MPa air, following rapid (R) pyrolysis at 1275 K. The normalization time parameter ($t_{0.5}$) is the time required to achieve 50% conversion. In both cases the maximum initial slope holds until $\approx 40\%$ conversion, with subsequently decreasing reactivity. In steam, at higher temperatures, calcium behaves in a similar manner¹⁰. However, potassium exhibits quite different behaviour. At 875 K, in 3.1 kPa H_2O , the Dem+K-chars prepared at 1275 K with residence times of 0.3 s and 5 min have practically the same reactivity, 0.20 versus 0.27 g/g/h, respectively, i.e., no deactivation is observed. In addition, the conversion versus time plots are linear up to as much as 90% conversion, as illustrated in *Figure 3*.

A meaningful comparison of the relative activities of the two catalysts analysed in the present study required, of course, the conversion of reactivities (per unit mass of daf char) to turnover frequencies (per unit active catalyst site). It was shown elsewhere^{3,5} that the high reactivity of the raw and Dem+Ca-chars is due to the catalytic effect of CaO. Under the present pyrolysis conditions, the dispersion of CaO in the Dem+Char-char was estimated to be $\approx 4.4\%$. At shorter pyrolysis residence times, say < 2 s (i.e., under rapid pyrolysis conditions), the dispersion was estimated to be $> 25\%$.

It was also shown that the commonly observed and empirically treated lignite char deactivation with increasing severity of pyrolysis conditions can be treated in a fundamental manner, by correlating it with a decrease in

CaO dispersion⁵. In the case of Dem+K-chars, attempts to identify the catalyst and estimate its dispersion by X-ray diffraction were not successful. However, the observed insensitivity of the reactivity in steam to changes in heat treatment conditions, being in agreement with the results of Mims and Pabst¹¹ and McKee *et al.*¹² that the K-catalysed steam gasification rate of coal chars is independent of the method of addition of K to, and therefore its dispersion on, the coal (or char), suggests that at steam gasification temperatures a phenomenon of redispersion of the K-species occurs¹³. It is noted that although the literature on K-catalysed carbon and char gasification is quite voluminous, not many authors address the fundamental issues of catalyst species identification and dispersion.

Wigmans *et al.*¹⁴ suggest the existence of a K-O-C surface complex. Mims *et al.*^{11,15,16} have recently presented evidence for the formation of this complex. This structure is consistent with the high, reproducible and carbon support-independent dispersion of the catalyst of ≈ 20 –25% measured by these authors in HCl chemisorption/poisoning¹¹ and surface derivatization/solid state n.m.r.¹⁶ experiments. Its formation also explains the above mentioned rate insensitivity to pyrolysis conditions and constancy with conversion at steam gasification temperatures.

McKee and Chatterji suggest a redox mechanism for the catalysis of the C- H_2O reaction by K, with the slow (and gasification) step being reduction of molten K_2CO_3 to metallic K by carbon¹⁷. Again good wetting and contact between the molten active K phase and the char surface would be expected. In contrast to the behaviour of K, *Figure 3* suggests a loss of contact between the catalyst and the carbon support in Ca-catalysis. This result, also reported by Lang and Neavel¹³, is a distinct disadvantage of Ca versus K as a catalyst in coal gasification processes. However, the apparent higher mobility of K-species on, and the greater degree of contact with, the char surface seems to be, at the same time, responsible for their

deactivation by interaction with the clays in the mineral matter to form insoluble aluminosilicates^{1,12,18}. With Ca no such deactivation occurs, as reported elsewhere¹⁰. The results of decreasing slope (rate) shown in *Figure 2* suggest that in contrast to the observed behaviour at higher temperatures in steam, at low temperatures the K-species are relatively immobile on the char surface, unable to form the surface complex and thus lose contact with the carbon support, similarly to the behaviour of CaO in raw lignite and Dem + Ca-chars.

The above discussion highlights the relative merits of K and Ca as char gasification catalysts. No matter how it is added to the coal or char, K seems to achieve relatively high dispersion at steam gasification conditions through chemical interaction with the carbon support. On the other hand, Ca is inherently present in low-rank coals, exchanged on the carboxyl groups; rapid pyrolysis conditions result in high initial catalyst dispersion. The mechanisms of deactivation of the two catalysts also seem to be different. Potassium primarily interacts with mineral components to form inactive aluminosilicates. Calcium, on the other hand, deactivates by sintering (crystallite growth). These results and interpretations are thought to have significance in the optimization of catalyst formulation in coal gasification processes.

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REFERENCES

- 1 Hirsch, R. L., Gallagher, Jr., J. E., Lessard, R. R. and Wesselhoft, R. D. *Science* 1982, **215**, 121
- 2 Walker, Jr., P. L., Matsumoto, S., Hanzawa, T., Miura, T. and Ismail, I. M. K. *Fuel* 1983, **62**, 140
- 3 Radovic, L. R., Walker, Jr., P. L. and Jenkins, R. G. *Fuel* 1983, **62**, 209
- 4 Radovic, L. R., Walker, Jr., P. L. and Jenkins, R. G. *Fuel* 1983, **62**, 849
- 5 Radovic, L. R., Walker, Jr., P. L. and Jenkins, R. G. *J. Catal.* 1983, **82**, 382
- 6 Radovic, L. R., Walker, Jr., P. L. and Jenkins, R. G. *Am. Chem. Soc. Div. Fuel Chem., Preprints* 1983, **28**(1), 1
- 7 Penn. State/DOE Coal Data Base, PSOC-246, Coal Research Section, The Pennsylvania State University
- 8 Radovic, L. R. *Ph.D. Thesis*, The Pennsylvania State University, 1982
- 9 Morgan, M. E., Jenkins, R. G. and Walker, Jr., P. L. *Fuel* 1981, **60**, 189
- 10 Radovic, L. R., Steczko, K., Walker, Jr., P. L. and Jenkins, R. G. *Fuel* in preparation
- 11 Mims, C. A. and Pabst, J. K. *Am. Chem. Soc. Div. Fuel Chem., Preprints* 1980, **25**(3), 258
- 12 McKee, D. W., Spiro, C. L., Kosky, P. G. and Lamby, E. J. *Am. Chem. Soc. Div. Fuel Chem., Preprints* 1982, **27**(1), 74
- 13 Lang, R. J. and Neavel, R. C. *Fuel* 1982, **61**, 620
- 14 Wigmans, T., Haringa, H. and Moulijn, J. A. *Fuel* 1983, **62**, 185
- 15 Mims, C. A. and Pabst, J. K. *Fuel* 1983, **62**, 176
- 16 Mims, C. A., Rose, K. D., Melchior, M. T. and Pabst, J. K. *J. Am. Chem. Soc.* 1982, **104**, 6886
- 17 McKee, D. W. and Chatterji, D. *Carbon* 1978, **16**, 53
- 18 McKee, D. W., Spiro, C. L., Kosky, P. G. and Lamby, E. J. *Chem. Tech.* 1983, **13**, 624

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Concern over coal samples

The value of much basic research published on coal is seriously undermined by lack of uniformity in the coal samples used. Many well-conceived, conducted and interpreted investigations on coal have not considered or accounted for the important effect of sample variability on results. This includes variability due to coal's inherent heterogeneous nature and failure to protect samples from changes during storage and repeated use. Meaningful correlations among various laboratory investigations can only be made when well characterized and preserved samples have been used.

The purpose of this communication is to bring to the attention of coal R&D bodies the need for greater care in the selection, preparation, storage and use of coal samples. While many experienced researchers are aware of this need, circumstances often prevent them from fulfilling it. Some workers may not fully appreciate the difficulty of obtaining and preserving standard samples and how failure to do so can influence experimental results. Both established and novice coal researchers must pay greater attention to the quality and integrity of the coal samples being employed for the sake of research quality.

While the lay community thinks of coal as a single entity, to the scientist it is a complex mixture of organic and inorganic compounds of variable composition. Thus, while research is often reported as being done with a specific type of coal, it must be recognized that the physical and chemical composition and properties of coals vary both vertically and horizontally within a given seam¹. Coals are also both kinetically and thermodynamically unstable and account must be taken of this reactivity.

Few investigators have control over a coal sample's integrity until it is received since they have to depend upon others to supply them with samples. It is, of course, not practical or desirable for each investigator to secure their own coal sample from the coal deposit. The investigator does have control once the sample is received, but here too, there is insufficient uniformity in the care and handling of samples.

The oxidation of coals by air at ambient temperatures is well documented and is apparently the most serious problem to consider with respect to sampling, preparation, storage and use of coal samples²⁻⁴. Even at ambient