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Synthesis, Characterization, and Catalytic Hydrogenation Activity of Highly Dispersed Fe, Rh, and Rh/Fe Powders

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The preparation of submicrometer-sized metal particles by chemical reduction of homogeneous solutions of metal salts in the absence of surfactants has been investigated. Reduction of $FeCl_3$ with $LiBEt_3H$ in THF resulted in the formation of solutions containing crystalline, monodispersed Fe particles with average sizes ~200 and 2–4 nm, depending on the reaction conditions. The reduction of $[(1,5\text{-COD})RhCl]_2$ (where 1,5-COD = 1,5 cyclooctadiene) with $LiBEt_3H$ in THF resulted in formation of a black solution containing 2–4 nm sized Rh particles, as shown by TEM and SAXS, together with small amounts of $[(1,5COD)RhH]_4$. Stepwise reduction of first $FeCl_3$ with $LiBEt_3H$ in THF followed by addition of $[(1,5COD)RhCl]_2$ resulted in formation of Rh/Fe particles. The particles were characterized by SEM, TEM, and X-ray diffraction experiments. The catalytic activity of these highly dispersed metals toward pyrene hydrogenation has been investigated. The 2–4 nm and agglomerated Rh particles showed an activity of 31.8 mg product/g catalyst/s and 4.8 mg product/g catalyst/s, respectively, while at 100°C, the Fe particles were inactive. The 2–4 nm Rh/Fe particles have shown pyrene conversion of 1.1 mg product/g catalyst/s, while larger ~150-nm-sized Rh/Fe particles exhibited lower reactivity, 0.076 g product/g catalyst/s. These activities were compared to those of hydrous titanate (HTO) supported Pd catalysts which have been used in studies of direct coal liquefaction. The results show that the activities of the highly dispersed metal colloids are comparable to those of supported metal catlaysts on a per-gram-of-metal basis.

I. INTRODUCTION

The formation of finely divided metal powders for catalytic applications has been the subject of much research interest. Most methods to control particle size involve the introduction of surfactants which may reduce the reactivity of the metal (*1*). Other synthetic methods include metal evaporation (*2*), electrolytic reduction (*3*), and chemical reduction of metal salts with electron carriers such as naphthalene and anthracene (*4*), often aided by ultrasound (*5*). These methods have resulted in formation of extremely reactive metal particles. More recently, the reduction of metal salts with alkali and alkaline earth metal borohydrides has been studied and shown to produce metal particles in the range 10–100 nm (*6*). Such colloids containing metal particles with dimensions <100 nm are generally only stable with respect to aggregation in the presence of surfactants. To this end, a refinement of this chemical reduction method has involved the use of $[NR_4]^+[BEt_3H]^-$, where $R = C_8H_{17}$, and resulted in the formation of stable 1–6 nm sized particles believed to be stabilized by the ammonium cations as surfactants (*7*). For catalytic applications, the presence of surfactant can be a disadvantage, because it may thermally decompose to poison the active metal surface (*1*). However, one advantage of this method is that coreduction of a homogeneous mixture of metal salts may lead to formation of highly disperse mixed metal powders or

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alloy phases with well-defined, controlled stoichiometry that bridge the gap between homogeneous and heterogeneous catalysis. For catalysis applications, this is invaluable since the synergistic effects of two metals is well documented (*8*).

In this work, we report preliminary results of an investigation of the formation of highly dispersed iron and rhodium particles by reduction of individual homogeneous solutions of metal salts or metal–organic compounds in the absence of traditional surfactants to form highly dispersed metal particles. The sequential reduction of first Fe(III) then Rh(I) has also been studied using these methods with the goal of forming catalyst metal particles consisting of Rh dispersed on Fe (*9*). The reactivity of these materials toward pyrene hydrogenation has been investigated.

2. EXPERIMENTAL

a. General Procedures

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. All hydrocarbon and ethereal solvents were dried and distilled from sodium benzophenone ketyl and stored over 4-Å molecular sieves under a nitrogen atmosphere prior to use. The starting material, $FeCl_3$, was purchased from Aldrich Chemical Company. The compound $RhCl_3 \cdot 3H_2O$ was obtained via the Johnson–Matthey Precious Metals Loan Program and converted to $[(1,5\text{-COD})RhCl]_2$ (where 1,5-COD = 1,5 cyclooctadiene) by the literature method (*10*).

b. Formation of Metallic Particles

Representative experimental procedures are given below for the preparation of iron, rhodium, and iron/rhodium particles.

(*i*) *200-nm Fe particles.* A solution of 4.64 g (28.6 mmole) of $FeCl_3$ in about 250 ml of THF was added slowly to 100 ml (100 mmole) of a rapidly stirred 1.0 *M* solution of $LiBEt_3H$ in THF cooled in an ice bath. The flask containing $FeCl_3$ was washed with 2 × 50 ml of THF and the washings transferred to reaction mixture. The reaction mixture was stirred at room temperature for 5 h. Black iron particles were separated from the clear reaction solution by filtration. The solid product was then washed with a mixture of 25 ml of THF and 25 ml of absolute ethanol until the evolution of gas ceased and filtered. Finally, the product was washed with 5 × 20 ml of THF and dried *in vacuo*. The yield was 85.5%.

(*ii*) *2–4 nm Fe particles.* Fifty milliliters of THF was added to an ice-cold Schlenk flask containing 0.83 g (5.1 mmole) of $FeCl_3$. The mixture was stirred at room temperature for 0.5 h and then left to stand overnight. The solution was filtered to remove any particulate material; 10 ml (10 mmole) of 1 *M* $LiBEt_3H$ in THF was added slowly to the rapidly stirred solution, which had been cooled in an ice bath to 0°C. The black sol was stirred at room temperature for 24 h. A further 8 ml of 1 *M* $LiBEt_3H$ in THF was added to the reaction mixture, and it was stirred for 6 h more at room temperature. A black solution containing 2–4 nm Fe particles was obtained.

(*iii*) *2—4 nm Rh particles.* Five milliliters of 1.0 *M* solution of $LiBEt_3H$ in THF were added slowly to a solution of 0.4939 g (1 mmole) of $[(1,5\text{-COD})RhCl]_2$ in 38 ml of THF cooled in an ice bath. The color of the solution changed immediately from yellow to black. The reaction mixture was then stirred at room temperature for 16 h. The solution is retained for catalysis experiment. When the volatile components of the Rh colloid solution were removed *in vacuo* and the residue was extracted with pentane, 0.085 g of $[(1,5\text{-COD})RhH]_4$ (~20% yield) were obtained from the pentane extractant. The pentane insoluble solid was washed with THF and separated by centrifugation, 0.1602 g of black agglomerates (77.8% yield) were obtained which were air-sensitive and pyrophoric.

(*iv*) *150-nm Rh/Fe particles.* A solution of 1.62 g (10 mmol) of $FeCl_3$ in 100 mL of THF was added slowly to 34 ml of a stirred

1.0 *M* (34 mmol) solution of $LiBEt_3H$ in THF in an ice bath. After stirring for 60 h at room temperature, the black iron particles were formed. To this solution 149 mg (0.30 mmol) of $[(1,5\text{-COD})RhCl]_2$ in 10 ml of THF was added. The dark brown suspension was stirred for 1 day. When the stirring was stopped, black particles were stuck to the stir bar. The brown solution was filtered by cannula. The solid product was then stirred with a mixture of 15 ml of THF and 15 ml of absolute ethanol until the evolution of gas ceased and was then filtered. Finally, the product was washed with 2 × 20 ml of THF and then 3 × 10 ml of THF. The yield of the metal powder after drying *in vacuo* was 95.1%.

(*v*) *2–4 nm Rh/Fe particles.* One hundred milliliters of THF was added to a Schlenk flask containing 1.63 g (10 mmole) of $FeCl_3$. The mixture was stirred at room temperature and then left to stand overnight. The solution was filtered and cooled to 0°C; 20 ml (20 mmole) of 1 *M* $LiBEt_3H$ in THF was added slowly to the rapidly stirred solution. The black solution was stirred for 6 h at room temperature. A further 14 ml of 1 *M* $LiBEt_3H$ in THF was added to the reaction mixture and it was stirred for a further 6 h at room temperature. To this solution 149 mg (0.30 mmole) of $[(1,5\text{-COD})RhCl]_2$ in 10 ml of THF was added. The mixture was stirred for 12 h. A small amount of precipitate was separated by centrifugation to give a black solution containing 2–4 nm Rh/Fe particles as determined by transmission electron microscopy (TEM).

c. Catalyst Characterization

The catalysts were examined in a Jeol 2000-FX transmission electron microscope by drying solutions of the catalysts on holey carbon films supported on 3-mm copper grids in a nitrogen-filled glove box. Care was taken to expose the samples to the atmosphere for the minimum amount of time possible on loading into the TEM instrument. Elemental analyses were performed using a Tracor Northern energy dispersive X-ray analyzer.

d. Catalyst Testing

The catalyst testing was performed in stainless steel batch-microreactors (~23 ml) equipped with thermocouples and pressure transducers. After the microreactors were charged with pyrene (100 mg), an inert solvent *n*-hexadecane (1000 mg), and catalyst (~0.5 ml, ~0.004 mg active metal), they were pressurized with hydrogen to 100 psi and heated to 100°C in a fluidized sand bath while being shaken horizontally at 160 cycles/min. Following the heating period, the reactors were rapidly quenched to ambient and the products subjected to analysis by capillary gas chromatography. The data treatment has previously been described in detail (*11*).

3. RESULTS

a. Catalyst Characterization

Iron particles were prepared according to the reaction

$$FeCl_3 + 3LiBEt_3H \xrightarrow{THF} Fe + 3LiCl + 3/2H_2 + 3BEt_3. \quad (1)$$

in yields of over 80%. Depending upon the reaction conditions, iron particles of different sizes could be formed as determined by electron microscopy. Under conditions where an excess of the reducing agent was used in a single step, larger ~200-nm agglomerates were formed, as shown by scanning electron microscopy (SEM). Examination of these agglomerates by TEM revealed that they were composed of smaller ~4-nm particles. A TEM micrograph of such an agglomerate is shown in Fig. 1. A higher magnification view is shown of the same sample is shown in Fig. 2 to emphasize the presence of smaller primary particles within this agglomerate. Electron diffraction patterns of samples removed from the reaction mixture at various times after addition of all the reducing agent revealed that the crys-

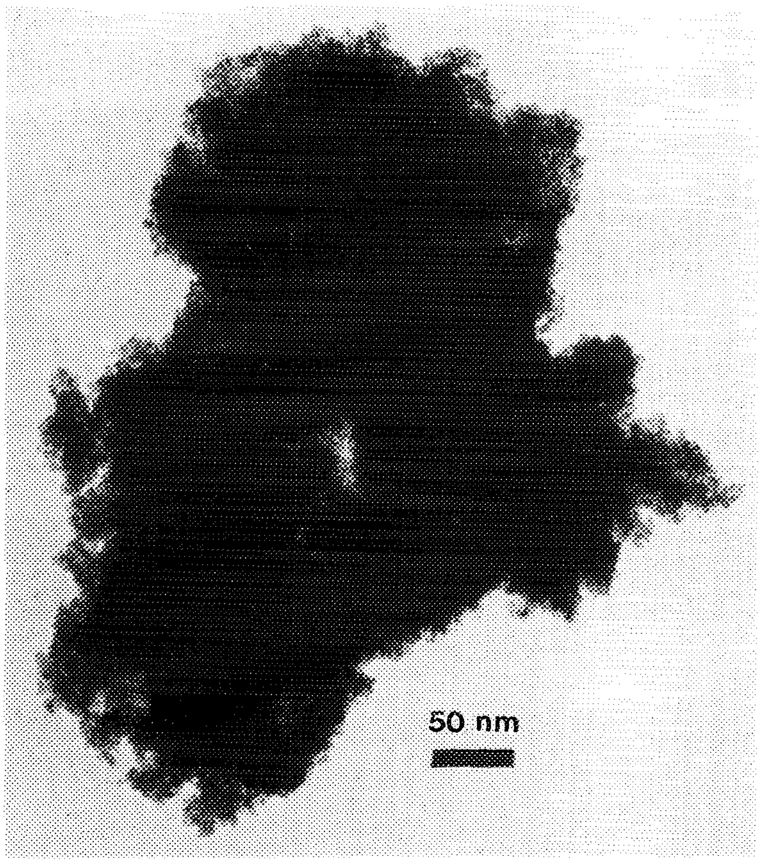

FIG. 1. Transmission electron micrograph showing a large iron agglomerate formed by the reduction method described here.

tallinity increased with time. The iron agglomerates formed by this method were isolated by filtration and found to be air-sensitive. Analysis of the electron diffraction pattern revealed that both α-Fe and γ-Fe_2O_3 crystalline phases were present. It seems likely that iron particles were initially formed and were oxidized on the short exposure to air on loading into the TEM instrument. Combustion elemental analysis showed that the powder contained less than 1% carbon and hydrogen as impurities. The BET surface area of this sample was found to be 57 m^2/g. This value is significantly higher than the geometric value expected for a powder consisting of ~200-nm particles and is more consistent with the rough surface and smaller primary particle size observed by TEM. When $FeCl_3$ was reduced in the two-step reduction process using insufficient reducing agent in the first step, as described in the experimental section, unagglomerated iron particles with sizes 2–4 nm, as determined by TEM, could be obtained.

The reduction of $[(1,5\text{-COD})RhCl]_2$ with $LiBEt_3H$ resulted in formation of a black homogeneous colloidal solution. TEM experiments on samples removed from this solution revealed the presence of 2–4 nm sized particles. Electron diffraction (ED) patterns showed the presence of a diffuse ring corresponding to a d-spacing of 2.2 Å, similar to the value of the most intense re-

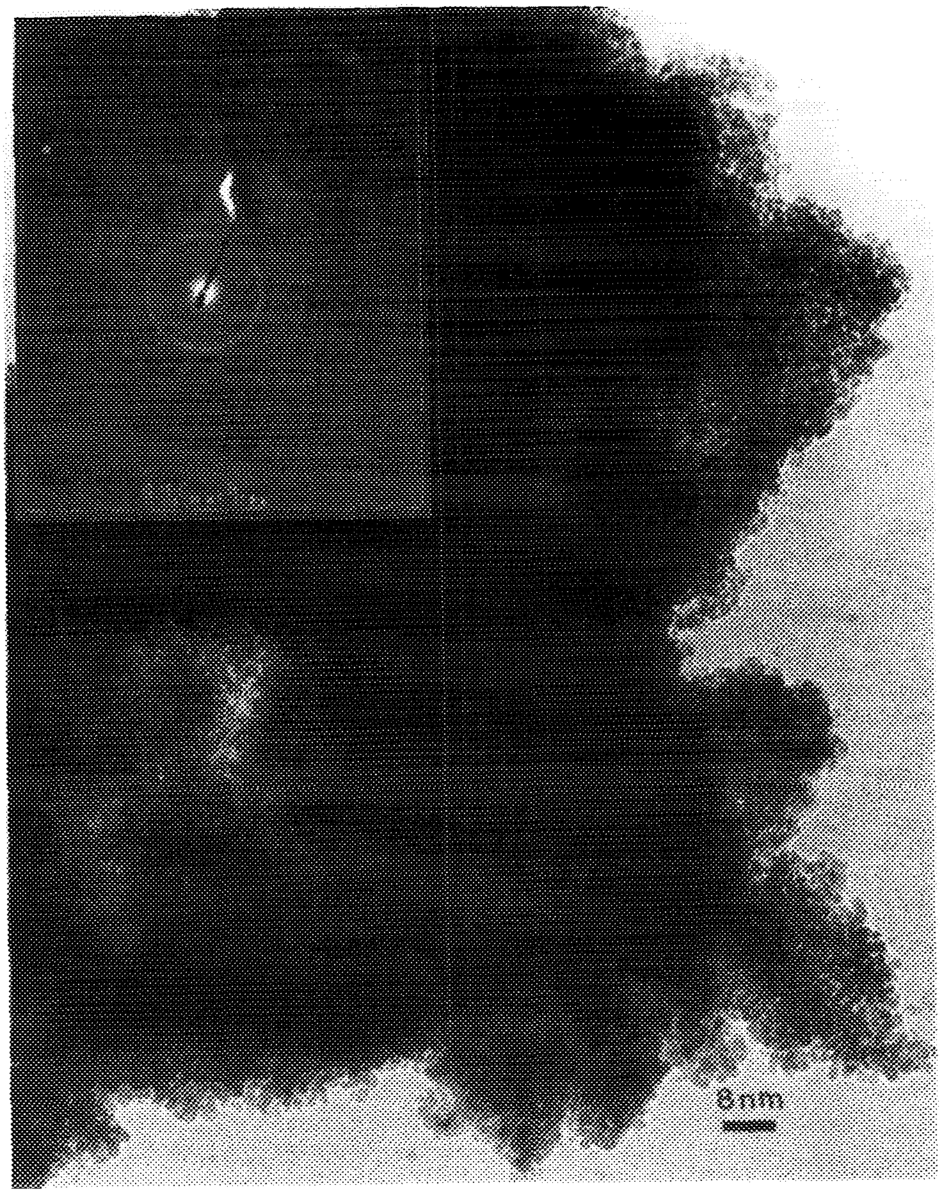

FIG. 2. Expansion of the region indicated in Fig. 1 emphasizing the particle morphology.

flection, d_{111} (2.19 Å), for Rh. Energy dispersive spectroscopy (EDS) revealed only the presence of Rh. Small angle X-ray scattering (SAXS) experiments confirmed that the average particle size of the colloidal was 4.3 nm, consistent with the TEM results.

When the volatile components were removed from the initial solution *in vacuo* and the residue was extracted with pentane, an ~20% yield of $[(1,5\text{-COD})RhH]_4$ was obtained (*12*). The pentane insoluble solid was washed with THF and separated by centrifugation to give a 78% yield of black agglomerates which were air-sensitive and pyrophoric. Examination of these agglomerates by TEM and ED revealed that they were composed of smaller ~2–4 nm particles and were crystalline. X-ray powder diffraction of the as-prepared samples showed the presence of a broad peak at ~2.2 Å, consistent with the electron diffraction data. To grow the crystallite size and so sharpen the X-ray diffraction peaks the isolated black powder was heated to 400°C for 2 h *in vacuo*. X-ray diffraction data revealed the presence of crystalline Rh.

Analogous $LiBEt_3H$ reduction experiments were then conducted in which a source of rhodium was added *after* the Fe particles had been prepared to form an Rh/Fe mixture with the goal of dispersing the Rh on the Fe surface. Large iron particles were prepared according to the method described above and after stirring for 60 h, a THF solution of $[(1,5\text{-COD})RhCl]_2$ was added to give a theoretical Rh : Fe weight ratio of 1 : 9. The reaction conditions were such that sufficient excess of reducing agent was present to completely reduce the added rhodium starting material. Under conditions of formation of larger size iron particles, SEM revealed that approximately 150-nm-sized spherical particles had been produced. TEM studies gave similar results to those of the pure iron particles. Energy-dispersive spectroscopy gave average Rh : Fe ratios of 1 : 7 and 1 : 5 for two different samples. Combustion elemental analysis gave higher carbon contents than typical values for the pure iron powder, in the range 2–4%, which may result from the presence of the 1,5-COD ligand still intact on Rh. However, no ν(C–H) bands were observed by IR spectroscopy. The surface area of such samples was found to be in the range 59–70 m^2/g by nitrogen adsorption. X-ray diffraction data for the as-prepared sample exhibited a broad peak corresponding to a *d*-spacing of 2.0 Å. After heating the sample to 400°C for 2 h *in vacuo* (10^{-2} Torr), to grow the crystallite size, sharp diffraction peaks were observed at only the *d*-spacings corresponding to α-Fe. No peaks corresponding to the presence of a crystalline Rh phase were observed. These data are consistent with the dispersion of Rh on Fe particles based on the observations above, that when a pure Rh sample was heated under the same conditions, crystalline Rh was observed.

Addition of $[(1,5\text{-COD})RhCl]_2$ to a suspension of 2–4 nm Fe particles containing an excess of $LiBEt_3H$ resulted in formation of 2–4 nm Rh/Fe particles as shown by TEM; see Fig. 3. Energy-dispersive spectroscopy revealed that the sample was homogeneous with an Rh : Fe ratio of 1 : 17, different from the expected ratio of 1 : 9.

b. Catalytic Reactivity

The Rh/Fe particles prepared by these methods were tested for their reactivity toward the catalytic hydrogenation of pyrene. This choice of catalyst testing is based on the premise that hydrogenated polynuclear aromatic hydrocarbons (PAHs) play an important role in coal liquefaction, since they function as hydrogen donor solvents. This latter class of solvents is largely responsible for bringing about the breakdown (liquefaction) of complex coal structures. The rate of hydrogenation of one PAH component found in coal-derived liquids, pyrene, has been found to be useful in illustrating the effect of reaction conditions on the kinetics and thermodynamics of catalytic hydrogenation of PAHs in liquefaction solvents (*13, 14*). Pyrene is particularly attractive because it can be quantitatively hydrogenated to donor-solvent products at temperatures as low as 100°C. From the rate of hydrogenation data, guidance for the establishment of optimum conditions for the hydrogenation of coal liquefaction process solvents can be obtained. We have conducted screening evaluations of the above described Rh/Fe powders by determining their low-temperature activity for hydrogenating pyrene.

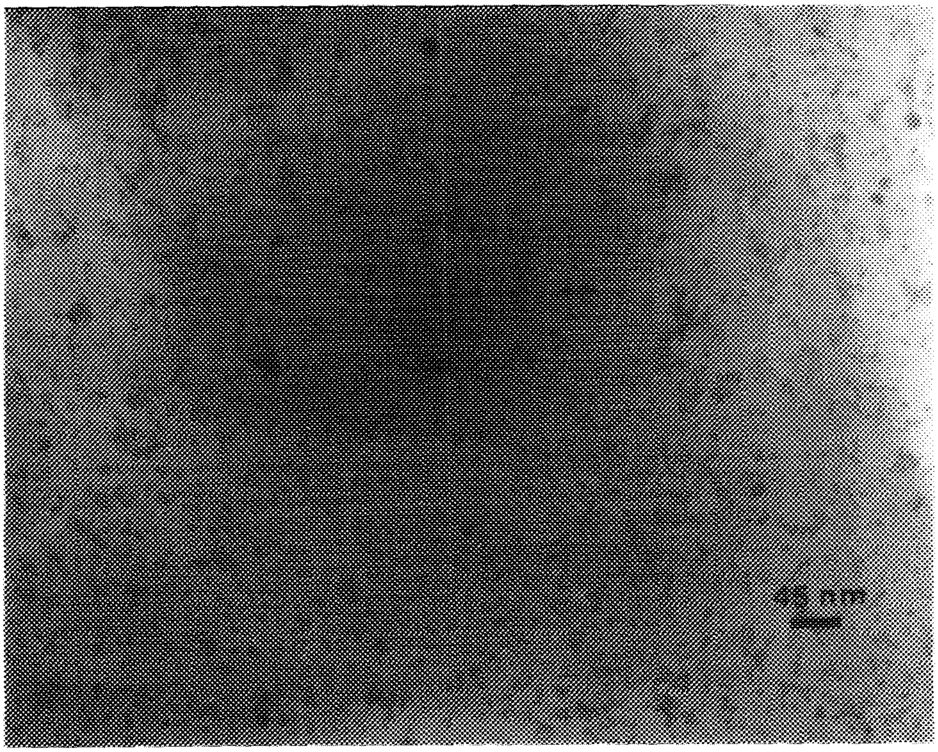

FIG. 3. Transmission electron micrograph showing the 2–4 nm sized Rh/Fe particles.

Previous studies (*11*, *15*) have shown that the catalytic hydrogenation of pyrene over a hydrous titanium oxide (HTO) supported palladium catalyst at 100°C and 100 psi of hydrogen pressure proceeds via a reversible reaction to form 4,5-dihydropyrene. Furthermore, the rate of hydrogenation of pyrene could be modeled by pseudo-first-order reversible kinetics. Based on the amount of 4,5-dihydropyrene detected in the reaction, pyrene conversion rates (mg product/g catlyst/s) were calculated. The results for the materials prepared in this work are presented in Table 1. The iron particles themselves have no detectable activity. The 4-nm Rh particles exhibit an activity of 31.8 mg product/g catalyst/s and the agglomerated Rh particles exhibit an activity of 4.8 mg product/g catalyst/s. However, the activity of the 2–4 nm Rh particles may be obscured by the presence of traces of $[(1,5\text{-COD})RhH]_4$, although we have shown this species is rapidly converted to Rh metal on exposure to H_2 (*12*). Therefore, this activity does not necessarily represent the activity of the 2–4 nm Rh particles and care was taken to remove $[(1,5\text{-COD})RhH]_4$ from other samples that were examined. Using the 2–4 nm unagglomerated Rh/Fe particles, an average conversion rate of 1.1 mg product/g catalyst/sec was obtained. In contrast, when the ~150-nm Rh/Fe ag-

TABLE 1

Sample	Activity (mg prod./g cat./s)	Activity (mg prod./g metal/s)
Fe	0	0
2–4 nm Rh	31.8	31.8
Rh (agglom.)	4.8	4.8
2–4 nm Rh/Fe	1.1	6.5
150 nm Rh/Fe	0.076	0.5
HTO–Pd	0.2	12

glomerated particles were used, a conversion rate of 0.076 mg product/g catalyst/s was obtained. A series of experiments using the HTO-supported Pd catalyst were also carried out under identical conditions for comparison. This system gave an average conversion rate of 0.2 mg product/g catalyst/sec, or approximately 12 mg product/g metal/s (see Table 1).

There are a number of explanations for the difference in activity of the different sized Rh/Fe particles. In addition to a difference in size, it is noteworthy that the rhodium loading on the smaller particles was observed to be less than that of the larger particles as determined by energy dispersive spectroscopy. However, the calculated activity per gram of rhodium metal is significantly different. Unfortunately it is not possible to compare the activity on an active site basis because we do not have the facilities to measure H_2 chemisorption on highly dispersed metal *in solution*. Furthermore, it has been shown by BET N_2 adsorption surface area measurements that the observed surface area is significantly lower than that predicted for the individual particle size from TEM measurements. We suspect that drying the powders and the outgassing pretreatment before N_2 adsorption causes agglomeration leading to a lower BET surface area. This makes it difficult to report activity per unit surface area of catalyst.

CONCLUSIONS

A convenient, single-step chemical reduction method for the formation of highly dispersed crystalline, metal particles has been demonstrated. These colloidal solutions were shown to contain 2–4 nm sized metal particles and are indefinitely stable in THF in the absence of a surfactant. The sequential reduction of $FeCl_3$ followed by $[(1,5\text{-COD})RhCl]_2$ resulted in the formation of metallic particles. At this stage the distinction between the formation of Rh dispersed on Fe and a mixture of individual Fe and Rh particles is not unambiguous, but we feel that Rh dispersed on Fe is more likely based on the X-ray diffraction data. The 2–4 nm Rh/Fe dispersion exhibited a similar activity to agglomerated 2–4 nm Rh particles based on the weight of the active metal. The activity of the colloidal metal solutions compare favorably to supported metal hydrogenation catalysts on a per-gram-metal basis. Further studies are in progress.

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