

Kinetics and FTIR Studies of the Catalytic Gasification of Coal Chars

by

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Introduction

Several mechanisms have been proposed to explain the catalytic effects of alkali metal salts in the steam gasification of coal chars. These include redox cycles involving alkali metals [1-2], alkali oxides [3-4], metal - carbon intercalates [5-6], and the formation of surface complexes which are the catalytic sites for water dissociation and carbon oxidation [7-8]. Our previous infrared work [9-11] with potassium salts have shown the formation of a common IR spectrum for all the salts impregnated on coal chars except for the inactive chlorides.

This paper described kinetic and FTIR studies of the gasification of coal chars by Na and K salts, which have led us to formulate a procedure to activate the otherwise inactive alkali chlorides.

Experimental

Kinetic experiments were performed by following the weight loss of the sample in a flow reactor equipped with an electrobalance. The infrared spectrum of coal char samples, pressed with KBr, was recorded using a fourier transform infrared spectrometer (FTIR). A spectrum was collected by co-adding fifty scans at resolution 4 cm^{-1} wavenumber ratioed out against a pure KBr disc used as a reference.

Results and Discussion

Conversion versus time results obtained during gasification of Illinois #6 coal treated with various Na and K salts at different catalyst loadings, were summarized in a plot of the gasification rate (at 50% conversion) versus metal/carbon ratio. All salts, except the chlorides exhibit good catalytic activity. The gasification rate of the sodium salts follows a linear relation with the sodium/carbon ratio until a saturation point at about $\text{Na/C}=0.12$ is reached. Furthermore, the method of introducing the salts into the coal does not change the gasification rate more than 10%. At the same metal/carbon ratio, potassium is about 70% more active than sodium for steam gasification of coal chars.

The IR spectrum of the sodium impregnated coal chars exhibits bands at 1450 and 880 cm^{-1} corresponding to Na_2CO_3 regardless of the parent

salt. Upon devolatilization, the intensity of these bands decrease, although they should have remained the same as those of the non-devolatilized sample, due to similar sodium and carbon losses during devolatilization. Moreover, upon further gasification to 25% conversion, the intensity of the carbonate bands decrease even further even though the Na/C ratio increases, and the same amount of sample was used in all the IR studies. The loss of IR absorbance intensity indicates that the carbonate has reacted with the carbon substrate to form a species which cannot be seen by IR, and which is presumably responsible for the catalytic activity. This is further demonstrated by the increase in the IR absorbance intensity of a sample gasified to 94% conversion. In this case the absorbance increases due to the release of sodium by the depletion of the carbon substrate.

The interaction of Na with the carbon was further demonstrated by thermogravimetric experiments of decomposition of Na_2CO_3 in He with and without a carbon substrate. The weight loss in the presence of carbon char starts at a much lower temperature than the carbonate decomposition temperature. However, the decomposition of NaCl in He was not affected by the presence of a carbon char.

The thermogravimetric and infrared results clearly shows that an interaction between the alkali metal and the carbon substrate occurs for all active salts except the chlorides. It thus can be inferred that the chlorides lack of catalytic activity is due to its stability which prevents a direct interaction of the metal with carbon. This point was further demonstrated by adding different amounts of gas phase HCL to a coal char treated with Na_2CO_3 . It was found that the activity, and IR absorbance intensity of the HCL treated samples, decreased as the amount of CL in the sample increased. These results shows that the formation of NaCl , which is IR inactive, was favored over the interaction of Na with the carbon substrate thus decreasing the catalytic effect.

A corollary of the above is that if Na could be freed from chlorine one can use NaCl or KCl as the source of Na or K to catalyze coal gasification. Accordingly, a procedure was devised whereby the chlorides of sodium and potassium were contacted with coal, and a suitable

solvent which reacts with chlorine, and frees the alkali metal for further interaction with the carbon substrate. The chlorine ions could be removed and the solvent regenerated and reused. All operations were performed at room temperature. *Gasification rates of coals treated with different amounts of NaCl and KCl using the activation procedure were found to be the same as rates obtained with Na₂CO₃ and K₂CO₃ impregnated coals chars.* The advantage of this procedure is that it uses the less expensive chloride salts as the source of the alkali metal. The fact that the same activity is obtained with the otherwise inactive chlorides, further substantiate the claim that the alkali-metal interaction is responsible for the catalytic effect. The specific nature of this interaction and the structure of the resulting species still awaits definite elucidation.

References

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