

Microscopic Studies on the Dispersion of Iron/Molybdenum Bimetallic Catalysts in Argonne Coals

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Abstract

The dispersion and reactivity of an iron/molybdenum coal liquefaction catalyst was investigated in three Argonne coals. Three coals (Blind Canyon, Wyodak and Pittsburgh #8) were impregnated with a 1 wt% Fe and 1 wt% Mo liquefaction catalyst using both ultrasonic and incipient wetness techniques. The yields of THF solubles in demineralized Blind Canyon coal indicate no significant advantage in the use of ultrasound as the impregnation technique. Results of electron probe microanalysis (EPMA) reveal that the catalyst is coated on the surface of the particles prior to hydrolysis at 350 °C and 2000 psig H₂. EPMA micrographs indicate that the catalyst occupies the interior of the coal particles after hydrolysis. Our results suggest that coal catalyst mobility occurs during hydrolysis and may be due to the liquid phase present in the coal and the amount of porosity.

Introduction

Catalyst dispersion remains an area in coal liquefaction research requiring a more thorough understanding.¹ Common sense suggests that the more evenly dispersed and the finer the size of the catalyst the more efficient the coal liquefaction. In other words, both the form of the catalyst and the manner in which it is introduced into the coal affect the coal liquids yields.

In this study we examine the role of the catalyst impregnation technique upon coal hydrolysis by comparing the incipient wetness technique with ultrasonic impregnation. A series of bimetallic catalysts were studied in three coals from the Argonne Premium Coal Sample Program. The dispersion of the catalyst was followed with electron probe microanalysis (EPMA) as in previous studies.² Electron probe microanalysis is a microscopic technique that allows one to examine on the micron scale the distribution of elemental species by detecting characteristic X-rays (Fig. 1).^{3,4}

Experimental

Samples of 100 mesh Blind Canyon, Wyodak and Pittsburgh #8 coals were obtained from the Argonne Premium Coal Sample Program

and stored at 0 °C until impregnation. In some studies involving Blind Canyon coal the coal samples were demineralized. The demineralization process occurred under nitrogen using warm (about 60 °C) solutions of concentrated HCl followed by concentrated HF and then concentrated HCl.

The following catalyst systems were studied: 0.05% Mo, 1% and 0.01% Fe, 1% and 0.01% Ni, 1% and 0.01% Fe/0.05% Mo and 1% and 0.01% Ni/0.05% Mo (note: these are all in wt%). Two methods of catalyst impregnation were compared: incipient wetness and ultrasound. For bimetallic catalysts the impregnation was done sequentially from aqueous solutions using first the ammonium tetrathiomolybdate, followed by the iron(III) chloride hexahydrate or nickel(II) nitrate hexahydrate. Hydroxypropylation was done in a shaken tubing bomb reactor in which samples were reacted for one hour at 350 °C and 2000 psig of H₂. In order to determine the product yields, the samples were Soxhlet extracted with tetrahydrofuran (THF) after hydroxypropylation.

Samples for electron probe microanalysis were prepared with Petropoxy, polished to a smoothness suitable for EPMA, and sputter coated with carbon to reduce point charging of the surface. Visual images of the samples were obtained from the secondary electron and back-scattered electron images with a CAMECA Model SX-50 detector (Courbevoie Cedex, France). The catalyst dispersion in the samples was determined by collecting the characteristic X-rays for iron, nickel, molybdenum and sulfur with an energy dispersive spectrometer detector. X-ray analysis was done using a Digimap program. Sample magnification was x1000 or x1500.

Results

The resulting yields are summarized in Tables 1 and 2. The first set of experiments involved the use of demineralized Blind Canyon coal. These first experiments were run in order to determine which method of impregnation was better, incipient wetness or ultrasound, and whether preextracting the coal with THF improved the yields. As seen in Table 1 no significant advantage exists for either impregnation technique and preextraction with THF actually decreases the yields of THF solubles upon hydroxypropylation. The rest of the experiments were all done with coals that had not been preextracted and had been impregnated by the incipient wetness technique and were performed in order to determine the efficiency for producing THF solubles of various Fe/Mo and Ni/Mo bimetallic catalysts. The results show that the bimetallic catalysts are much more efficient than either metal alone (Table 1). More importantly, even when the loading of the Fe/Ni promoters is decreased by two orders of magnitude significant amounts of THF solubles are still produced.

These images are of samples that have been impregnated with 1 wt% Mo because the 0.05 wt% loading of Mo results in a Mo concentration too close to the detection limits of the EPMA for accurate micrographs. The EPMA images for iron, nickel and molybdenum show that all three of the cationic species behave in

a similar manner. Before hydropyrolysis the catalyst species are located on the surface of the coal particles (Fig. 2). After reaction the catalyst species occupy the interior of the coal particles (Fig. 3). This is true for the iron, nickel and molybdenum catalytic species.

The second set of experiments involved three different Argonne coals: Wyodak, Pittsburgh #8 and Blind Canyon and were done in order to determine whether the choice of catalyst impregnation technique seriously affected the yields of THF solubles. The coals were used as received from the Argonne Premium Coal Sample Program. The catalyst system used was 1 wt% Fe/1 wt% Mo with the same reaction conditions as given previously. For the Pittsburgh #8 and Blind Canyon coal samples there was no significant difference in the yields of THF solubles between samples impregnated by incipient wetness or by ultrasound (Table 2). A significant difference occurs for Wyodak coal. The samples impregnated by incipient wetness exhibit a 13% higher yield of THF solubles. As described in the case above, before hydropyrolysis the catalytic species are found on the surface of the coal particles. After hydropyrolysis these species are found in the interior of the coal particles.

Discussion

Sulfided molybdenum can provide a reasonably efficient coal liquefaction catalyst.^{5,6} Recently, Li and coworkers,⁷ using a fixed-bed reactor, found that a MoS₂ loading of 0.5% produces a 35% oil yield under hydropyrolysis conditions of 3 M Pa and 798 K for 30 minutes. As they note in their conclusion, a Mo loading of 0.5% is commercially unrealistic due to its high cost and the sulfur added to the hydropyrolysis products.⁷

The yields reported in the present study (Tables 1 and 2) result from a procedure using lower Mo loadings (0.05%) and mild hydropyrolysis conditions. The presence of the iron/nickel promoters appears to increase the efficiency of hydropyrolysis (Table 1). These results seem to indicate that one of the most promising routes to commercially feasible coal liquefaction involves the use of bimetallic catalyst systems with loadings of less than 1% and the use of mild hydropyrolysis conditions. The mild conditions would permit a catalytic rather than thermal breakdown of the coal structure.

The EPMA experiments lead to two main conclusions: First, catalyst mobility occurs during hydropyrolysis for these coals and catalytic species. Second, because these catalysts are mobile species during hydropyrolysis, the choice of catalyst impregnation technique probably will not significantly affect the coal liquefaction yield.

What does affect the liquefaction yield is the rank of the coal. The best yields were obtained from a subbituminous coal, Wyodak coal, which is 75% C.⁸ Blind Canyon coal, a high volatility bituminous coal which is 81% C, provided the next best yield of THF solubles. Pittsburgh #8 with a carbon content of 83% provided the lowest yields of THF solubles (Table 2). As has been pointed out

by Derbyshire,⁹ the rank of a coal and its carbon content correlate with the porosity of the coal structure. Upon heat treatment the open pore structure of low rank coals is preserved whereas higher rank coals undergo increasing degrees of graphitization. We believe this effect helps to explain our results. If, as we surmise, catalyst mobility occurs during hydroxyprolysis then a more efficient catalyst dispersion process will occur in the low rank coals resulting in a higher yield of THF solubles. Higher rank coals will have less efficient catalyst dispersion during hydroxyprolysis and hence lower THF soluble yields. This is precisely what we find for the yields of Wyodak versus Blind Canyon and Pittsburgh #8 coals (Table 2).

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Table 1. Catalytic Hydropyrolysis of Blind Canyon Coal
THF^c

Catalyst ^a	Impregnation ^b	Sol.	Insol.
0.05% Mo	U	40	52
0.05% Mo	I	42	52
1% Fe + 0.05% Mo	I	55	41
0.01% Fe + 0.05% Mo	I	50	43
1% Ni + 0.05% Mo	I	50	46
0.01% Ni + 0.05% Mo	I	52	45

^aCatalyst loadings are given in wt%

^bImpregnation: U=ultrasound, I=incipient wetness

^cYields are given as % of maf coal

Table 2. Comparison of Yields and Impregnation Technique
THF^b

Coal	Impregnation ^a	Sol.	Insol.
Wyodak	U	55	36
Wyodak	I	68	20
Pittsburgh #8	U	53	45
Pittsburgh #8	I	56	42
Blind Canyon	U	62	36
Blind Canyon	I	63	38

^aImpregnation: U=ultrasound, I=incipient wetness

^bYields are given as % of maf coal

Electron Probe Microanalysis Schematic

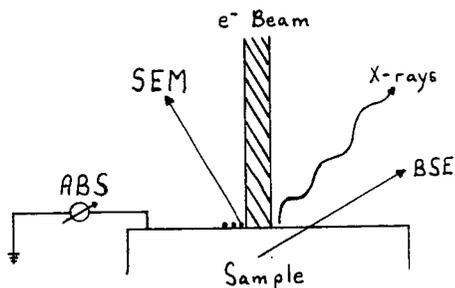


Figure 1. This illustration portrays the various signals generated by EPMA. An e⁻ beam of 10-30 keV impinges upon the sample surface resulting in three "visual" signals and characteristic X-rays. The secondary electron image (SEM) results when the incoming electron beam causes the loosely bound surface electrons to leave the sample. Back-scattered electrons (BSE) have entered the sample and through atomic interactions are emitted from the sample. The absorption image (ABS) is read as a current from the sample and accounts for those electrons of the incoming electron beam that are not back-scattered.

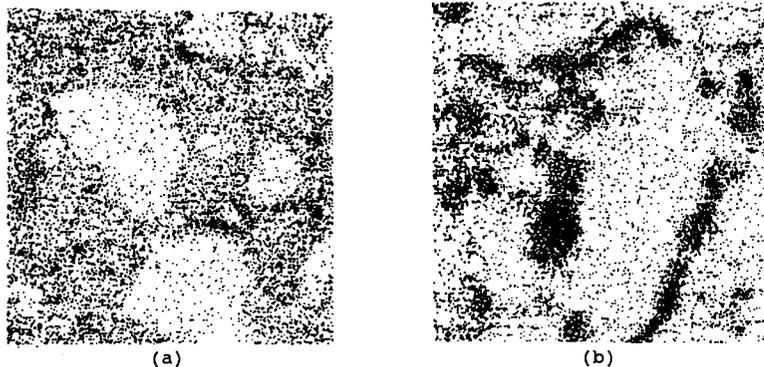
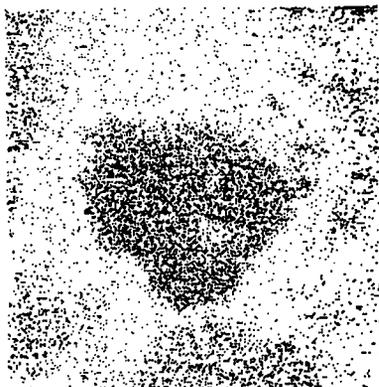


Figure 2. These EPMA micrographs are 97 x 97 microns. Figure 2a is of 1 wt% Fe impregnated Blind Canyon coal before reaction. Figure 2b is of 1 wt% Ni impregnated Blind Canyon coal before reaction. The cationic species have not entered the particles, they are located on the surfaces of the coal particles as seen by the rings and ghost images of particles.



(a)



(b)

Figure 3. The EPMA images here are 97×97 microns. Figure 2a is an image of Blind Canyon coal after impregnation with 1 wt% Fe and hydrolysis. The iron is now evenly dispersed throughout the coal particle in the center of the image. Figure 2b is an image of Blind Canyon coal after impregnation with 1 wt% Ni and hydrolysis. The nickel species has entered the coal particle in the lower-right corner of the image and is less evenly dispersed.