

FREE RADICAL INVESTIGATIONS OF DIRECT COAL LIQUEFACTION WITH Fe-BASED CATALYSTS USING ELECTRON SPIN RESONANCE SPECTROSCOPY

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ABSTRACT

Using a recently fabricated in-situ high pressure/high temperature electron spin resonance (ESR) apparatus, we report the variations of the ESR parameters of free radicals (density N , linewidth ΔH and g -value) in the hydrogenation of Blind Canyon coal at 440°C and 415°C and as a function of H_2 pressure up to 600 psi. More efficient hydrogenation is observed at 440°C as the decrease in N with H_2 pressure is much higher at 440°C than at 415°C. A corresponding decrease in ΔH with H_2 pressure is also observed. Similar experiments but with loadings of Fe_2O_3/SO_4 catalyst, elemental sulfur and hydrogen donor 9-10 dihydrophenanthrene are now being carried out.

SUMMARY OF RESULTS/PROCEDURES

It is now generally accepted that direct coal liquefaction involves the interaction of thermally/catalytically generated free radicals in coals with the available hydrogen [1,2]. Some of these free radicals can be detected by in-situ electron spin resonance (ESR) spectroscopy. Recently we have fabricated a high pressure/high temperature in-situ ESR cavity system in order to investigate the free radical chemistry of direct coal liquefaction under more realistic conditions used in coal liquefaction experiments [3]. Experiments have been carried out from ambient to 500°C and for gaseous pressures up to 600 psi at X-band frequencies (~9 GHz). The density N of the free radicals and their g -values g and linewidth ΔH are measured as a function of temperature and pressure. The experimental procedures for measuring these quantities have been described in a recent paper [4].

In Fig. 1, we show the variation of the free radical density N in Blind Canyon coal as a function of H_2 pressure at two temperatures viz. 415°C and 440°C. The decrease in the free radical density with H_2 pressure signifies hydrogenation since capture of H_2 by free radicals quenches them and makes them undetectable by ESR. Comparing the results at 440°C with those at 415°C shows that hydrogenation is considerably more efficient at 440°C than at 415°C since considerably larger decrease in N with H_2 pressure is observed at 440°C. The significance of these results is that these experiments are providing a direct evidence for the process of hydrogenation.

The variation of the g -value and the linewidth ΔH of the free radicals with H_2 pressure is shown in Fig. 2 for the experiments at 440°C. Whereas the g -value is essentially independent of H_2 pressure, the linewidth decreases as the H_2 pressure increases. The g -value, in favorable circumstances, can provide some information on the nature of the free radicals. However since there is no change in the observed g -value with H_2 pressure (Fig. 2), no additional information on the chemical nature of free radicals is readily apparent from this experiment. The observed decrease in the linewidth with H_2 pressure may be related to the decrease in the free radical density with H_2 pressure observed in Fig. 1.

To simulate the conditions used in direct coal liquefaction, experiments are now underway in which the Blind Canyon coal is successively loaded with the catalyst (e.g. Fe_2O_3/SO_4), elemental sulfur, and the hydrogen donor 9-10 dihydrophenanthrene (DHP). Free radical ESR

parameters are then monitored as a function of temperature in flowing H₂ gas and at fixed temperature as a function of H₂ pressure. In Fig. 3, we show one set of such results in flowing H₂ gas in which N vs T is plotted for the Blind Canyon coal, and for the coal loaded with Fe₂O₃/SO₄ and sulfur, and coal loaded with Fe₂O₃/SO₄, sulfur and DHP. The loading by weight was in the ratio coal: Fe₂O₃/SO₄:sulfur:DHP = 100:1.44:2.02:200. These loadings are chosen so as to give the ratios Fe/coal = 1/99 (~1%), Fe/S = 1/2, coal/DHP = 1/2. These preliminary results in Fig. 3 show that the catalyst and sulfur promote cracking since N is higher compared to the unloaded coal at all temperatures. With loading of DHP, magnitude of N is lowered as compared to the unloaded coal for temperatures below 260°C. Above this temperature, N values with DHP loading are essentially identical to the coal + catalyst + sulfur case as if the DHP is no longer present. To verify this, we carried out a thermogravimetric experiment on DHP in flowing H₂ gas. This experiment showed that by 290°C all DHP is evaporated, confirming the above argument. The lower values of N below 260°C in DHP are simply due to hydrogenation since it is well known that hydrogenation caps the free radicals, at least some of them. Experiments are now in progress under H₂ pressures up to 600 psi to simulate direct liquefaction conditions. Under H₂ pressures, evaporation of DHP at lower temperatures should be suppressed. Results of these experiments will be reported elsewhere in the near future.

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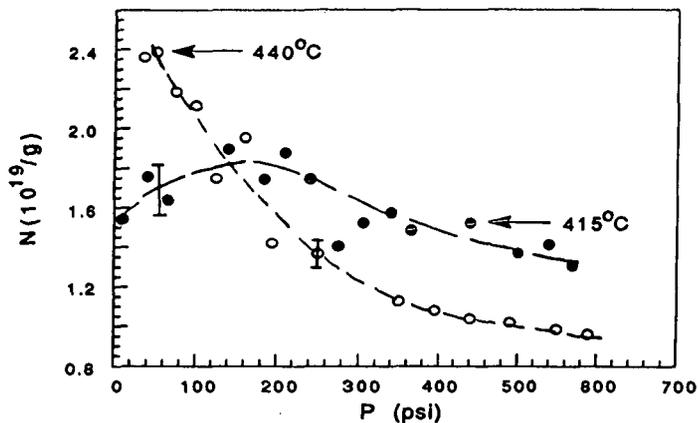


Fig. 1. Variation of N in Blind Canyon coal with H_2 pressure at two temperatures.

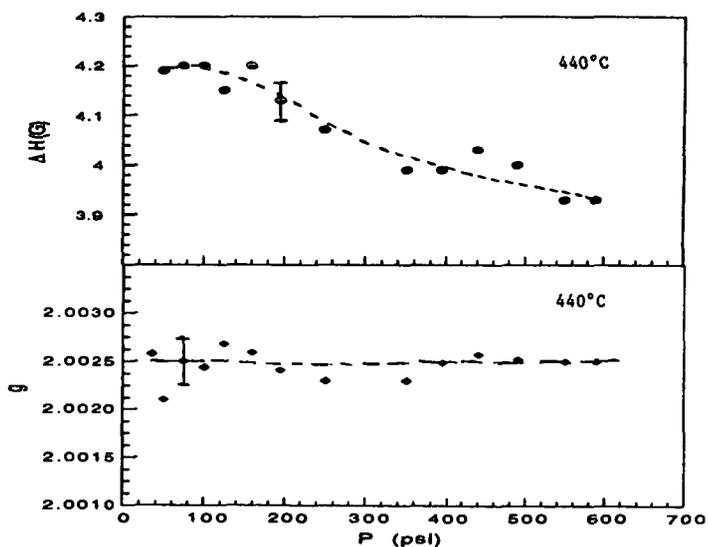


Fig. 2. Variations of the g-value and linewidth ΔH with H_2 pressure.

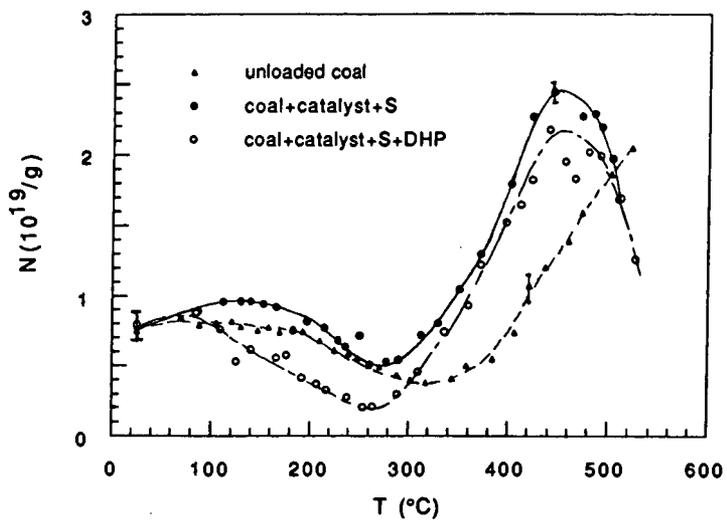


Fig. 3. Variation of free radical density N with temperature for unloaded and loaded coal. See text for details.