FTIR STUDIES OF THE EFFECT OF ALKALI METAL SALTS AND THE USE OF ALKALI METAL CHLORIDES IN THE CATALYTIC GASIFICATION OF COAL CHARS

Shang Jung Yuh and Eduardo E. Wolf*

Department of Chemical Engineering
University of Notre Dame
Notre Dame, Indiana 46556

INTRODUCTION

Catalytic gasification of coal provides a direct route for producing synthetic natural gas (SNG). It has long been known that certain alkali metal salts can catalyze the steam gasification of carbonaceous materials(1-2). As a result, lower gasification temperatures can be employed creating a thermodynamically favorable condition for methane production. Several interpretations have been proposed to explain the catalytic mechanism of coal gasification by alkali metal salts. Various redox cycles involving alkali metal(3-5), alkali oxide(6-8), and alkali metal-carbon intercalates(9-10) as the reaction intermediates, have been suggested. Alternatively, Mims and Pabst have proposed that surface complexes such as -C-O-K, -C-K are possible sites of catalytic activity during coal gasification(11-13). Our previous infrared studies of partially gasified coals originally treated with alkali salts showed the presence of a common infrared spectrum for all salts except for the inactive chlorides(14-15).

In the Exxon catalytic coal gasification (CCG) process, only about two-third of the original K_2CO_3(or KOH) catalyst can be recovered by water leaching from the ashes due to the formation of insoluble aluminosilicates(11). Procedures to activate the less expensive alkali salts have been investigated. Wood et al.(16) reported that at modest temperatures, a steam pretreatment of KCl-impregnated carbon may activate this otherwise inactive but inexpensive salt. Lang and Pabst(17) showed that high gasification rates can be attained by employing mixtures of strong acid salts of potassium and, any weak acid salts or certain strong acid salts of sodium as the catalyst. Chauhan et al.(18) found that coal treated with CaO using NaOH at an elevated temperature is much more reactive than that impregnated with aqueous CaO slurry. Lang and Neavel(19) also concluded that calcium must be atomically dispersed throughout the coal to obtain good activity.

This paper describes kinetic and infrared studies of the steam gasification of coal catalyzed by alkali metal salts. These studies have subsequently led us to the formulation of a procedure by which alkali metal chlorides are used as the source of alkali metals for catalytic coal gasification.

* To whom correspondence should be addressed.

EXPERIMENTAL

Kinetic experiments were performed in a quartz flow reactor equipped with a Cahn RG 2000 electrobalance which can continuously monitor the weight loss of the sample as it reacts with flowing steam. During the course of the gasification, effluent gas was periodically analyzed by a gas chromatograph. The infrared spectra were recorded on a Digilab FTS-15C fourier transform infrared spectrometer (FTIR) using coal samples pressed with KBr at a ratio of 1:400. A spectrum was obtained by co-adding fifty scans at a resolution of 4 cm^{-1} wavenumber using a pure KBr disc as the reference. In all experiments, reagent grade chemicals and high purity gases were used as received. Further details about the experimental apparatus, operating procedures, and sample preparation have been described elsewhere(14).

RESULTS AND DISCUSSION

Figure 1 summarizes the gasification rates at 20% conversion and 750°C versus metal/carbon ratio. The data were obtained using an Illinois #6 coal treated with various sodium salts and different catalyst loadings. All sodium salts studied, except NaCl, exhibit good catalytic activity for steam gasification of coal. The gasification rate follows a linear relation with sodium/carbon ratio until a saturation point at about Na/C=0.12 is reached. This trend is similar to the observation reported by Mims and Pabst(11) for K_2CO_3 with various carbon substrates. The dependence of the gasification rate on the catalyst contacting method, namely incipient wetness, aqueous impregnation, and mechanical mixing is not significant. Figure 1 shows that the gasification rate varies at most 10% among three contacting methods. Furthermore, based on the same metal/carbon ratio potassium salts are more effective than sodium salts. However, untreated NaCl and KCl are inactive as catalysts for steam gasification of coal.

The infrared spectrum of Na_2CO_3-impregnated coal is shown in Figure 2A. The absorption band at 1610 cm^{-1} has been assigned to the chelated conjugated carbonyl structure and carboxylates contained in coal(20) whereas the 1450 and 880 cm^{-1} bands are due to sodium carbonate(21). Upon devolatilization, the 1610 cm^{-1} band disappeared while the carbonate bands were still present but less intense as shown in Figure 2B. Since about 44% of the Na initially loaded was lost after devolatilization along with 34% release of volatile matter, the Na/C ratio of the devolatilized sample should have remained the same as that of the impregnated sample. Thus, the decrease in infrared absorbance of the carbonate bands in the devolatlized sample indicates that the missing fraction had reacted with the carbon substrate. Moreover, upon partial gasification to 25% conversion, the intensity of the carbonate bands decreased even further as shown in Figure 2C, even though the Na/C ratio increased due to the carbon consumption. Furthermore, the infrared spectrum of an almost completely gasified sample(94% conversion, Figure 2D) shows an increase of intensity of the carbonate bands as well as the appearance of additional

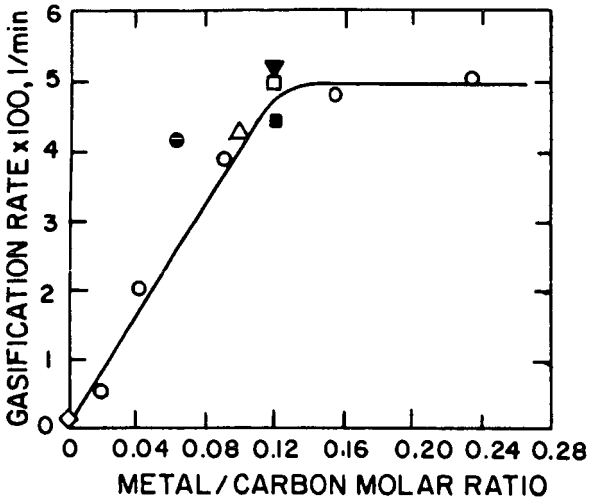

Figure 1 Effects of loading, anion, and contacting method of catalyst on the gasification rate. O, NaOH; Δ, Na_2CO_3; ▼, $NaNO_3$; □, $NaHCO_3$ (incipient wetness); +, $NaHCO_3$ (aqueous impregnation); ■, $NaHCO_3$ (mechanical mixing); ●, K_2CO_3; ◇, without catalyst.

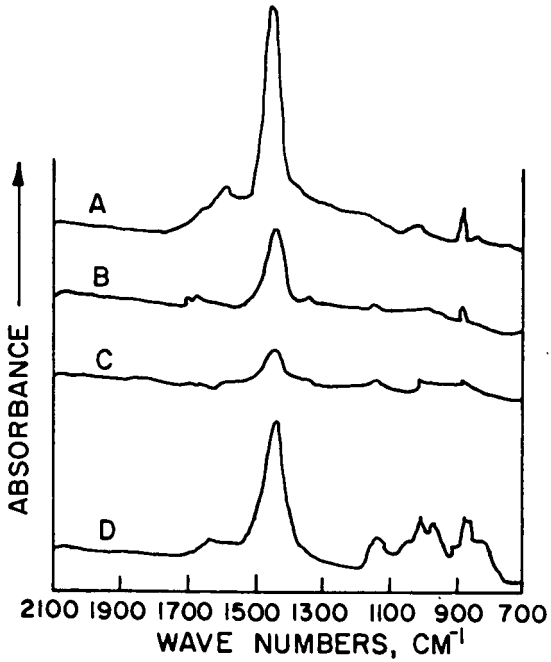

Figure 2 FTIR spectra of Na_2CO_3 coal samples. A, impregnated; B, devolatilized; C, partially gasified (25% conversion); D, gasified (94% conversion).

bands in the 1200-800 cm^{-1} region which corresponds to mineral matters. Atomic absorption measurements of the sodium contained in this sample gave a similar percentage of Na losses(43%) as in the devolatilized sample demonstrating that the interaction of sodium with the carbon substrate occurs at the initial stages of gasification but it disappears at the end with the release of sodium due to the depletion of carbon. It is also interesting to note that all devolatilized and partially gasified samples treated with catalytically active sodium salts exhibit a common infrared spectrum regardless of the anion of the parent salt(15).

In addition, the interaction of sodium and carbon substrate has also been documented by our and other's thermogravimetric results(4,11,15). We found that the weight loss of Na_2CO_3-char in helium starts at temperature much lower than the melting point of Na_2CO_3(851^oC), with CO and CO_2 being the gas products. In the case of char impregnated with NaCl, the temperature at which the weight loss begins is similar to that of NaCl, without any detectable gas product. The infrared and thermogravimetric results clearly demonstrate the importance of the direct interaction of coal with the alkali metal in catalytic activity. Thus, the lack of catalytic activity of alkali metal chlorides results from the high stability of the alkali metal-chlorine bond which prevents the interaction of the carbon substrate with the alkali metal. Further proof of this point is illustrated in Figure 3 in which HCl was added to three Na_2CO_3-treated chars. It can be seen that as the amount of chlorine increases, the catalytic activity decreases accordingly. Moreover, infrared spectra of the HCl-treated samples show a corresponding decrease in the intensity of the carbonate absorbance indicating that the reaction of sodium to form chloride which is infrared inactive, was favored over the interaction of sodium with the carbon substrate.

A corollary of the above results is that Na has to be freed from the chlorine ion in order to use NaCl as the source of Na to catalyze coal gasification. On this basis, we have developed a process which ultilizes alkali chlorides as the source of alkali metals for catalytic coal gasification. The process consists of slurrying the coal with an aqueous solution of the chlorides and a suitable solvent, and subsequent saturation with CO_2. The solid is separated, washed, and dried and is then ready for gasification. All operations except drying are carried out at room temperature. The chlorine ions could be removed in the form of $CaCl_2$ and the solvent can be regenerated and reused. The advantage of this procedure is that the consumption of CO_2 required can be supplied by the gasification itself and alkali chlorides are less expensive than other alkali salts.

Figure 4 shows the gasification rates (at 20% conversion and 750 ^oC) of coals treated with different amounts of NaCl and KCl according to the above mentioned procedure, versus metal/carbon ratio. The sodium and potassium loadings were determined by an atomic absorption spectrophotometer(Perkin-Elmer, Model 305). As expected the KCl-treated coals show higher activity than NaCl-treated coals. Also included in Figure 4 are points obtained with Na_2CO_3-impregnated and K_2CO_3-impregnated coals showing that the activities of these samples are equivalent to those obtained with chloride-treated samples.

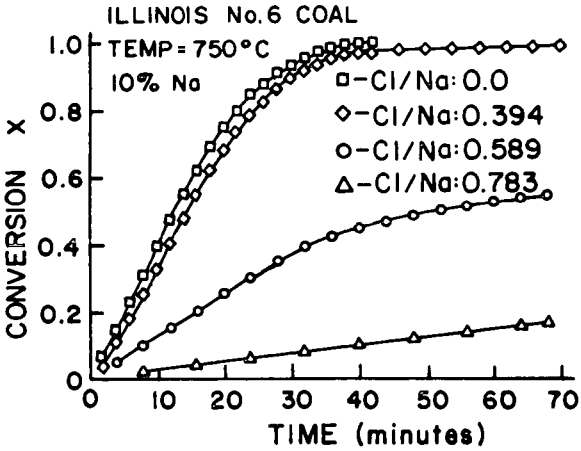

Figure 3 Effect of chlorine addition to Na_2CO_3 coal samples.

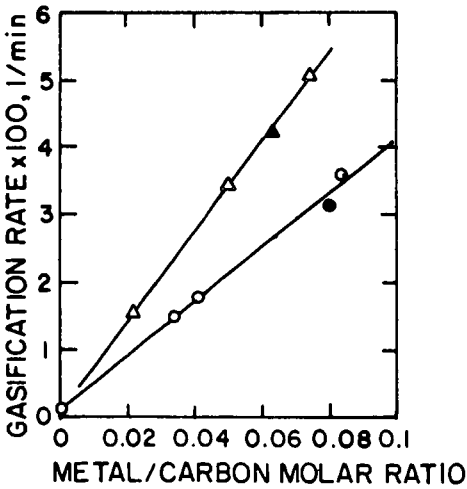

Figure 4 Gasification rates of KCl treated coals (△), NaCl treated coals (O), K_2CO_3 impregnated coal (▲), Na_2CO_3 impregnated coal (●).

CONCLUSION

Laboratory results demonstrate that alkali metal chlorides can provide the source of alkali metals required for catalytic steam gasification of coals via a process involving contact of coal with an aqueous solution of alkali chloride, a suitable as well as regenerable solvent, and CO_2. The catalytic activities of the samples prepared by this procedure are equivalent to those impregnated with other alkali salts.

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