

Title: FORMATION AND CHARACTERIZATION OF HIGHLY DISPERSED METAL COLLOID CATALYSTS

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Objective: The objective of this research is to explore the feasibility of using small metal colloids, in microemulsions, as catalysts. The product of this work will be a new concept for tailoring highly dispersed materials to specific catalytic reactions. The knowledge gained from the proposed research will be broadly applicable to variety of reactions, including hydrogenation, synthesis gas conversion, and hydrogen conversion. To achieve this objective, a plan has been formulated to prepare and characterize catalyst particles in organic solvents and to explore the use of catalyst particles.

INTRODUCTION

The development of new or improved catalysts is predicated on the design of new catalytic materials. While most of the materials research in catalyst synthesis has concentrated in recent years on microporous crystalline aluminosilicates (zeolites), it is clear that other materials (elements and compounds) could also be produced in high surface area forms. The development of new synthetic methodologies for catalytic materials and major efforts of characterizing the kinetics of their formation, their thermodynamic properties, structure, and bonding should lead to improved understanding of catalytic materials and to the discovery of new materials. In addition, improved activity of new catalytic materials for coal liquefaction and selectivity in cleaving certain C-C bonds in model compounds may be achieved in highly dispersed systems.

A microemulsion system may be thought of as a small (~100 Angstroms) micellar reaction vessel in which various chemical reactions (e.g., reduction of a metal) may take place. The surfactants composing the micelles fall into three general families: nonionic surfactants of the type $\text{CH}_3(\text{CH}_2)_{i-1}(\text{OCH}_2\text{CH}_2)_j\text{OH}$ (hereafter abbreviated C_iE_j , or the industrial appellation Brij), anionic surfactants, (e.g. sodium-bis(2-ethylhexyl)sulfosuccinate (common name Aerosol-OT, AOT), and cationic surfactants (e.g. didodecyldimethylammonium bromide, DDAB). Early in this project we prepared small highly-dispersed metallic gold, platinum, iridium, palladium, and mixed gold/platinum colloids¹ by introducing the appropriate aqueous salt solution into an oil continuous inverse micelle system consisting of nonionic surfactants in a continuous hydrocarbon phase. More recently, we have prepared iron, iron sulfide, nickel, molybdenum sulfide, and rhodium colloids from cationic-based microemulsions. In these microemulsion systems, the salt compounds go to the interior of the transparent micellar solutions and swell the micelles. The ability of the surfactants to solubilize large amounts of water containing the metallic salt, in the form of 4-10 nm spherical droplets, has allowed us to reduce the metal salts to highly-dispersed metal colloids using either chemical reduction, thermal decomposition or photochemical decomposition. By controlling the solution microstructure, the kinetics of metal reduction and the concentration of metal ions in the micelle, we can control the size and shape of the colloids over a wide range. The nanometer-sized metal colloids represent a totally new class of materials since they are composed of 100 - 1000 atom clusters. Such materials

while having the potential for a variety of valuable applications² also are in the size-regime of certain model compounds and the three-dimensional structure of bituminous coal. In this paper, we will discuss the use of inverse micelles to solubilize significant quantities of metal compounds in hydrocarbon solvents and their reduction, decomposition, and sulfidation to give colloidal catalytic materials. We will also discuss in detail the characterization of these materials, present preliminary results for the catalytic hydroxyprolysis of coals, and discuss the results of our evaluation of selected metal colloids in catalytic hydrogenation of pyrene.

EXPERIMENTAL PROCEDURES

General

All manipulations involving the use of air/moisture-sensitive reagents such as lithium borohydride (LiBH_4) in organic solvents were performed in septum-sealed glass vials (typical volume 25 mL). Undried reagent grade solvents such as tetrahydrofuran and toluene were used. These solvents were filtered through a 0.2μ filter prior to use. Chemical reduction techniques were performed using modified Schlenk-line techniques. For thermal decomposition of metal compounds in micelles, the micellar solutions were immersed in an oil bath maintained slightly above the decomposition temperature³ of the respective metal compound. The decomposition process was monitored until no further optical changes and particle size growth could be observed. Photochemical decomposition reactions were performed at ambient by irradiating the micellar salt solutions for short times (~ 1 min.) with a 350 nm pulsed laser light source (Argon Ion CW laser, 1/2 W power). The photochemical reaction process was similarly monitored by UV-visible and light scattering techniques.

Preparation of Metal Colloids

The preparation of iron metal colloids using the DDAB/toluene system inverse micelle will be described. Similar preparative procedures were used for other metal colloids. Initially, a 5-10% wt% solution of DDAB was prepared in toluene. Static and dynamic light scattering (DLS), or small angle neutron scattering (SANS) can be used to demonstrate that this system produces the smallest micelles of all the available surfactant types. Transmission electron microscopy (TEM) confirms that nanometer-sized colloids are produced from these micelles. The surfactant concentrations are chosen to be above the critical micelle concentration (CMC). A CMC is defined as the concentration at which micelles first form. The iron-containing salt, FeCl_3 , was added directly with stirring at ambient for the desired metal concentration. In this project, we have typically varied the concentration between 1×10^{-5} and 0.05 M. The sample was then purged for several minutes with argon. Several methods of reduction are applicable, the optimal type depending on the particular metal and solvent/surfactant system chosen. In the case of iron, either solid NaBH_4 or LiBH_4 reducing agents were used. Aqueous-based NaBH_4 or organic-based LiBH_4 may also be used. The latter reducing agent gave faster reactions and smaller final colloid size because of the increased solubility in the oil-continuous phase.

Preparation of Metal Sulfide Colloids

Most metal sulfides are prepared by the reaction of a previously formed metal salt in an inverse micelle system with either aqueous Na_2S or Li_2S . Thus when $\text{Fe}(\text{ClO}_4)_2$ in the C_{12}E_5 micelle system was reacted with 1.0 M Li_2S , colloidal FeS_x ($x = 1-2$) was obtained. Only nonionic surfactants were used because of the necessity to solubilize significant amounts of water during the process. Two equivalents of S^{2-} were required for complete reaction indicating that colloidal FeS_2 was likely formed.

Catalytic Hydrogenation of Pyrene

Batch reactions were performed in stainless steel microreactors⁴, equipped with thermocouples and pressure transducers. Pyrene and n-hexadecane, an inert solvent for pyrene, were used as received from Aldrich Chemical Co. For hydrogenations involving precious metal-containing catalysts sulfur-free pyrene was used. The reactors were charged with 1000 mg of hexadecane, 100 mg of pyrene, and 500 mg of catalyst solution. Based on the concentration of metal salts in the inverse micelle and assuming 100% reaction to colloid, the amount of metal colloid in 500 mg of catalyst solution is typically less than 1 mg. After the reactors were charged with the reactants and catalyst, they were pressurized with hydrogen and heated to temperature (100°C) (heat-up time ~ 1 min.) in a fluidized sand bath while being shaken horizontally at 160 cycles/min. Temperature and pressure were recorded with a digital data acquisition system during the course of the experiment. Following the heating period, the reactor vessels were quenched (quench time ~ 10 sec.) to ambient temperature, and the products were removed. The products were washed from the reactor with toluene, filtered to remove the catalyst and transferred to a volumetric flask. Following the addition of an internal standard (2-methyl naphthalene), the product solution was brought to 50 mL and analyzed by capillary GC. An external standard consisting of a solution of the internal standard, pyrene, n-hexadecane and 1,2,3,6,7,8-hexahydropyrene was used to establish FID response factors relative to the internal standards. The weights of each component of the product mixture were calculated from the chromatograph area. Previous work here⁵ has shown that at low hydrogen pressures (100 psi) and temperature (100°C) various catalysts obey zero-order kinetics for the hydrogenation of pyrene. Thus, assuming zero-order kinetics, rate constants (g product/gram catalyst-sec) for each catalyst studied were calculated. It should be mentioned that the weight of catalyst used in these calculations is based on the above discussed assumptions.

Catalytic Hydrolysis of Coal

The palladium colloids used for catalytic hydrolysis testing were prepared as described above in toluene and octane. Those colloids dispersed in octane used the nonionic surfactant, C₁₂E₅, while another colloid sample included the anionic surfactant AOT. All palladium colloids prepared in toluene had DDAB as the surfactant. Ground (-100 mesh) Herrin Burning Star No. 2, a U.S. bituminous coal, was wetted with the colloidal palladium in the desired concentrations and vacuum dried at 90-110°C prior to testing. The weight of the coal prior to wetting with the solution and after vacuum drying was compared to ensure that the solvent and surfactant was satisfactorily minimized. Solvent swelling studies were performed on the Herrin Burning Star coal with toluene and octane to determine if pore structure changes occurred.

Fixed-bed Hydrolysis Test Procedure

Fixed-bed hydrolysis tests were conducted in an apparatus similar to that described by Snape, et al⁶. A temperature of 520°C and a pressure of 150 bar of hydrogen was chosen. These operating conditions were shown previously in tests on a U.K. bituminous coal to maximize tar yield with sulfided Mo catalyst⁷. Approximately five grams of 65°C vacuum dried coal was mixed with 10g of sand in a reactor tube, which was resistively heated at 5°C/sec. Gas from the reactor was analyzed for C₁-C₄ hydrocarbons, CO, and CO₂. After each experiment, char and ash remaining in the reactor tube were removed and weighed. The daf coal basis yield of tar for each experiment was calculated as the weight of material recovered in the system cold trap less the weight of water produced, divided by the initial daf coal weight.

RESULTS AND DISCUSSION

Inverse micelles are distinguished from inverse microemulsions by the absence of water in the former system. Both systems consist of surfactant aggregates (micelles) with the hydrophobic tail groups facing an oil-continuous (organic solvent) medium. For the preparation of inverse micelles, a solution consisting of the surfactant in an organic solvent is first made. Typical concentrations of surfactant are 0.05 M to 0.2 M. The exact choice of surfactant will depend on a number of factors, among them, the type of organic solvent being used, the desired metal particle size and the required concentration of metal salt in the inverse micelle. Metal salt concentrations up to 0.05 M may be obtained while retaining homogeneous and transparent solutions when the appropriate choice of surfactant is made. From numerous experiments, we have determined that the surfactants achieve size control primarily through intermicellar interactions, i.e., their phase behavior. An observed disadvantage, therefore, of nonionic surfactants is that colloids formed in a given solvent (e.g. octane) cannot be diluted into a different solvent without aggregation. For use as dispersed catalysts, this aggregation is undesirable since it reduces the available catalyst surface area. Thus, we looked for a surfactant system whose stabilization properties were superior. Since stabilization of colloids occurs through steric and/or electronic repulsions between colloidal surfaces, we selected a charged surfactant with two long chain hydrocarbon hydrophobic groups. This cationic surfactant, DDAB, formed stable clear inverse micelles in toluene. While DDAB is only sparingly soluble in saturated hydrocarbons, it shares with the nonionic family of surfactants the ability to directly solubilize large amounts (0.01 M to 0.05 M, depending on the salt type) of metal salts. Once the phase behavior of for a given metal salt/surfactant/solvent system is understood, the growth and size properties of of the final colloid are highly reproducible and predictable.

Control of Colloid Size via the Reducing Agent

The growth of metal colloids in inverse micelles or microemulsions is achieved by either chemical reduction, thermal decomposition, photochemical decomposition or sulfidation of the metal compounds. Initial studies¹ using chemical reducing agents utilized aqueous solutions and pure hydrazine and sodium borohydride stabilized in water by NaOH. Approximately stoichiometric amounts of reducing agent were used to reduce the metal salts to elemental metal. Rapid stirring was required during the addition of reducing agent. It was determined that the small size of the DDAB inverse micelles could not allow adequate solubilization of the reducing agent leading to much slower reduction reactions than had been observed in the corresponding nonionic micelle system. To improve this reaction rate and decrease the resultant particle size, four types of reducing agents were tested, LiBH_4 (solid), NaBH_4 (solid), KH(oil slurry), and LiAlH_4 (solid). In each case the, the reaction used no water with the reducing agent. It was found that NaBH_4 decreased the final size of Pd colloids to ~ 2.5 nm and increased the reduction rate considerably. LiBH_4 was even better, reducing the size to 1.4-1.6 nm, with no larger particles observed. We attribute at least some of this size reduction to improved solubilization of the reducing agent in the micelles. This increases the initial nucleation rate, the number of small, critically sized nuclei, and the final colloid size. Both KH and LiAlH_4 produced extremely slow reactions and thus were deemed unsatisfactory. This cannot be explained by their poor reducing strength (KH is a very strong reducing agent) but rather their failure to mix into the micelles effectively. To increase the solubilization of the reducing agents, commercially available lithium and sodium-based boro- and aluminum hydrides in tetrahydrofuran or triglyme (triethylene glycol dimethyl ether) were used. These organic solvent-based reducing agents gave small metal colloids in a much shorter time. For example, using solid LiBH_4 , the reduction process required times in excess of an hour while with LiBH_4 in THF only ca. 30 seconds was required. Thus using the latter reducing agent considerably reduced the time required to form metal particles. We have used principally 2.0M lithium borohydride in tetrahydrofuran to reduce the metal salts in the

micellar solutions. However, in one reaction (Pd#22, Table 1), 2.0M sodium borohydride in triglyme was also used. Consistent with our expectations, we have been able to produce small (1.4-1.8 nm) Pd particles using LiBH_4 . Table 1 shows that, in general, we have not been able to obtain comparable small particles in the anionic surfactants AOT and the nonionic surfactant Brij30.

Formation of FeS Particles

FeS particles were prepared by the addition of aqueous solutions of either lithium sulfide or sodium sulfide to a nonionic inverse micelle system [$\text{C}_{12}\text{E}_5(10\%)/\text{octane}/\text{Fe}(\text{ClO}_4)_2$]. The use of a nonionic surfactant was required because of the aqueous-based sulfiding reagent (Li_2S). Similar to experiments where separate inverse micelles of the salt and sulfiding agent were reacted, 3.2 nm green colloidal particles were obtained. The exact crystal structure and chemical composition of this colloid is presently unknown but we are attempting to analyze them by analytical TEM. We have performed UV-vis spectroscopy on the FeS colloids and its salt precursor, i.e. the unsulfided micelle. The optical spectra of the colloid was vastly different from the precursor and exhibited electronic absorption bands at 430, 530 and 630 nm⁸. Unlike bulk FeS which is a black unreactive opaque solid, these green colored suspensions were quite oxygen sensitive and could be reverted (by observation of a color change) to their original oxidation state if exposed for short time periods to air. This high chemical reactivity suggests that there an extremely large percentage of atoms with coordinative unsaturation at the surface sites in these small metal particles which could lead to high catalytic activity. DLS measurements have established that FeS can be diluted by other solvents with the retention of the particle size provided that stabilizers such as cyclohexyl mercaptan or adamantane mercaptan are present. Interestingly, DDAB was found to be just as effective in stabilizing the colloids as the mercaptans.

Formation of MoS₂ Particles

We have used a surfactant/acetonitrile system to thermally decompose molybdenum oxalate in the presence of sodium sulfide and hydrazine. In addition to DDAB (1%) and tridodecylmethylammonium chloride (TDAC, 10%), ethylhexylammonium bromide (10%) surfactants were used to prepare MoS₂ colloids. Instead of being opaque, clear solutions of these 1 - 3 nm colloids vary in color from blue to light yellow. Correspondingly, the optical spectra of these colloids were found to be blue shifted indicating an increase in the bandgap from that normally observed in bulk MoS₂.

Effect of Precursor Salt Type

A variety of metal salts (precursor salts) were looked at in our study. In the Pd system, we investigated three precursor salt types, PdSO_4 , PdCl_2 , and Na_2PdCl_4 . In the Rh system, two salt types were investigated, RhCl_3 and Na_2RhCl_6 . While in the case of iron, we examined FeCl_3 , FeCl_2 , and FeBr_3 . For Pd, we found from TEM and DLS analysis that the number average size of colloids formed, using NaBH_4 as the reducing agent, increased slightly in the order $\text{PdSO}_4 < \text{PdCl}_2 < \text{Na}_2\text{PdCl}_4$. The biggest difference was that the inverse micelle system with the PdSO_4 precursor was monodispersed, but the other two systems showed increased amounts of polydispersity, with some significantly large particles (>50 nm) observed. Thus, the effective surface area per gram of starting material was less with these systems. In the Rh system very similar results were obtained for both starting complexes, the number average size being 2-5 nm, with no particles larger than 20 nm observed in either case. We note for comparison that Rh colloids produced in the nonionic system, $\text{C}_{12}\text{E}_5/\text{octane}$, were fairly monodispersed but about 20-25 nm in size. Finally, in the iron system the smallest colloids were obtained from FeCl_3 , with both FeCl_2 and FeBr_3 being both larger in average size and more polydispersed. Similar to the size and

stability already achieved in the Pd, Ni, NiB, and Rh systems in DDAB/toluene, the iron system has also been optimized to obtain the desired 3-5 nm colloids.

Control of Size via Metal Precursor Salt/Surfactant Ratio

We performed two experimental series in the Pd system using the precursor salt PdCl₂ and NaBH₄ as the reducing agent to test the effect of different initial salt concentration on the final colloid size. In similar experiments with nonionic surfactants we found that addition of large amounts of salt altered the intermicellar attractive interactions, often producing unfavorable final size distributions in the resulting colloid populations at high (e.g. > 0.01 M) salt concentrations. Both salt and temperature have a much less profound effects on cationic micelle systems, so we expected that these nascent phase separation effects could be obviated in the DDAB systems. In the first experimental series we confirmed this expectation and we actually found larger sized, more polydisperse Pd colloids at low salt concentrations than at high ones. In the second series we held the precursor salt concentration constant while varying the surfactant concentration between 1 and 10 wt%. We discovered that the relevant variable controlling the mean size was the metal to surfactant ratio. Colloid sizes between 2 nm and 20 nm were produced, but improvements in size distribution control at the high end (low salt concentration) are still needed. This method looks encouraging for future attempts to control final catalyst particle size. One goal for this work is to provide a means to systematically investigate the effect of particle size on catalyst activity.

Use of Phase Behavior to Extract Ion Byproducts and Excess Surfactant

When the Pd metal precursor salt is reduced, the ionic byproducts, being insoluble in the organic phase, remain in the micelle interior. In the case of DDAB, some of this bulk surfactant which contains the ionic species can be precipitated out of solution by addition of a non-solvent for the surfactant, (e.g. hexadecane) or a highly polar solvent such as water. With water a three phase emulsion system is formed with the hydrophobic Pd colloids remaining in the upper toluene phase. The middle phase contains a mixture of surfactant, oil, and water, while the bottom is a water phase with the excess surfactant and ionic byproducts. The upper phase which contains the purified Pd colloid can be removed, dried and used as a dispersed catalyst. Potentially, the surfactant could also be recycled by recrystallization. TEM measurements indicate that the colloids retain their small initial size during this extraction process. We have found it extremely difficult to precipitate these colloids from solution, so it appears the DDAB is strongly bound to the surface.

Characterization of Colloids

The characterization of colloids prepared in the inverse micelle system has turned out to be a rather challenging task. This is especially true for colloids in the 1-2 nm size range. While in-situ measurements such as DLS and SANS have provided valuable information concerning the size, shape, and size distribution, ex-situ techniques such as x-ray diffraction and high resolution TEM have provided limited data. This is not unexpected considering that particles in this size regime and preparative conditions (presence of surfactants) may be approaching the limits of these techniques. For these reasons, we have relied mainly on static and dynamic light scattering for size information in the prepared materials. TEM measurements have been used to confirm the values of colloid size obtained from the light scattering studies. Table 1 provides a summary of selected colloid preparations together with some of their properties. Concentrating on the iron samples in Table 1, it can be seen that iron colloids mostly in the 1.4-20 nm range were obtained from both cationic and nonionic surfactants. Values for molecular weights were derived from the intensity data of the respective light scattering experiments. The cluster size for the Fe colloids in this size range appears to be 26 to ~3460 Fe atoms. In view of the known high chemical reactivity of finely divided iron, it is not surprising that these colloidal solutions,

containing much smaller iron, exhibited high reactivity. Typically, solutions formed with colloidal size greater than ~2.5 nm were black in color and are opaque to visible light. However, when prepared in an inverse micelle system with an extremely strongly bound surfactant (e.g. DDAB), these initially yellow solutions turn completely clear. As Table 1 illustrates, both the type of metal salt used and the type of reducing agent influences the final colloid size. However, the largest effect occurs on changing surfactant from cationic to nonionic (e.g. compare Fe#10 with Fe#6). Attempts to characterize the Fe colloids from inverse micelles by x-ray techniques have been unsuccessful. However, bulk powder diffraction on powders formed from larger colloids indicate crystallinity but the crystal structure cannot be indexed directly to bulk Fe, Fe₂O₃ or FeB structure. Initial electron diffraction studies on Fe colloids prepared without the use of surfactants, have suggested γ -Fe as the main phase in these >200 nm particles. Further studies concerning the type of metal present in the colloids are required. We have also attempted to characterize the our colloids using traditional UV-vis spectroscopic techniques. We have observed that depending on the metal colloid and its size, absorption bands are observed in the visible region of the spectrum. The wavelength of maximum absorbance (λ_{max}), where observed, is shown in Table 1. The origin of these bands is not understood presently. However, if these spectral features are related to colloid size, we have an alternative method for characterizing the colloids.

Table 1. Colloid Preparations and Properties

Sample	Surfactant	Oil	Salt	Reducing Agent	λ_{max} (nm)	Size ¹ (nm)	M.W. ² (a.u.)
Pd#21	DDAB(6%)	toluene	PdSO ₄	LiBH ₄ /THF	347	1.4 ³	4,560
Pd#22	DDAB(6%)	toluene	PdSO ₄	NaBH ₄ /TRIG	346	13 ³	26,900
Pd#35	DDAB(10%)	toluene	Pd(NO ₃) ₂	LiAlH ₄ /THF	350	1.5 ¹	8,000
Pd#39	AOT(10%)	toluene	Pd(NO ₃) ₂	LiBH ₄ /THF	none	25	80,000
Pd#41	AOT(10%)	octane	Pd(NO ₃) ₂	LiBH ₄ /THF	none	12	20,000
Pd#24	AOT(10%)	toluene	Pd(NO ₃) ₂	LiBH ₄ /THF	none	>30	106,000
Pd#34	Brij30(10%)	decane	Pd(NO ₃) ₂	LiBH ₄ /THF	none	1.2 ¹	14,000
Fe#6	C ₁₂ E ₅	octane	FeCl ₃	N ₂ H ₄	n.m.	20	194000
Fe#19	C ₁₂ E ₅ (10%)	octane	Fe(ClO ₄) ₂	LiBH ₄ /THF	n.m.	2.1	
FeS #21	C ₁₂ E ₅ (10%)	octane	Fe(ClO ₄) ₂	Li ₂ S/H ₂ O	n.a.	3.2	
Fe#8	DDAB(10%)	toluene	Fe(ClO ₄) ₂	LiAlH ₄	n.m.	2.9	11,900
Fe#10	DDAB(10%)	toluene	FeCl ₃ (0.01M)	LiBH ₄	clear	1.4	
Fe#27	DDAB(10%)	toluene	FeCl ₃ (0.01M)	LiBH ₄ /THF	n.m.	2.4	1,940
Fe#28	DDAB(1%)	toluene	FeCl ₃ (0.001)	NaBH ₄ /H ₂ O	n.m.	1.4	1,490
Co#5	DDAB(10%)	toluene	CoCl ₂ (0.01M)	LiBH ₄ /THF	700	4.6	10,300
MoO ₂ #9	C ₁₂ E ₅ (10%)	octane	MoO ₂ Br ₂	N ₂ H ₄	none	9.5	
MoO ₂ #13	DDAB(10%)	toluene	MoO ₂ Br ₂	LiBH ₄ /THF	none	2.0	7,750
MoS ₂ #3	DDAB(10%)	toluene	MoO ₂ Br ₂	decomp.	n.m.	3.4	
Rh#9	DDAB(10%)	toluene	RhCl ₃	LiBH ₄ /THF	n.m.	2.6	
Rh#15	DDAB(10%)	toluene	RhCl ₃	LiBH ₄ /THF	n.m.	1.6	24,300
Sn#14	DDAB(10%)	toluene	SnBr ₂ (0.01M)	LiBH ₄ /THF	n.m.	6.5	

¹number average from TEM

²relative weight average molecular weight from light scattering

³estimated size based on light scattering, TEM results not yet analyzed

Hydropyrolysis of Coal

Preliminary results with the Herrin Burning Star coal indicate that this coal can be satisfactorily tested in a fixed-bed hydropyrolysis reactor. Its free-swelling-index is less than 2, thereby avoiding problems with coal swelling in the reactor tube. The coal, an Illinois

bituminous coal, also shows large differences in conversion and tar yield between catalyzed and uncatalyzed hydrolysis. Pd colloid catalysts were tested because their small nm size suggested the potential for uniform dispersion and also high activity at low concentrations.

A summary of results performed on the Herrin Burning Star coal and incorporating both the metal hydrous titanium oxide and highly dispersed catalysts is provided in Table 2. The molybdenum disulfide catalyst, run as a baseline to compare the results from the other catalysts, performs well as expected at a concentration of 1% by weight of active metal. The Pd metal colloids were prepared in toluene and octane. It was found that toluene swells the coal slightly (swelling ratio of 1.1 relative to original coal) while the octane did not measurably swell the coal. Tests on control samples of the Herrin Burning Star coal that were wetted with the toluene or octane solvents showed no significant difference in yield relative to the untreated coal. The Pd particles formed in the octane solution were 1.2 nm in size while those in toluene ranged in size from 1.9 to 12 nm. Control samples of Herrin Burning Star treated with the two solvents and the surfactant achieved yields similar to the coal with no pretreatment, indicating that the solvent and surfactant did not affect the hydrolysis process. The results in Table 2 show that the colloidal Pd catalysts do significantly increase conversion and tar yield, even at concentrations less than 0.1% (by weight of Pd). There appears to be no difference between using the toluene and octane solvents; solvents that significantly swell the coal structure might enhance the metal colloid dispersion. Additionally, comparable results are obtained with the nanometer-sized Pd colloids and the Pd-HTO catalysts.

Table 2. Summary of Catalytic Hydrolysis Results on Herrin Burning Star Coal No. 2

<u>Treatment</u>	<u>Nominal Active Metal Concentration (%)</u>	<u>Conversion (%)</u>	<u>Tar Yield (%)</u>	<u>C1-C4 Gases (%)</u>
Initial Herrin Burning Star Coal	None	55.1	38.3	11.2
MoS ₂	1	80.4	64.1	11.1
Pd-HTO	0.09	80.5	65.1	11.7
Pd-HTO	0.07	78.1	62.6	12.6
Pd-HTO	0.02	79.0	66.3	11.8
Pd-HTO	0.01	76.5	59.3	11.1
Pd-HTO	0.005	71.8	56.0	13.2
Toluene	None	52.0	38.1	8.5
Octane	None	55.2	43.7	8.9
Pd colloids in toluene	0.09	78.9	63.0	10.4
Pd colloids in toluene	0.02	68.6	51.2	9.3
Pd colloids in toluene	0.004	57.0	43.2	13.8a
Pd colloids in octane	0.08	77.7	61b	9.4
Pd colloids in octane	0.02	59.6	50.7c	13.6a
Pd colloids in octane	0.004	49.7	36.3	13.6a

aHigher gas yield possibly due to slower heating rate in these 3 runs.

bWater could not be determined accurately.

cTotal liquid yield including water.

Hydrogenation of Pyrene

We are developing a series of reliable tests to evaluate the prepared colloids for catalytic activity and selectivity. Most of our studies to date have involved the evaluation of the metal and metal sulfide colloids as hydrogenation catalysts. As a model reaction, the hydrogenation of pyrene at moderate temperatures and pressures was studied for direct comparison with other successful Sandia and commercial catalysts. Since an essential reaction during coal liquefaction is the cleavage of covalent bonds, we have selected another model reaction, the hydroxylation of 4-(1-Naphthylmethyl)biphenyl⁹ to test the selectivity of our colloids. Because these studies have just recently been initiated, we will not discuss any results here but will review our catalytic hydrogenation of pyrene.

Early experiments with Pd colloids prepared in octane or hexane using the nonionic surfactant C₁₂E₅ were frustrated by agglomeration of the Pd colloids at elevated temperatures. The use of a more strongly binding cationic surfactant, DDAB, in toluene or hexadecane solution eliminated this problem. Additionally, using the latter surfactant/solvent combination permitted the preparation of Pd colloids with smaller average sizes (typically 1.4 to 15 nm). In order to develop an understanding of the effects of colloid size, method of preparation and metal/surfactant composition as well as the effect of removal of excess surfactant, the palladium system was used as a model system. These model studies with Pd guided the development of other catalytically active metals such as Fe, Mo, Co and Ni. Initial results on the hydrogenation of pyrene at 100°C and 100 psi H₂ pressures, showed an increase in relative activity with decreasing particle size. Furthermore, it was observed that the removal of excess surfactant from 5 nm Pd colloids brought about nearly the doubling of the catalytic activity. The latter effect, while not totally unexpected, pointed to the catalyst deactivation by surfactant. Subsequently, we assessed the extent of Pd catalyst deactivation by testing Pd-HTO prepared by others at SNL for pyrene hydrogenation with and without added DDAB. In the presence of DDAB (10% w/w), the Pd HTO catalyst was nearly seven times less active than the same catalyst without DDAB present. A comparison of the Pd HTO activity in the presence of DDAB with dispersed Pd colloid catalyst at the same DDAB concentration (10%) shows that the HTO catalyst is approximately 18 times as active. The smaller Pd particle size in the Pd HTO catalyst likely accounts for the difference in activity. These results strongly suggest that surfactant removal strategies need to be developed for the dispersed catalyst particles in order to improve their activity. Such strategies would involve the displacement of the surfactant molecules in the micelle with "capping" species. Capping reagents such as PdL_x (L = a suitable ligand) could be used in the Pd system. In metal sulfide systems or for those metal colloids where the catalytically active species is a sulfide, sulfur containing compounds such as adamantane mercaptan, cyclohexyl mercaptan or trimethylsilylthiobenzene might be used to cap the formed colloids.

In view of the relative low cost of iron catalysts compared to precious metal catalysts, we have carried out a number of reactions to obtain Fe colloids. From the knowledge gained studying Pd colloids, we were able to use nearly identical solvent/surfactant systems and similar chemistries to obtain 1.4-20 nm Fe colloids as shown in Table 1 above. Although iron or its compounds are known not to have catalytic hydrogenation activity, we wanted to evaluate our nm-sized materials for pyrene hydrogenation activity. This motivation was based on the literature supported indications that metal clusters on the size scale of ~40 atoms have different properties than bulk materials. For the Fe, FeS_x and MoS_x colloids obtained, the catalytic pyrene hydrogenations were carried out using more aggressive reaction conditions of temperature and hydrogen pressure. Most reactions were performed at 300°C and 500 psi H₂ pressure. The results of these studies are given in Table 3. As can be seen, both Fe and FeS_x colloids have rather low activities. It is interesting, however, that the FeS_x samples appear to be more active than the Pd colloid samples. Furthermore, even the FeS_x samples appear to have somewhat greater activity than the Fe colloids. However, in view of the low activities obtained for all these colloids, we will concentrate on

evaluating the catalytic hydropyrolysis reactions of the Fe colloids on the model compound 4-(1-naphthylmethyl)bibenzyl using both "capped" and uncapped colloids.

Table 3. Pyrene Hydrogenation Results with Selected Colloids

<u>Sample</u>	<u>Surfactant</u>	<u>Oil</u>	<u>Salt</u>	<u>Reducing Agent¹</u>	<u>Size (nm)</u>	<u>Activity (g prod./g of cat.-sec)</u>
Pd#20	DDAB	Toluene	PdSO ₄	LiBH ₄	n.a.	2.55x10 ⁻⁵
Pd#20X ⁴	DDAB	Toluene	PdSO ₄	LiBH ₄	n.a.	1.25x10 ⁻⁴
Fe#24	DDAB	Toluene	FeCl ₃	LiBH ₄ /THF	2.5	9.31x10 ⁻⁴
Fe#31	DDAB	Toluene	FeCl ₃	LiBH ₄ /THF	2.4	4.97x10 ⁻³
FeS ² #10	DDAB	Toluene	FeCl ₃	LiBH ₄	1.2 ³	2.64x10 ⁻³
FeS ²	DDAB	Toluene	FeCl ₃	LiBH ₄	1.2 ³	2.49x10 ⁻³
MoS ₂ ²	DDAB	CH ₃ CN	Mo oxal.	Thermal/NaS ₂	n.a.	1.5

1 Solid reducing agent

2 Carbon disulfide sulfiding agent added to reactor prior to hydrogenation

3 Pre-sulfided value

4 Twice extracted with water

CONCLUSIONS

We have demonstrated that chemical or photochemical reduction of various metal compounds in oil-continuous (organic solvent-based) inverse micelles leads to the formation of small, 1 - 100 nm, highly-dispersed colloids. Controlled growth and aggregation of the metal and metal sulfide colloids in inverse micelles results in the formation of nm-sized particles having narrow size distribution. Control of the colloid size was achieved by variation of the surfactant-to-metal-surface binding. The latter effect is important in preventing increases in colloid size through further aggregation of the metal colloids. When selected metal colloids such as molybdenum and iron were subsequently reacted with sulphiding agents, the respective highly dispersed metal sulphide colloids in organic solvents were obtained. Initial results for catalytic hydropyrolysis using these materials, show that even at low concentrations of active metal, high yields of liquid products can be obtained. In addition, since we have shown that nm-sized colloids can be prepared in various organic solvents, increased dispersion processes leading to higher conversions in coal may be possible. While catalytic hydrogenation of pyrene have been less satisfactory, we will concentrate on the evaluation of these materials in the catalytic hydropyrolysis of the model compounds, 4-(1-naphthylmethyl)bibenzyl. Furthermore, with the achievement of nm-sized "capped" colloids, it may be possible to re-evaluate the hydrogenation activities of the various metal colloids.

FUTURE PLANS

There are a large number of potential catalytic applications for highly dispersed metal/metal sulfide colloids. Among these are coal preconversion and solubilization, hydrogenation, hydrogenolysis, hydrodesulfurization and hydrodenitrogenation. After our evaluation of hydrogenolysis and hydrogenation activity, we will proceed with the following program elements: 1) Development of more effective methods of colloid preparation and characterization, 2) Development of reliable tests for the evaluation of hydropyrolysis and hydrogenation activity, 3) Preparation and testing of mixed-metal, metal-on-metal oxides microemulsions (e.g. Ni-Mo, Rh-on-SnO₂), and ultra-dispersed (e.g. very small Rh-on-larger Fe particles), 4) Study of catalyst activation, including presulfidation of metal microemulsions, 5) Use of computer-aided molecular modeling to design micelles for controlled catalytic reactions, 6) Reactions with coal and coal-derived solvents to evaluate

use of microemulsions for the solubilization of coal and 7) Evaluation of the most active catalysts in a flow microreactor system.

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