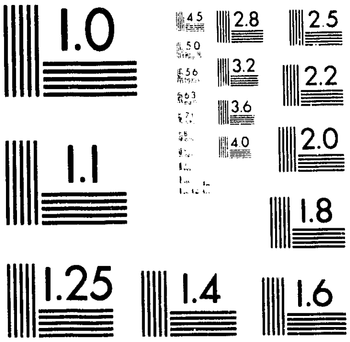
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SYNTHESIS AND CATALYTIC PROPERTIES OF METAL AND SEMICONDUCTOR NANOCLUSTERS*

J. P. Wilcoxon, T. Martino, E. Klavetter, and A.P. Sylwester, Organizations 1153 and 6211, Sandia National Laboratories, Albuquerque, N.M. 87108.

Abstract: The synthesis of metal or semiconductor nanoclusters in the microheterogeneous environment of oil-continuous inverse micelle systems is discussed. We focus on the synthesis and catalytic properties of palladium, iron, and iron sulfide nanoclusters. Cluster size control is achieved by changing the micelle size. The size of various micelles used for synthesis was determined by small angle neutron scattering(SANS) and was chosen to produce cluster in the size range of 1-20 nm. Cluster sizes were determined by either transmission electron microscopy (TEM) or small-angle x-ray scattering (SAXS). Cluster structure was determined by either x-ray or electron diffraction. In the case of Fe nanoclusters the crystal structure depended on the chemical nature of the surfactant micelle used in the synthesis, illustrating the important role of the surfactant during the growth process. Results of *in-situ* pyrene hydrogenation using size-selected Pd clusters show a significant increase in activity/total surface area as the size decreases. These clusters also proved to be effective as unsupported catalysts for direct coal hydropyrolysis, even at very low metal concentrations. The synthesis and optical features of a new semiconductor cluster material, FeS_2 is discussed with regard to its use in photocatalysis. The application of FeS_2 in coal hydrogenolysis reactions has improved yields of short chain hydrocarbons significantly compared to conventional FeS_2 powders.

Introduction: Surfactants have many industrially valuable properties and are widely used as wetting agents, emulsifiers etc.[1] One of their most remarkable properties is the ability to allow mixing of otherwise incompatible solvents, e.g. water and oil to form clear homogeneous solutions called microemulsions. This is the basis for their use as tertiary oil recovery agents. For example, the anionic surfactant AOT can solubilize nearly 100 molecules of water for each surfactant molecule in a solution of decane. This paper discusses the use of inverse micelles to solubilize significant quantities of metal salt, which can then be reduced to colloidal metal form by a variety of techniques.

Metal salts are insoluble in oils and consequently techniques of metal colloid formation have focused primarily on inorganic chemistry in polar solvents such as water. It has been recognized for years that formation of small, narrow size dispersion colloids requires homogeneous nucleation and growth and requires the addition of stabilizers such as polymers to prevent precipitation. In our method[2], by a suitable choice of solvent and surfactant we form a inverse micelle system which consists of 1-10 nm size surfactant aggregates called micelles which have non polar tail groups forming an interface with the oil-continuous organic phase and polar head groups directed toward the interior of the micelle. The interior of the droplet-like micelle is capable of solubilizing significant amounts of charged metal salts. It also serves as a center for nucleation and growth during the reduction of the metal. Growth of the colloid proceeds by a complex process of collisions between micelles, material interchange, and final stabilization by the surfactant. This growth stage is strongly influenced by the presence of phase boundaries and the strength of interactions between the micelles[3] and these features, properly understood, can be used to control the size and polydispersity of the final product.

Palladium Clusters; Size control and Hydrogenation Activity: Surfactants used in the preparation of palladium clusters fall into three general families; nonionic surfactants of the type $CH_3(CH_2)_{i-1}(OCH_2CH_3)_jOH$ (hereafter abbreviated C_iE_j, industrial appellation Brij), the anionic surfactants (e.g. Sodium-Bis(2-ethylhexyl)sulfosuccinate, (common name AOT)), and the cationic surfactants, (e.g. didodecyldimethylammonium bromide, (called DDAB)). We describe the preparation of some palladium metal colloids using the DDAB/toluene system inverse micelle system. A 5-10 wt% solution of DDAB is prepared in toluene. Static and dynamic light scattering, or small angle neutron scattering (SANS) can be used to demonstrate that this system produces the smallest micelles[4], and TEM (see Figure 1) demonstrates that very small, highly dispersed clusters are produced. $PdCl_2$ is added directly with stirring to a desired metal concentration, typically between 1×10^{-5} and .05 M. The sample is then purged for several minutes with Ar gas. Several methods of reduction are then available, the optimal type depending on metal and

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solvent/surfactant system. In the case of palladium either $NaBH_4$ or $LiBH_4$ dissolved in tetrahydrofuran (THF) is used. Absorbance measurements to monitor the $[Pd(II)]$ have established that the reactions are complete under these conditions. The number average size of these clusters was $\langle D \rangle_n = 1.2$ nm. This corresponds closely to the available interior volume of DDAB micelles as measured by small angle neutron scattering (SANS).

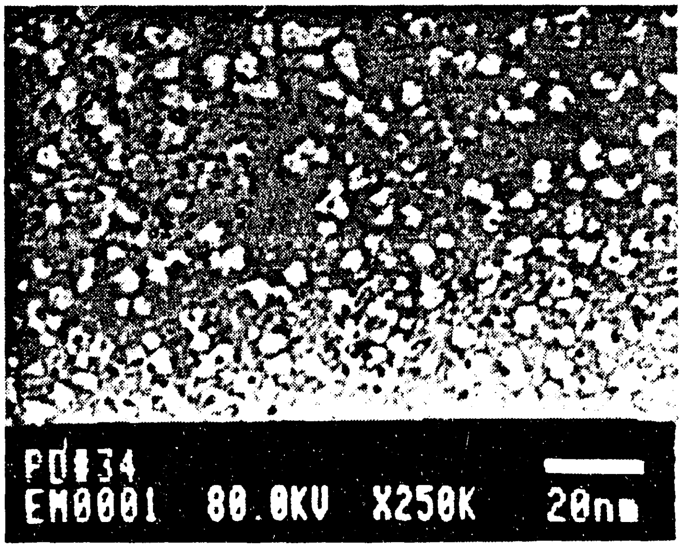

Figure 1. Transmission electron micrograph (TEM) of palladium clusters formed by reduction of $PdCl_2$ encapsulated in the interior of the water-free inverse micelle system described in the text.

We vary the size of the palladium clusters by using various micelles whose dimensions have been determined previously by SANS. For example, using the nonionic surfactant $C_{12}E_5$ dispersed in octane we obtain palladium clusters whose size was determined to be D~12.2 nm by small angle x-ray scattering. Figure 2 shows a Guinier analysis of such data. The advantage of this approach to size characterization is that the z-average size of the entire ensemble is measured automatically. This removes some of the subjectivity inherent to TEM size analysis. Also, independent of particle shape, the small wavevector (Q) portion of the x-ray scattering should obey $\ln I \sim 1/3(Q^2 R_g^2)$, so a semilog plot of the scattering vs Q^2 gives the radius of gyration, R_g. In addition, a detailed analysis of the large wavevector portion of the scattering allows an analysis of the size polydispersity. Preparations of palladium clusters in inverse micelles typically have between 5 to 10% variation about the mean size.

Selected area electron diffraction (SAD) from palladium nanoclusters grown in inverse micelles demonstrated that the clusters had a fcc lattice as expected with the bulk lattice constant. These results were confirmed by x-ray diffraction (XRD). We mention this observation since, as we shall demonstrate in the case of iron nanoclusters, the presence of the surfactant during the cluster growth process can result in non-bulk crystal structure.

Although SAXS measurements of size can be very useful for metal clusters, for certain materials the absorbance is too strong at conventional x-ray wavelengths (e.g. the Cu($K\alpha$) at 1.54 Å can not be used to study iron nanoclusters). Never-the-less, the possibility of obtaining both cluster size information from SAXS and structure via wide-angle diffraction makes this technique quite attractive.

Palladium as a conventional supported (heterogeneous) material is known to be a very good hydrogenation catalyst. Our nanoclusters, being fully dispersed in organic solution, require no support. In a sense, they span the gap between molecular (homogeneous) catalysts and heterogeneous catalysts. Since very little is known about such materials we decided to investigate the effect of size on catalytic activity for a series of size-selected Pd nanoclusters.

We synthesized a series of palladium nanoclusters with sizes between 2 and 13 nm by variation of the micelle size. We tested these nanoclusters for activity for the hydrogenation of pyrene.[5] This polycyclic molecule was chosen because of our interest in screening catalysts for coal liquefaction applications. The results of these experiments are shown in figure 3. The reactions were all carried out under identical conditions. A very dramatic size effect was observed, with activity increasing nearly 3 decades as the size decreased from 13 to 2 nm. Even when corrected for the increase in geometric surface area, the effect is considerable.

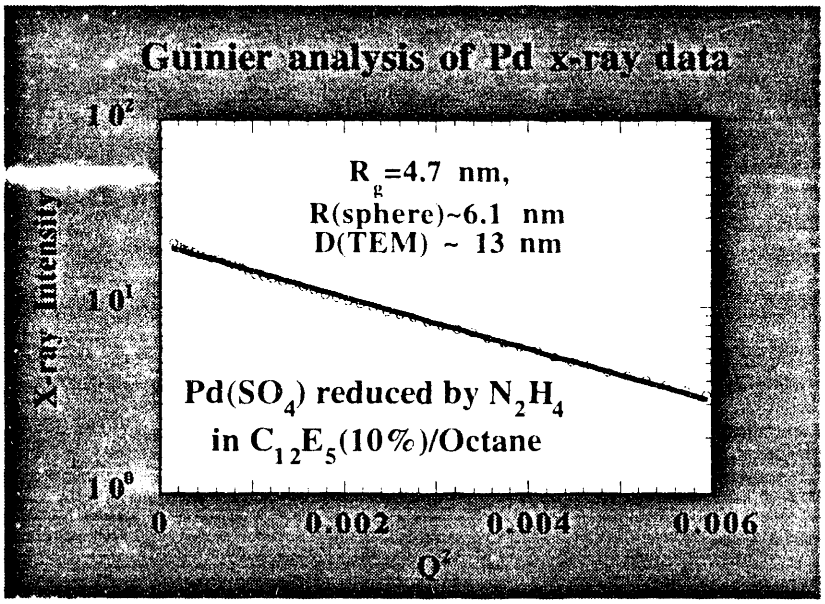

Figure 2. Guinier analysis of the scattering from palladium clusters grown in inverse micelles.

There are two possible explanations for these observation. The first is an increase in special types of surface sites on the cluster surface which are especially active for pyrene hydrogenation. The second explanation is a consequence of our method of cluster size control which required us to synthesize several of the clusters in chemically distinct micelle systems. The surfactants in the different systems may very well bind preferentially to special sites on the cluster surface and compete with the pyrene molecules, altering the inherent catalytic activity. Since the surfactants were required to bind strongly enough to prevent cluster aggregation during the reaction, this is a strong possibility. Never-the-less the results of figure 3 encouraged us to further investigate the catalytic behavior of these clusters in a reaction in which the surfactant on the surface would play a more minor role.

The reaction we chose, direct coal hydropyrolysis, is a very attractive method for conversion of coal into tars and gases. This process would be the first stage of coal liquefaction since the tars could then be further refined to produce liquid hydrocarbons fuels. For such a process to be successful a catalyst must be dispersible directly onto coal powder. This makes nanoclusters which are synthesized in hydrocarbons ideal. Since there is little or no chance to recover the catalyst after the process, the catalyst must be both cheap and relatively environmentally benign. In the our initial experiments, we examined two sizes of palladium clusters which had been synthesized using inverse micelles in toluene and octane. Toluene is known to swell the coal slightly, but did not by itself increase the yield during determinations of the baseline conversion.

Figure 4 shows the conversion of coal into tars using palladium nanoclusters as a function of weight % metal. Also shown are the results of using conventional supported Pd and MoS_2 catalysts, the latter at a order of magnitude higher concentration. It is clear that these novel catalysts can match the performance of the best available supported materials. Also encouraging is the fact that significant conversion above baseline occurs at very low weight % metals. Not shown is the gas yield which is quite high at 13-15% even at 0.02% Pd. One of the most promising results shown in figure 4 is the conversion obtained using 2.5 nm sized iron nanoclusters.[6] No iron catalyst previously tested had shown any conversion above baseline. When the price of iron is compared to palladium this result is even more promising. We expect that the development of a commercially viable coal hydropyrolysis catalyst will require alloying of an inexpensive base material like iron, with a material with better hydrogenation activity such as palladium. Our future research in this area will focus on such nanocluster alloys. In the narrow size range of palladium clusters tested there seems to be only a minor size effect on the conversion efficiency as shown in this figure. The slight increase in conversion for the 2.5 nm clusters in toluene may be a consequence of better penetration of the clusters into the coal structure due to the swelling effect of toluene.

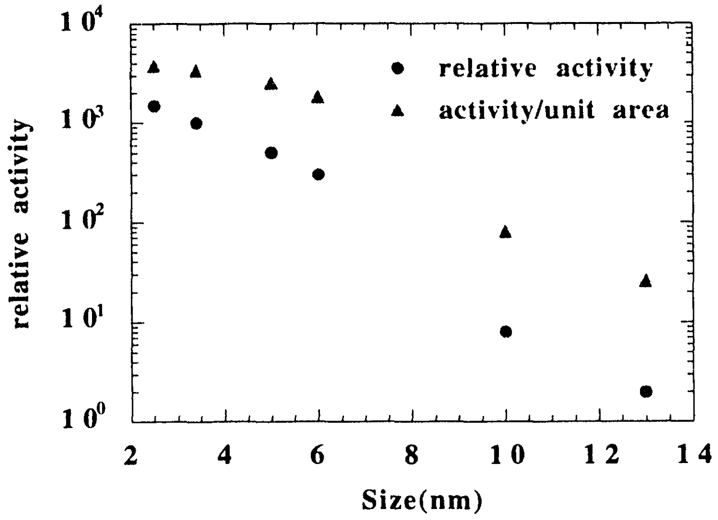

Figure 3. Pyrene Hydrogenation Activity as a function of Palladium Nanocluster Size.

Iron Nanoclusters: Our method of Fe colloid formation exploits the inherent size differences between different micelle systems to control the final particle size. In effect, the size of the surfactant head group coupled with the interaction between the surfactant hydrophobic tails and oil determines the interior volume of the inverse micelles. This is most easily illustrated by the nonionic systems C_iE_j, where the ratio of i/j controls the micelle size in a given solvent. Low ratios result in small aggregation numbers and micelles sizes, or by fixing i/j and increasing the length k of the hydrocarbon C_k solvent the same effect can be achieved. Since the ionic precursor salts are only soluable in the interior hydrophilic volume of the inverse micelle, all cluster growth occurs within and is limited to this volume. The reducing agent when added diffuses through the micellar interface and rapidly reduces any metal ions present in the interior. Following this rapid reduction process diffusion of the micelles and collisions between micelles allows exchange and growth of iron clusters, provided, of course, that such exchange does not exceed the available volume of the micelle. Thus, a narrow size distribution of cluster sizes results.

Optimization of solvent/surfactant compatibility during the colloid growth process (e.g. $C_{12}E_3$ with C_{16} or $C_{12}E_8$ with C_8) allows a broad range of final cluster size. SANS measurements, such as shown in figure 5 demonstrate the changes in size of the precursor micelles that are possible by this strategy, and these measurements allow selection of desirable systems for use in forming metal clusters of a chosen size. The intercept at Q=0, yields the mass, while the shape of scattering curve at large Q yields the surface/volume ratio, which gives information concerning the shape of the precursor micelle. In this case it indicates a slightly non-spherical (disc-like) shape which is consistent with the surfactant geometry and packing considerations for the micelle aggregate. Unfortunately, SANS or SAXS measurements on the final Fe colloid solutions are difficult because of the significant absorbance cross-section of iron for the neutron or x-ray wavelengths available. Thus, we have relied on TEM and dynamic light scattering DLS for these measurements. DLS is possible when the light absorbance is small enough to allow detection of the relaxation of concentration fluctuations due to cluster diffusion. Often, for small clusters the contribution of the micelles to the light scattering does not allow direct size determination by this rapid, in situ method. If static light scattering is possible, however, the intensity/unit concentration of metal is directly proportional to the cluster mass, and relative cluster masses can be quickly determined. These measurements yield the weight average mass, M_w, and thus are particularly sensitive to the cluster size polydispersity. Thus relative sizes can be easily obtained if the particle sizes are small enough that light extinction is not a problem. Table I summarizes some results of Fe nanocluster formation in inverse micelle systems.

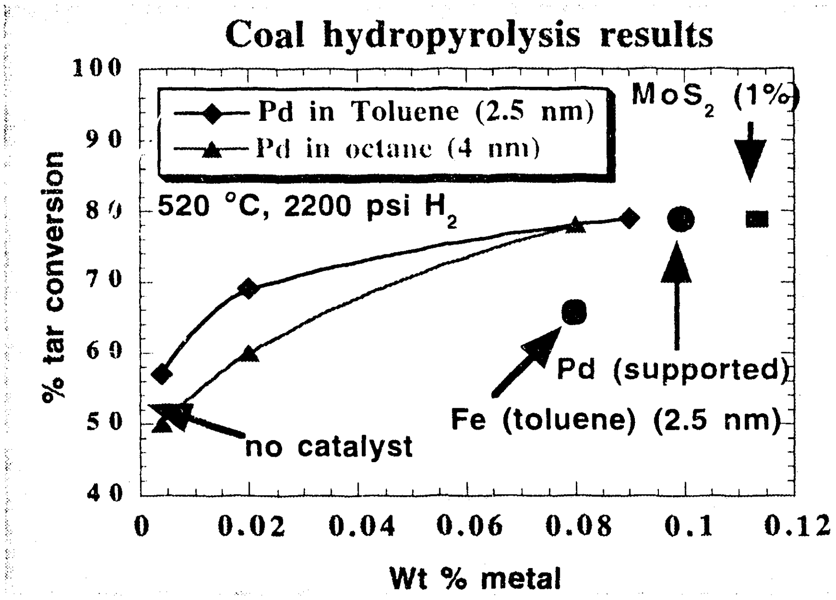

Figure 4. Results of coal hydropyrolysis testing of palladium and iron nanoclusters.

The formation of Fe colloids is of singular importance from an economic standpoint. The materials costs would be low enough to obviate the need for recovery after use in a catalytic process such as direct coal liquefaction. However, nanosize iron clusters are extremely reactive and oxygen sensitive so transfers to coal powders for catalyst testing were affected, where feasible, under anaerobic conditions. The encouraging results of such tests were indicated in figure 4, where we noted that no previous Fe catalysts tested had shown any activity above baseline.[6]

When Fe(III) is reduced using $NaBH_4$ in aqueous solution which has been purged of O_2, XRD shows that the expected bcc α-Fe phase results. In many cases, this same equilibrium phase is obtained by the analogous reduction in an inverse micelle. However, we have observed at least one system in which 6-8 nm size iron clusters showed electron diffraction which was consistent with the high temperature γ-Fe phase which has the fcc structure. This result was quite surprising but may indicate that during the cluster growth process, the presence of the surfactant on selected sites of the growing cluster may induce unexpected structural changes in the cluster. All metal borides have complex orthorhombic or tetragonal structures whose symmetry yields vastly different electron diffraction compared to simple fcc structures. Thus, our identification is unambiguous and no metal borides ever form in water-free inverse micelles. If this process can be better understood and controlled, this would allow control of both size and phase in selected nanocluster systems. To date we have not systematically investigated the effect of Fe nanocluster structure on catalytic activity. Such studies are planned for the future.

Formation and Catalytic Activity of Iron Sulfide: Colloidal FeS_x (x=1-2) was formed by addition of an aqueous solution of either Na_2S or Li_2S (1.0 M stock), to a previously formed Fe(II) salt encapsulated in an inverse micelle system. Two equivalents of S^{-2} were required for complete reaction suggesting colloidal FeS_2 was formed. The green to yellow colored solutions had optical spectra as shown in figure 6 consistent with that of a semiconductor but the band-gap was shifted significantly from the bulk value (~1 eV or 1240 nm). By comparison, bulk pyrite (FeS_2) has black color since it absorbs throughout the visible regime. SAD from 10 nm FeS_x

clusters formed in an inverse micelle system allowed identification of 14 diffraction rings which were unambiguously assigned to the cubic pyrite structure, confirming its structure. The band-gaps shifts we observed as similar to those we have reported[6,7] in colloidal CdS, and MoS_2. We note that, although we plan on using iron sulfide for coal liquefaction, this semiconductor in colloidal form has been proposed for many solar-based photocatalysis applications.[9] Our colloids are quite unique, however, because of their remarkably small sizes and huge surface areas as shown in the TEM of figure 7. Unfortunately, due the small number of atoms in each cluster of figure 7, SAD give only two or three broad rings and we can only say the structure is consistent with that obtained from larger FeS_2 clusters.

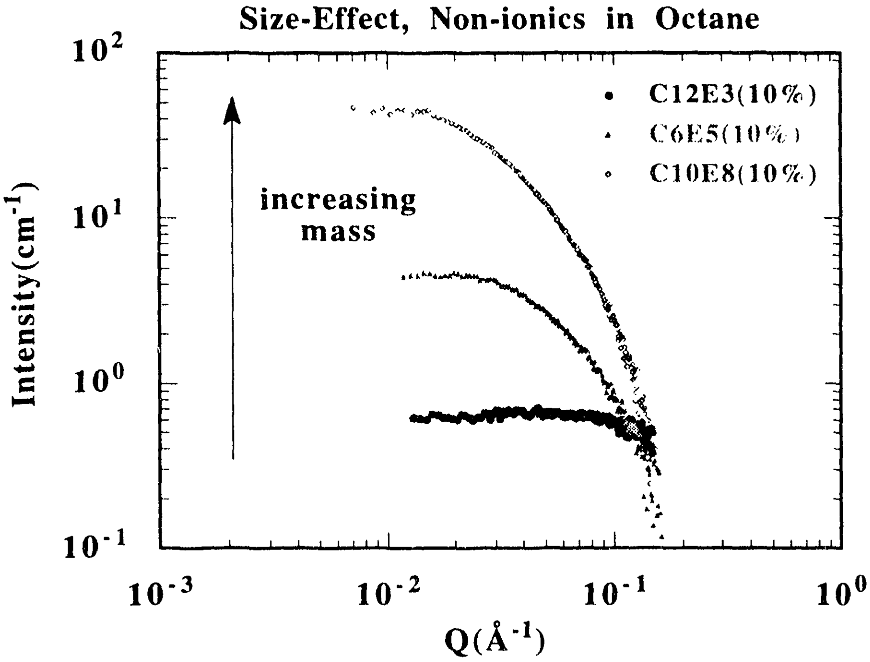

Figure 5. SANS intensity vs momentum transfer Q for three non-ionic surfactant inverse micelle systems.

Table I. Selected Fe Colloids and their Sizes.

sample	Surfactant	Oil	Salt	Reducing Agent	size[1] (nm)
Fe #6	$C_{12}E_5$	octane	$FeCl_3$	N_2H_4	20
Fe #7	$C_{12}E_8$	octane	$FeCl_3$	N_2H_4	25
Fe #8	DDAB	toluene	$Fe(ClO_4)_2$	$LiAlH_4$	2.9
Fe #10	DDAB	toluene	$FeCl_3$	$NaBH_4$	1.4
Fe #12	C12E4	octane	$FeCl_3$	$NaBH_4$	2.4
Fe #13	C12E6	octane	$FeCl_3$	$NaBH_4$	3.4
Fe #14	C12E8	octane	$FeCl_3$	NaBH4	4.4
Fe #15	C12E8	hexdecane	FeCl3	$NaBH_4$	6.4

[1] number average from TEM

The sample shown in figure 7 was converted into a powder under anaerobic conditions and then dispersed onto a coal powder. Since coal differs considerably from one source to another we used a standard type selected by the Department of Energy called DECS-17, from Blind Canyon.

The hydrogen in the hydrogenolysis process is provided by a hydrogen donor solvent, 9,10 decahydropyrene, which is consumed during the process. As in direct coal hydropyrolysis, the catalyst is inevitably lost during the breakdown of the coal and thus an inexpensive, disposable material is required. This effectively limits the choices to iron, iron oxides, or iron sulfides. The success of the reaction can be essentially gauged by the one-step conversion of the coal into useful, low molecular weight hydrocarbon products. To be effective, a catalyst must successfully break carbon-carbon bonds (hydrogenolysis) as well as performing hydrogenation on unsaturated entities in the coal macromolecule.

In the absence of any catalyst, at 400 ^{o}C and 800 psi pressure about 30% of the coal is converted into heptane soluable sols. These are the low molecular weight hydrocarbon products desired. When commercial FeS_2 powder is used as a catalyst, (Aldrich), no increase in yield is found. However, use of the nanoclusters shown in figure 7 increased the yield of heptane soluable sols to 45%. This increase of 50% for the desired products is accompanied by a decrease in the yield of undesirable THF soluable products, which illustrates these nanoclusters can provide some reaction selectivity. Although these results are preliminary and the process requires further research to increase yield, the ability to use nanocluster materials such as FeS_2, which are non-catalytic in bulk form, may allow coal liquefaction to become an economically viable process in the future.

Photocatalysis Applications: For a number of years researchers have been interested in the use of semiconductor materials to perform photocatalytic reactions such as splitting of water into hydrogen and oxygen as well as in solar detoxification (the removal of organic contaminants from water).[10] Such a process, if sufficiently efficient, would provide new forms of environmentally benign fuels. The requirement for such a process includes, high quantum efficiency for generation of hole-electron pairs under solar illumination, low rate of recombination of these pairs once formed, and a high efficiency for transfer of the electrons and holes to the chemical reactants. The most commonly used material, TiO_2, has too wide a band-gap (~3.1 eV, ~400 nm absorbance onset), to efficiently generate hole-electron pairs using sunlight. Also, the powders typically available are large in size which increases the rate of recombination compared to the probability for trapping at defect sites on the cluster surface. The latter probability is obviously increased considerably when the total number of surface sites is large (e.g. for nanosize powders).

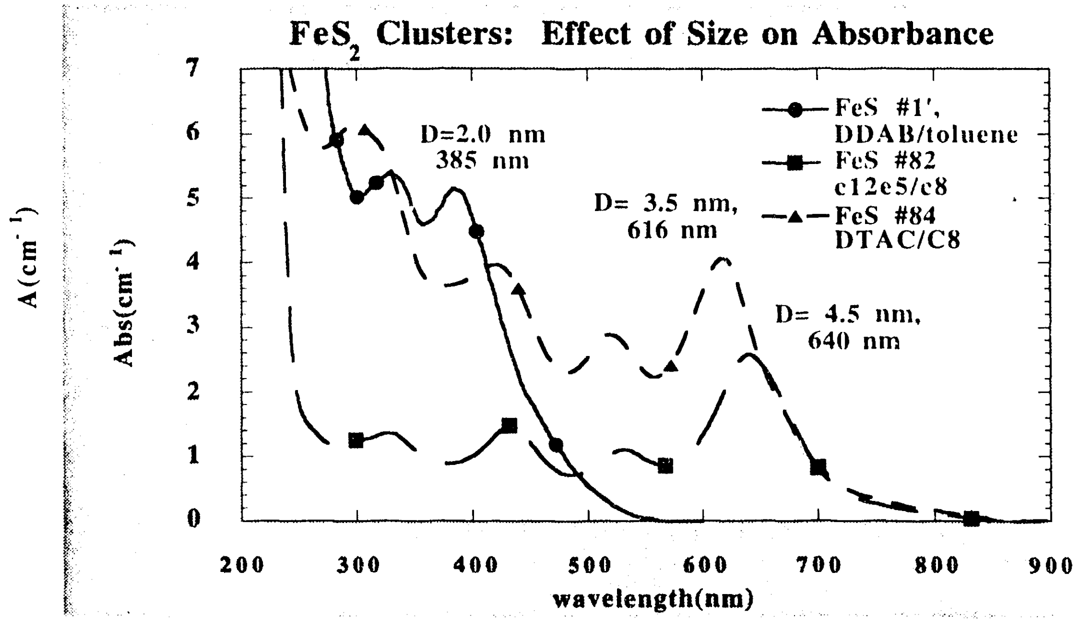

Figure 6. UV-Visible spectra of colloidal FeS_2 shows a size-dependent absorbance edge and discrete exciton transitions due to the narrow cluster size distribution and small size.

The ability to synthesize new types of nanosize semiconductors such as FeS_2 and MoS_2 can increase the efficiency of photocatalysis since these materials in the bulk are IR semiconductors whose band-gap shifts to the visible region when made in nanosize form. At the same time, their small size reduces light scattering which interferes with the generation of exciton pairs throughout the entire dispersion. As can be observed from figure 6, 3.5-4.5 nm sized FeS_2 has nearly the ideal absorbance characteristics to match the solar spectrum. However, the extreme sensitivity to oxidation of this nanocluster material means that only certain chemical reactions may be viable. A possible example is the splitting of H_2S into hydrogen and elemental sulfur. In such a reaction the presence of reactants S^{-2} and HS^- may trap holes and prevent oxidation of the material.[11] Using our synthesis method is may also be possible to selectively coat these nanoclusters with metals such as platinum to reduce oxidation and increase reduction efficiency.

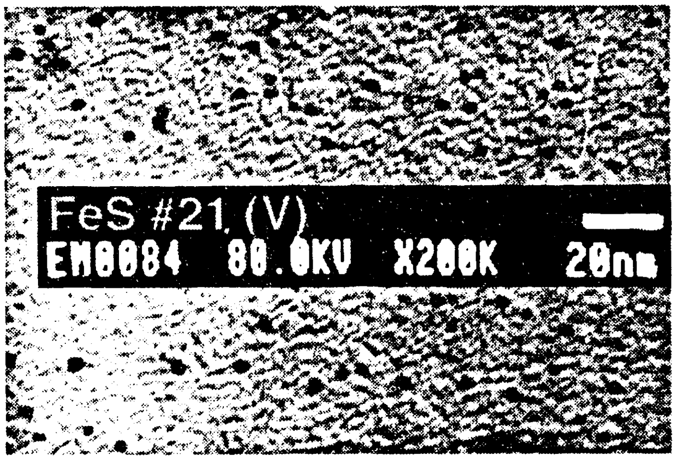

Figure 7. TEM of colloidal iron sulfide

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