

## SULFUR-PROMOTED METAL OXIDES AS COAL LIQUEFACTION CATALYSTS

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### ABSTRACT

This paper reports an investigation of the activities of iron and tin oxides treated with varying amounts of sulfate for the direct liquefaction of a bituminous coal (Illinois No. 6 from the Argonne Premium Coal Sample Bank). The work described here also attempts to correlate the physico-chemical properties of the sulfate-promoted oxides before the reaction and the types of active phases formed under liquefaction conditions with their apparent activities for hydrocracking of coal.  $\text{Fe}_2\text{O}_3\cdot\text{SO}_4^{2-}$  was found to be an effective catalyst for coal liquefaction even when used in small concentrations (<0.7 wt % iron). It resulted in an 86 wt % (maf basis) conversion of Illinois No. 6 coal at 400°C and 1000 psig hydrogen (initial); more than 50 wt % of the products consisted of oils (n-pentane solubles). Addition of elemental sulfur to the same catalyst (at 0.35 wt % Fe) enhanced the overall conversion to 90.3 wt % with more than 60 % of products consisting of oils. Similar results for coal conversion were obtained for a solid superacid made from tin,  $\text{SnO}_2\cdot\text{SO}_4^{2-}$ . These conversions were much higher than those obtained in a thermal run under the same reaction conditions (% conversion = 52 %, wt % oils = 16). For both iron and tin oxides, sulfated forms containing between 1.5 wt % to 6 wt % of  $\text{SO}_4^{2-}$  group on the surface were more active than their respective unsulfated forms. Promotional effects of sulfate group are believed to be due to an increase in "catalyst-dispersion" and surface acidity.

### INTRODUCTION

Catalysts in highly dispersed form are believed to be very active for conversion of coal to liquids via direct coal liquefaction.<sup>1,2,3</sup> Understanding the effects of catalyst dispersion (catalyst surface area per mass) and composition on catalyst performance is still far from complete. In direct coal liquefaction, the supported metal catalysts such as Co-Mo/ $\text{Al}_2\text{O}_3$  may suffer from poor contact with the feed and rapid deactivation.<sup>4</sup> Unsupported dispersed catalysts derived from finely divided solid precursors offer efficient contact of coal-solvent slurries with catalyst surfaces. Addition of a low surface area solids requires high catalyst concentrations.<sup>5</sup> Particulate pyrite ( $\text{FeS}_2$ ) with average particle size of several microns is not very effective at low catalyst concentrations. A catalyst with a high specific surface area and fine particulate size can be utilized even at very small concentrations<sup>6</sup> for achieving better performance in terms of overall coal conversion and selectivity to lighter products (oils) in direct coal liquefaction. A cheap disposable catalyst such as iron is highly desirable.

High dispersions of catalysts have been obtained by different methods such as the impregnation technique<sup>3</sup>, use of water-soluble<sup>1</sup> or oil-soluble precursor<sup>2</sup>, and use of finely divided powders.<sup>9</sup> All these methods allow the formation of finely dispersed active inorganic phases under reaction conditions. Maximum interaction of coal, vehicle, and  $\text{H}_2$  can occur on the catalyst surface with a highly dispersed catalyst. One method of increasing dispersion of a catalyst is to introduce it as a very finely divided solid

(average particulate size of a few nanometers) to the coal-solvent reaction mixture. Such finely divided powdered precursors are believed to achieve good distribution throughout the coal-solvent slurry and are converted to active inorganic sulfide phases. The high dispersions of active phases thus achieved is believed to allow the use of catalyst concentrations below 1.0 wt % with good performance.<sup>10</sup>

We chose to study the catalytic activity of sulfate-treated iron and tin oxides and its relation to catalyst properties. These oxides have been claimed to be "superacidic"<sup>11,12</sup> as have the oxides of other transition metals such as Ti, Zr, Hf. These oxides have a Hammett acidity function,  $H_0 < -12.0$  and catalyze a variety of hydrocarbon transformations at low temperatures.<sup>12</sup> It is believed that the bidentate sulfate group on the oxide surface increases its acidity. It is also known<sup>13</sup> that the sulfate anion prevents sintering of ceramic oxide powders during calcination, thereby reducing the degree of crystallinity and lowering the average crystallite size of these oxides. It was reported first by Tanabe et al.<sup>14,15</sup> that a sulfate-promoted iron oxide ( $Fe_2O_3 \cdot SO_4^{2-}$ ), claimed to be a solid superacid, was active for promoting C-C bond cleavage in coals and therefore for the hydrocracking of a bituminous Akabira coal (% C = 83.0) at 400°C and under 1000 kg/cm<sup>2</sup> of H<sub>2</sub>. A sulfated iron oxide with about 2 wt % sulfate group ( $SO_4^{2-}$ ) on its surface was found as active as a well known hydroprocessing catalyst CoO-MoO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>. The iron oxide in its sulfated form gave about 75 wt % coal conversion (with 31 % "oils") as compared to unsulfated iron oxide which resulted in only 60 wt % coal conversion with 20 % of "oils". Later work reported by Kotanigawa et al.<sup>16</sup> mentions the use of sulfate-treated iron oxide for some model compound reactions and for direct coal liquefaction reactions. They attributed higher activity of the sulfate-promoted iron oxide to the possible synergism between sulfate ( $S^{6+}$ ) and sulfide ( $S^{2-}$ ) phases of iron formed under coal liquefaction conditions. Mariadassou et al.<sup>17,18</sup> have reported the use of finely divided iron oxides/oxyhydroxides (avg. particle size = 50 nm) such as FeOOH, FeOOH-Al<sub>2</sub>O<sub>3</sub> sulfided *in situ* by addition of CS<sub>2</sub> for the hydroliquefaction of a high volatile bituminous coal. They observed an increase in the activity of iron sulfide with decrease in the particle size of iron oxide added as precursor. They also reported that sintering of the oxide particles at high temperatures of coal liquefaction was inhibited by the textural promoter effects of coal. The same group recently reported the activity of finely divided tin oxide-sulfur systems for coal liquefaction.

## EXPERIMENTAL

**Chemicals:** Illinois No. 6 hvB bituminous coal ground to below 100 mesh (<120 μm) was obtained in ampules and under N<sub>2</sub> storage from the Argonne Sample Bank and used as received. Tetralin (99+% pure) was obtained from the Fisher Scientific Co. Illinois No. 6 coal contained 4.8 % sulfur of which 46 % was organic and 54 % was pyritic. It had a composition of 77.7 % C, 5.0 % H, 13.5 % O, 4.8 % S, and 15.5 % ash. The starting materials used for the catalyst preparation were iron alum, urea, 28 % ammonia water which were purchased from the Aldrich Chemical Co. and tin(IV)chloride and iron(III)nitrate were purchased from the Strem Chemical Co.

**Catalyst Preparation and Characterization:** The sulfate treated oxides of iron and tin were prepared starting from their respective sulfate or chloride salts precipitated with either ammonia water or urea. Both homogeneous as well as heterogeneous coprecipitation routes were followed to prepare the intermediate oxyhydroxides of iron and tin. These oxyhydroxides were then treated with sulfuric acid in varying concentrations. The resultant powders were then dried and calcined at appropriate temperatures. The preparation conditions of these catalysts are indicated in Table 1. The catalysts thus prepared were characterized by various techniques such as BET-surface area analysis, sulfur analysis, thermogravimetry (TGA), X-ray diffraction, and electron microscopy. A Phillips X-ray Diffractometer using Cu-Kα radiation at 30 kV and 25 mA was used to obtain the powder diffraction patterns of the catalysts.

Table 1. Summary of Preparation Conditions of Sulfate Treated Metal Oxides

| Cat.Code | Catalyst   | Starting Salts                       | Norm. H <sub>2</sub> SO <sub>4</sub> | Calcination, T°C |
|----------|--|--------------------------------------|--------------------------------------|------------------|
| FeCat1   | Fe <sub>2</sub> O <sub>3</sub>                               | Fe(NO <sub>3</sub> ) <sub>3</sub>    | -                                    | 500              |
| FeCat4   | Fe <sub>2</sub> O <sub>3</sub> SO <sub>4</sub> <sup>2-</sup> | Fe(NO <sub>3</sub> ) <sub>3</sub>    | 1.0                                  | 500              |
| FeCat7   | Fe <sub>2</sub> O <sub>3</sub> SO <sub>4</sub> <sup>2-</sup> | Fe Alum*                             | -                                    | 500              |
| FeCat8   | Fe <sub>2</sub> O <sub>3</sub> SO <sub>4</sub> <sup>2-</sup> | Fe Sulfate                           | -                                    | 700              |
| SnCat1   | SnO <sub>2</sub>   | SnCl <sub>4</sub> ·5H <sub>2</sub> O | -                                    | 600              |
| SnCat3   | SnO <sub>2</sub> SO <sub>4</sub> <sup>2-</sup>               | SnCl <sub>4</sub> ·5H <sub>2</sub> O | 1.0                                  | 600              |
| SnCat5   | SnO <sub>2</sub> SO <sub>4</sub> <sup>2-</sup>               | SnCl <sub>4</sub> ·5H <sub>2</sub> O | 6.0                                  | 600              |

\* Urea was used as a precipitating agent in this preparation.

Average crystallite sizes were calculated from line broadening of the peaks, corrected for instrumental broadening. A Cahn electrobalance was used for thermogravimetric analyses and acidity measurements of catalysts. Transmission electron microscopy(TEM) and scanning electron microscopy (SEM) were carried out for structural investigation of the catalysts using JEOL 35 CX SEM and JEOL 200 CX TEM models. The residues of coal liquefaction experiments were also analyzed using X-ray diffraction and a JEOL 2000 FX STEM (100 kV beam) with an energy dispersive X-ray spectrometer. for the composition and dispersion information about the catalytic phases formed under liquefaction conditions.

**Reaction Studies:** Direct coal liquefaction experiments were carried out in a 300 ml stainless steel autoclave (Autoclave Engineers) agitated by a turbine impeller and heated by a tube furnace. Illinois No. 6 coal (10 g), tetralin (40 g), and 0.35 or 0.7 wt % Fe or Sn (added as their respective sulfate-treated oxides) were mixed first manually in a beaker and then placed into the reactor, which was flushed with helium and pressurized with 1000 psig hydrogen at room temperature. Stirring was started at room temperature to allow for hydrogen dissolution in the coal-solvent slurry and proper mixing of the reactants. After about 30 minutes, the reactor was heated with furnace heater to 400°C in approximately 35-40 minutes, and held at that temperature for 60 minutes while stirring about 1400 rpm. The reactor was then cooled to below 300°C in about five minutes. Soxhlet extraction with CH<sub>2</sub>Cl<sub>2</sub> was used to determine the coal conversion. Soluble products were recovered by rotary evaporation at 45°C under vacuum. Pentane solubles (oils) were determined by adding 40 volumes of n-pentane to CH<sub>2</sub>Cl<sub>2</sub> solubles and using Soxhlet extraction with n-pentane. Pentane-insoluble but CH<sub>2</sub>Cl<sub>2</sub> soluble material was referred to as asphaltenes. Methylene chloride insolubles (residues) were recovered and stored for further characterization.

## RESULTS AND DISCUSSION

**Catalyst Characterization:** The iron and tin oxides treated with different amounts of sulfate were characterized by the different techniques mentioned above. Interestingly, the average crystallite size of the oxide particles was found to decrease upon treatment with 2 to 6 wt % sulfate anion. A distinct broadening of the X-ray diffraction peaks was observed for these oxides with the increasing sulfate group loadings. At the same time a corresponding increase in the specific surface areas of these oxides was observed when liquid nitrogen physisorption was carried out on the catalysts for determining the surface areas using the BET equation. A linear relationship was observed between the concentration of sulfuric acid used for sulfate treatment and the final amount of SO<sub>4</sub><sup>2-</sup> group that remained on the surface. The decrease in the crystallite size can be explained if we hypothesize that a bulky sulfate group on the surface of the intermediate oxyhydroxide particles prevents the agglomeration or sintering of the oxide particles

at high temperature. It also probably delays crystallization. Evidence for acidity enhancement of these oxides upon the sulfate-treatment was also observed from pyridine adsorption experiments carried out using a Cahn electrobalance. From X-ray diffraction studies for iron oxides,  $\alpha$ - and  $\gamma$ - $\text{Fe}_2\text{O}_3$  were found out to be the most abundant crystalline phases, while for tin oxides, the most abundant phase was crystalline  $\text{SnO}_2$ . Catalyst characterization results are listed in Table 2. The values of onset liquefaction temperatures of Illinois No.6 coal using different sulfate-treated oxides as catalysts have also been listed in this table. These temperatures were determined using a high pressure, high temperature polarizing light microscope with flowing hydrogen at 300 psig pressure.

Table 2. Effect of Sulfate Loading on Surface Area [ $S_g$ ] and Crystallite Size [ $D_{\text{average}}$ ]

| Cat.Code | Wt % $\text{SO}_4^{2-}$ | $S_g$ , m <sup>2</sup> /g | XRD: $D_{\text{avg}}$ | TEM : $D_{\text{avg}}$ | Onset* L.T., °C |
|----------|-------------------------|---------------------------|-----------------------|------------------------|-----------------|
| FeCat1   | 0.0                     | 26.82                     | 46 nm                 | 60-70 nm               | 415             |
| FeCat7   | 3.4                     | 81.72                     | 16 nm                 | 20-25 nm               | 410             |
| FeCat4   | 6.1                     | 79.50                     | 12 nm                 | 20-30 nm               | 400             |
| SnCat1   | 0.0                     | 60.50                     | 19 nm                 | —                      | 410             |
| SnCat3   | 1.8                     | 97.48                     | 9 nm                  | 15-20 nm               | 395             |
| SnCat5   | 3.9                     | 146.23                    | 5 nm                  | 10-15 nm               | 385             |

\* Onset liquefaction temperature for a thermal run was about 450°C.

As seen from this table, the average crystallite sizes determined for both the sulfated and unsulfated iron and tin oxides based on the X-ray line broadening agree fairly well with those determined with transmission electron microscopy (TEM) using the bright field. Scanning electron micrographs of these catalyst samples were also taken to determine their particle size distribution and surface structure morphology. It was found from both the TEM and SEM images that sulfate-treated iron oxide consists of a bimodal-type distribution of crystallites, with some crystals being rod-like while other are plate-like. The average crystallite size was about 20 nm. Sulfate-treated tin oxides have a porous structure with a sausage-like surface morphology. Their average crystallite size was found to be 15 nm.

**Reaction Studies:** The coal liquefaction reactions were carried out in a 300 ml stainless steel autoclave. Initially a thermal run was carried out to determine the catalytic activities of the mineral matter (especially pyrite) inherent to coal, i.e., without addition of any external catalyst. This resulted in 52 wt % (maf) total conversion of Illinois No.6 coal, with about 16 wt % n-pentane solubles (oils). The total coal conversion values are calculated based on the weight of the final residue. The sulfate-treated iron and tin oxides were then used in very small concentrations for the liquefaction reactions. One of the iron oxides, Fe Cat 4 (wt % sulfate = 6.1) resulted in a substantially high coal conversion of 86 wt % with 39 wt % conversion to n-pentane solubles. A comparative experiment with Fe Cat 1, which did not contain any sulfate group gave 74 wt % total conversion and 23 wt % conversion to oils. Less than 0.7 wt % Fe was used with respect to coal in these experiments. Similar experiments were run with tin oxides treated with sulfate to determine their efficacy for direct coal liquefaction reactions and to determine the promotional effect of the sulfate group on the activity of the oxides. About 0.8 to 0.9 wt % of tin was used in these runs with respect to coal. Two bar-charts demonstrating conversions and product-distributions for different oxide catalysts based on iron and tin are shown in Figure 3.

As can be seen from the bar-charts in Figure 1, addition of 0.7 wt % Fe in the form of oxide to the reaction mixture enhances total coal conversion as well as conversion to lighter oils. Both sulfate-treated oxides of iron, Fe Cat 4 and Fe Cat 7, were found to increase the total conversions to 86 % and 79 % respectively as compared to 74 % obtained with  $\text{Fe}_2\text{O}_3$  alone (unsulfated form). Importantly, the amounts

of oils increased from about 23 % for  $\text{Fe}_2\text{O}_3$  alone to about 38 to 40 % for  $\text{Fe}_2\text{O}_3\cdot\text{SO}_4^{2-}$  catalysts. Promotional effects of sulfate groups on catalytic activities of oxides for coal liquefaction were seen for sulfate-treated tin oxides as well. As seen in Figure 1, Sn Cat 5 (wt % sulfate=3.9) resulted in about 85 % total coal conversion with more than 40 % of the products consisting of oils. These values were again higher than those obtained for the unsulfated  $\text{SnO}_2$ , which gave 72 % total coal conversion with 32 % oils. A run was also made using iron oxide prepared directly from ferric sulfate by calcination at 700°C (Fe Cat 8). It resulted in about 80 % total coal conversion with 32 % conversion to oils. Some reactions were made at much reduced wt % of Fe and Sn but in the presence of an elemental sulfur added to the reaction mixture. The amount of sulfur added was enough (about 1.1 times the quantity that is required for complete sulfidation of added Fe as  $\text{Fe}_2\text{O}_3\cdot\text{SO}_4^{2-}$ ) to bring about complete *in situ* conversion of oxides to sulfides.<sup>19</sup> Fe Cat 1 and Fe Cat 7 were used separately with the added sulfur. The amount of catalyst was 0.35 wt % with respect to coal. As shown in the Figure 1, total conversions as high as 90+ % were obtained with both the sulfated (Fe Cat 7) and the unsulfated (Fe Cat 1) forms of iron oxides, but the former catalyst resulted in higher conversion to oils (47 %) than the latter one (28 % oils). This suggests that the non-stoichiometric iron sulfides (detected later by XRD) formed from sulfate-treated iron oxide were more active for the conversion of asphaltenes to lighter oils than those formed from unsulfated oxide ( $\text{Fe}_2\text{O}_3$ ). Comparison of two runs, one with Fe Cat 7 (0.7 % Fe) and other with Fe Cat 7 + S (0.35 % Fe), shows an enhancement in conversion levels (Figure 3). Elemental sulfur was used with one of the sulfated tin oxide for coal liquefaction (wt % Sn=0.4), but no significant effect on conversion was observed. The enhancements in total conversions as well as conversions to oils obtained with sulfate-treated oxides over the unsulfated ones might be attributed mainly to the enhanced "dispersions" (surface area/gm) of the oxides upon the sulfate treatment. Due to increase in the specific surface area and decrease in the average particle size of the oxides upon the addition of small amounts of the sulfate group, the conversion of oxides to active catalytic sulfide phases, especially non-stoichiometric sulfides for iron, is facilitated.<sup>19</sup> (Pyrrhotite, a non-stoichiometric sulfide of iron, is a semiconductor. One wonders whether this property of pyrrhotite has any bearing upon its catalytic activity for coal liquefaction.) More of the active catalyst surface of these sulfides probably becomes available for reaction.

**Product Characterization:** The  $\text{CH}_2\text{Cl}_2$  insolubles (residues) recovered from the coal liquefaction reactions were analyzed to determine the composition of metal-sulfide phases formed under coal liquefaction conditions. X-ray diffraction was carried out on these residues to determine their composition and the particle sizes of the inorganic phases formed. Residues recovered from the reactions which employed sulfate-treated iron oxides invariably showed the presence of non-stoichiometric iron sulfides (pyrrhotites) as the major constituent along with traces of  $\text{FeOOH}$  and  $\text{Fe}_3\text{O}_4$ . The average crystallite size of the pyrrhotite formed was found to be about 25 to 30 nm. Autoclave runs with sulfate-treated tin oxides resulted in residues rich in  $\text{SnS}$  with a small amount of pyrrhotite formed by the decomposition of pyrite in coal. These tin sulfides were found to have an average crystalline diameter of about 30 nm. A run was also made with one of the iron oxides (Fe Cat 7) in the presence of activated carbon instead of coal to characterize the dispersions using scanning and transmission electron microscopy (STEM). Some of the liquefaction residues were also characterized using STEM and energy dispersive microanalysis (EDX) and found to contain well dispersed iron-containing particles with particle sizes ranging between 10 to 100 nm. A typical TEM-mode image of iron-containing particles on activated carbon and the X-ray microanalysis are shown in Figure 2. This TEM-image shows a distribution of fine iron-containing particles over the activated carbon support. The EDX spectrum of one of the liquefaction residues indicates the presence of both Fe and S in these fine particles. Further detailed investigation of these liquefaction residues by Mossbauer spectroscopy and EXAFS is in progress.

The composition of  $\text{CH}_2\text{Cl}_2$  solubles was determined by elemental analysis which was performed by Galbraith Laboratories Inc. (Table 3). Methylene chloride solubles consisted of a mixture of recovered tetralin (GC-analysis) (about 50 wt %, H/C=1.2), naphthalene (about 35 wt %, H/C=0.8) and soluble products from coal (about 15 wt %).

Table 3. Elemental Analysis of  $\text{CH}_2\text{Cl}_2$  Solubles Obtained from Liquefaction Reactions Employing Different Catalysts

| Analysis by Wt % as Received |       |      |       |       |      |           |
|------------------------------|-------|------|-------|-------|------|-----------|
| Catalyst                     | % C   | % H  | % N   | % S   | % O  | {H/C}atom |
| Thermal                      | 83.97 | 6.37 | 1.85  | 1.23  | 6.76 | 0.91      |
| FeCat4                       | 84.69 | 7.68 | <0.50 | 0.084 | 0.74 | 1.09      |
| FeCat1                       | 88.98 | 8.94 | 1.30  | 0.21  | 1.09 | 1.20      |
| FeCat7                       | 86.25 | 8.47 | <0.50 | 0.28  | 1.25 | 1.18      |
| SnCat3                       | 87.94 | 8.80 | <0.50 | 0.24  | 1.32 | 1.20      |
| SnCat5                       | 87.44 | 9.10 | <0.50 | 0.25  | 1.07 | 1.25      |

All the iron and tin oxides used as catalysts for the reaction under the same conditions yielded  $\text{CH}_2\text{Cl}_2$  solubles with an enhancement in H/C ratios (about 1.2) along with a significant heteroatom removal. This could be due to the increased acidic character of these oxides. A very small amount of both nitrogen (Wt % < 0.5) and sulfur (Wt % < 0.28) was obtained in the solubles from almost all the catalytic runs. From these results, both iron and tin oxides (after transformation into their respective active sulfide phases) seem to function as good hydrogenation and hydrogenolysis catalysts.

### CONCLUSIONS

Our experimental work on sulfate-treated metal oxides has shown that the sulfate group immobilized on the surface of these oxides helps increase its surface acidity and promotes the catalytic activity of these oxides for direct coal liquefaction reactions, probably by causing reduction in their average particle diameter and subsequent increase in the specific surface area available for catalysis. The sulfate-treated iron and tin oxides resulted in better coal conversions and product slates than the unsulfated oxides. It appears that finely divided sulfate-treated oxides are effective for overall coal conversion as well as the conversion of the asphaltenes to lighter oils. The oxides seem to convert themselves in to their respective metal-sulfides with nano-size particles (10 to 100 nm), which is an indication of good catalyst-distribution during coal liquefaction reaction. These sulfate-treated oxides of iron and tin also seem to function as better hydrogenolysis catalysts for hydrodesulfurization and hydrodenitrogenation reactions.

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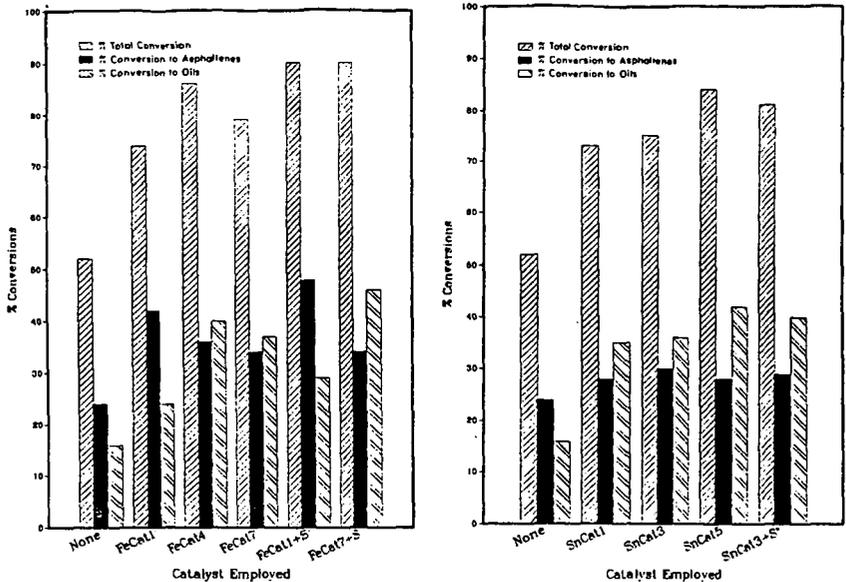


Figure 1. Activities of The Sulfate-Treated Iron and Tin Oxides for Liquefaction of Argonne Illinois No.6 Coal at 400°C, 1000 psig H<sub>2</sub>, 1 hr run time

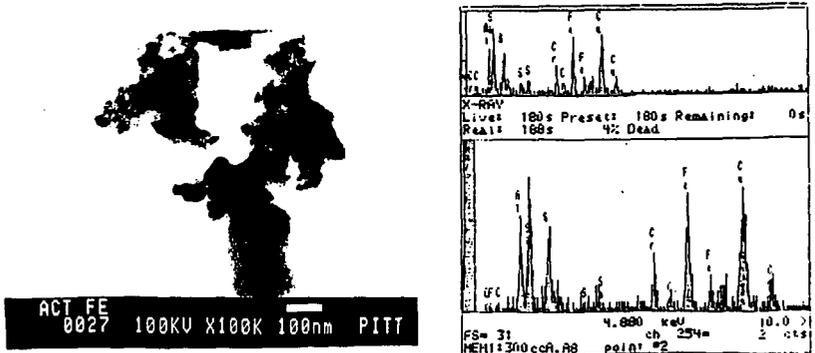


Figure 2. TEM-mode image of iron-containing particles on activated carbon and EDX Spectrum of Coal Liquefaction Residue using sulfated Iron Oxide Catalyst

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