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Catalysis Today 89 (2004) 237–244

CATALYSIS TODAY

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Plasma torch generation of carbon supported metal catalysts

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Abstract

Novel plasma torch generated Pd/C, and PdAg/C catalysts were tested for reactivity for two hydrogenation reactions and characterized using a number of techniques. The general conclusion reached was that the metal catalysts created in this fashion were extremely highly dispersed (>50% in some cases) and had concomitantly high activity on a gram basis. The PdAg/C catalysts exceeded the selectivity of PdAg/Al_2O_3 catalysts for selective hydrogenation of acetylene. The selectivity of Pd/C catalysts for 1-butene isomerization was equal or better than that of catalysts prepared by conventional means, and the activity nearly as high. One surprise was the finding that plasma generated PdAg/C catalysts had no apparent activity for 1-butene isomerization. A second surprise was the finding that the plasma treatment did not increase the crystallinity of the carbon but did result in the loss up to 30% of the surface area.

Keywords: Plasma torch; Metal catalysts; Hydrogenation reaction

1. Introduction

The use of an atmospheric pressure torch to produce supported metal catalysts from an aerosol containing alumina support and metal precursor molecules was first demonstrated about 5 years ago [1]. Surprisingly little work has gone into exploring this new technology since the original invention; given that the little data available suggest there are both potential advantages and disadvantages to the technique [2]. On the advantage side of the ledger was the finding that the selectivity of Pd/Al_2O_3 catalysts produced with the torch was far higher for 1-butene isomerization than conventionally generated Pd/Al_2O_3 catalysts of the identical composition. On the disadvantage side of the ledger was the finding that on alumina the plasma generated catalysts were far less active over the temperature range of interest than catalyst prepared by conventional means. With more effort some unique and valuable catalysts can be produced using this technology.

The relatively low activity of the plasma generated alumina supported catalysts was shown to reflect a loss of surface area of the support alumina and concomitantly the supported metal. The support melted as it passed through the hot zone of the plasma, $T > 3000\,K$ [3], leading to the loss of much of its porosity, and likely the 'burial' of metal particles in closed pores, when the alumina 'refroze' in the cool afterglow. The positive change in selectivity also appeared to reflect a change in the support. In this case, the transformation by the plasma of the support from γ to α phase dramatically impacted the selectivity.

The finding that the plasma technique is capable of producing highly dispersed metal particles on transformed supports suggests additional avenues for study. This study represents a first effort to use the lessons learned in the earlier studies to design plasma generated catalysts with unique structure and properties. Specifically, a support that will not melt (carbon) was employed instead of a refractory oxide. The expectation was that this would lead to the creation of high surface area, high dispersion catalysts. In fact, the resulting catalysts were found to have these features, although there was more transformation of the carbon support than anticipated. The net result was the production of plasma generated catalysts showing high activity and selectivity for two different selective hydrogenation reactions.

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doi:10.1016/j.cattod.2003.11.033

Table 1
Key conditions employed in catalysts preparation

Catalyst	Concentration of Pd (wt.%)	Concentration of Ag (wt.%)	Plasma and aerosol gas	Flow rate of plasma gas (l/min)	Flow rate of aerosol gas (l/min)
Pd/C (400 W)	1	0	Argon	0.81	0.36
Pd/C (500 W)	1	0	Argon	0.81	0.36
Pd/C (600 W)	1	0	Argon	0.81	0.36
Pd/C (700 W)	1	0	Argon	0.81	0.36
PdAg/C (500 W)	0.5	0.5	Argon	0.81	0.36
PdAg/C (600 W)	0.5	0.5	Argon	0.81	0.36
PdAg/C (700 W)	0.5	0.5	Argon	0.81	0.36
Pd/Al_2O_3[a]	0.5	0	NA	NA	NA
$PdAg/Al_2O_3$[a]	0.5	0.5	NA	NA	NA

[a] Pd/Al_2O_3 and $PdAg/Al_2O_3$ catalysts were prepared by incipient wetness impregnation and coimpregnation, respectively.

2. Experimental

Palladium, silver and palladium–silver supported metal catalysts were generated by passing a physical (completely dry, no solvents) mixture of crushed Norit C carbon (particle size order of 50 μm) and nitrates of palladium and/or silver as an aerosol (<0.1% solid) in an argon feed stream through a vertically oriented plasma. The plasma torch and the aerosol system are described in detail elsewhere [4,5]. Indeed, Pd/Al_2O_3 catalysts were prepared in a virtually identical manner [1,2]. Thus, only the key features will be noted here. The aerosol (carbon particles + nitrates in Ar) enters the plasma (approximately 700 Torr pressure) through a central alumina tube (3 mm i.d.) near the center of the coupler region, where the plasma is probably above 3500 K [3]. This gas, 'aerosol gas', mixes with a second gas (also Ar in this case), called the 'plasma gas', at the center of the coupler region. The plasma gas enters the torch (17 mm i.d.) from below in the annular region surrounding the central alumina tube. The aerosol gas appears to form a jet within the (incompletely) mixed stream, and this jet carries the particles out of the hot zone of the torch, and into the afterglow, in less than 0.1 s. The catalytic material that forms during this rapid passage of the aerosol is then captured downstream on filter paper.

The mechanism of catalysts generation is presumed to include the following steps. First, the precursors nitrate decomposes due to the high temperatures encountered. Second, the metal atoms released by the decomposition adsorb on the carbon particles also presented in the aerosol. Third, high velocity diffusion of atoms on the carbon surface leads to particle formation. High velocity diffusion and particle growth ceases in the cool afterglow.

Pd/Al_2O_3 and $PdAg/Al_2O_3$ catalysts were prepared by incipient wetness impregnation and coimpregnation respectively using solutions of Pd nitrate and Ag nitrate in deionized water. After impregnation, the slurry was dried in an oven at 100 °C overnight and then calcined at 500 °C in air for 6 h. Table 1 summarizes the catalyst preparation condition.

3. Reaction tests

3.1. Selective hydrogenation of acetylene

For polymerization reactors to create the highest quality polyethylene, all acetylene must be removed from the feed stream [6,7]. A catalyst able to selectively remove this species without converting ethylene to ethane is required.

The selective hydrogenation test reaction was performed on a premixed gas consisting of 35% C_2H_4, 0.5% C_2H_2, 1000 ppm CO, and the balance N_2 obtained from Scott Specialty Gases; the mixture was designed to mimic the feed conditions found in industry. This gas mixture together with hydrogen gas was passed over catalyst loaded in a fixed-bed quartz micro-reactor of about 3 mm i.d. with 25 mg of catalyst loaded into the reactor and retained between quartz wool.

Comparisons were made between catalysts prepared in the plasma torch and $PdAg/Al_2O_3$ catalysts prepared by incipient wetness with the same metal weight loading as the plasma generated catalysts. All alumina supported catalysts were given a pretreatment, generally consisting of oxidation in 20% O_2 and 80% He at 500 ± 5 °C, for 4 h, followed by reduction in flowing H_2 at 500 °C for 4 h before introduction of the reaction mixture. In some cases a lower temperature was employed in the H_2 treatment, as noted. This treatment protocol was selected because it improves the performance of $PdAg/Al_2O_3$, as prior work clearly shows [7,8]. Carbon supported catalyst were just reduced at moderate temperatures (100 °C).

The premixed gas (10 sccm) was mixed with 2 sccm of UHP H_2 to make the reaction mixture. For each reaction run, the reaction was started at temperatures in which the initial acetylene conversion was between 40 and 50%, a temperature far below the 'clean up' temperature (temperature at which 99% of acetylene in the feed has been converted). Reaction temperature was then increased to study the influence of increased acetylene conversion and increased temperature on product distribution. By starting the reaction at a low temperature and exposing all catalysts to the reaction mixture for about 2 h, we sought to ensure that all catalysts had comparable levels of carbonaceous deposit.

An on-line HP 5890 gas chromatograph was used to analyze the composition of the reaction effluent. The products were separated on a PLOT capillary column, CP-Al_2O_3/Na_2SO_4 25 m × 0.25 mm × 4 μm, from Chrompack. Only hydrocarbon products are detected by the flame ionization detector, hence selectivity and conversion were based on analysis of the hydrocarbons alone.

The selectivity of catalysts for ethylene hydrogenation was defined as:

$$\text{selectivity} = \frac{C_2H_4\ (\text{outlet}) - C_2H_4\ (\text{inlet})}{C_2H_2\ (\text{inlet}) - C_2H_2\ (\text{outlet})}$$

As the practical concern is the selective removal of acetylene, activity is not of great interest, however relative activity data is shown in Fig. 2.

3.2. *Selective hydrogenation of 1-butene*

Alkylation is widely employed to create gasoline range hydrocarbons (e.g. C-8) from smaller molecules. In the case of C4 alkylation, the highest octane product is formed if the input olefins are 2-butenes, as the alkylation of 2-butenes creates 'branched' chains (e.g. *iso*-octane), whereas the alkylation of 1-butenes creates lower octane straight chains. Thus in many alkylation processes the C4 stream is 'pretreated' to convert 1-butene to 2-butene [9,10]. The preferred catalyst for pre-treating a C4 olefin stream is Pd/Al_2O_3, hence we use the activity and selectivity of these catalysts as a benchmark for evaluating the quality of the plasma generated Pd/C catalysts.

The selective 1-butene isomerization reaction was also performed in a fixed-bed quartz micro-reactor with 25 mg of solid (mixture of 5 mg of supported catalyst and 20 mg of carbon with no metal) retained between quartz wool. This bed was pretreated in flowing H_2 at 100 °C for 2 h before introduction of the reaction mixture. Several gases were used in this experiment: UHP hydrogen and helium, and 99.99% 1-butene, purchased from Tri-Gas. MKS mass flow controllers meter were used to obtain a feed stream consisted of 500 cm^3/min of helium, 90 cm^3/min of hydrogen and 10 cm^3/min of 1-butene. All reaction test were carried out at a temperature of 30 °C.

An on-line HP 5890 gas chromatograph coupled with a thermal conductivity detector was used to analyze the composition of the reaction effluent. The products were separated on an ALLTECH packed column, 0.19% piric acid on carbograph 2AP 80/100 mesh. The selectivity of catalysts for 1-butene isomerization was defined as:

$$\text{selectivity} = \frac{\begin{array}{c}(\textit{cis}\text{-butene} + \textit{trans}\text{-butene})\ (\text{outlet}) \\ -(\textit{cis}\text{-butene} + \textit{trans}\text{-butene})\ (\text{inlet})\end{array}}{(1 - \text{butene})\ (\text{inlet}) - (1 - \text{butene})\ (\text{outlet})}$$

Table 2
BET areas and metal dispersion by chemisoprtion

Catalyst	Total area (m^2/g cat.)	Total metallic area (m^2/g cat.)	Dispersion (%)
Carbon	1338	–	–
Pd/C (500 W)	1029	153	57
Pd/C (600 W)	1096	169	63
Pd/C (700 W)	1108	148	52
PdAg/C (500 W)	964	33	15
PdAg/C (600 W)	951	35	17
PdAg/C (700 W)	985	28	13
Pd/Al_2O_3	337	65	49
PdAg/Al_2O_3	327	71	53
Ag/C	1128	–	–

4. X-ray diffraction

Powdered samples were analyzed by X-ray diffraction (XRD) in the XRD Laboratory in the Department of Earth and Planetary Sciences at the University of New Mexico, using a Scintag Pad V diffractometer with DataScan 3.1 software (from MDI, Inc.) for system automation and data collection. Ni-filtered Cu Kα radiation (40 kV, 35 mA) was used with a Bicron Scintillation detector (with curved graphite-crystal monochromator). Data were analyzed with Jade 5 Software (from MDI, Inc.) using the ICDD PDF2 database [11].

5. Surface area determination

An Accelerated Surface Area and Poroimetry (ASAP) 2010 system was used to measure the surface area. A 125 mg catalyst sample was placed in a Pyrex cell holder, heated to 100 °C, and evacuated to 1×10^{-6} bar. The full adsorption–desorption isotherm was obtained at 77 K, using UHP nitrogen as the adsorbing gas. Surface areas were calculated using the BET equation. Carbon monoxide chemisorption was used to measure the palladium dispersion on the catalyst sample. All data were judged reliable as a minimum of six data points were always collected during the isotherms and there the resulting linearized plots were very linear ($R^2 > 0.99$). It is generally believed that Ag will not adsorb CO [8,12–18]. The stoichiometry of CO:Pd is assumed to be 1:1 for this study. There is some controversy in the literature and some workers suggest lower values for this ratio (between 0.7 and 1.0), reflecting the fact that a mixture of bridged and linear forms of CO are found on the surface [19,20]. Thus, the dispersion given in Table 2, are minimum dispersions.

6. Transmission electron microscopy

A 200 kV JEOL 2010F high resolution transmission electron microscope with point-to-point resolution of 0.19 nm was used for this work. Samples were prepared by dipping

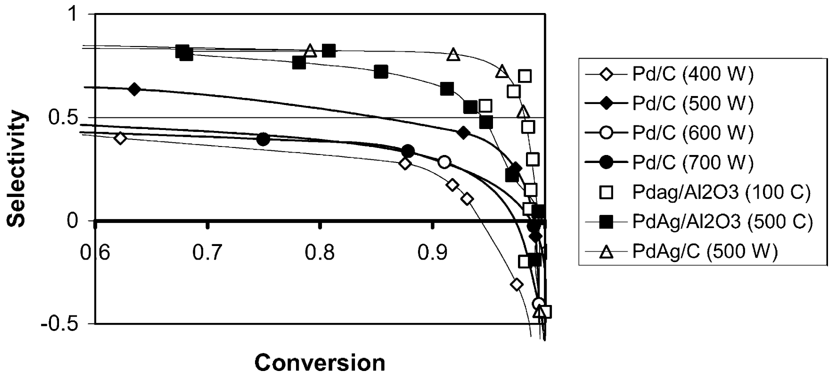

Fig. 1. Near the point of total conversion of the acetylene the plasma generated PdAg catalyst is as good, as the optimum alumina supported catalyst (pretreated at 500 °C) and clearly better than non-optimized alumina supported catalysts (pretreated at 100 °C). Pd only catalyst have lower selectivity. Note: the fonts are larger than the measurement errors.

a copper grid in an ethanol solution in which mechanically ground, plasma generated carbon supported catalysts were well dispersed.

7. Results

Fig. 1 shows the effect of preparation method on the selectivity of Pd and PdAg catalysts supported on carbon an alumina for acetylene hydrogenation in a large excess of ethylene. A positive selectivity near the temperature at which 99+% of the acetylene is converted indicates that acetylene is being converted to ethylene more rapidly than ethylene is hydrogenated. The plasma generated PdAg/C catalysts are at least as selective as the best PdAg/Al_2O_3 catalyst. In this figure it is shown that at the point at which nearly all the acetylene is converted, the selectivity of the plasma generated PdAg/C catalyst is as good as the catalyst of the same metal composition on alumina made by a conventional route. Not surprisingly, the monometallic Pd/C catalysts are not as selective as PdAg alloy catalysts made using either the plasma or the standard approaches [7]. See Table 1 for more detail on catalyst preparation.

Fig. 2 shows the effect of preparation method on the activation energy of Pd and PdAg catalysts supported on carbon and alumina for ethylene hydrogenation. These values are important in evaluating catalysts for industrial use. Clearly the plasma generated catalysts have the lower activation energy. Also, it is clear that the PdAg catalysts generally are less active for this reaction than the Pd only catalysts. Note the rates of acetylene hydrogenation were not measured as the concentrations were very low and the conversion virtually complete. This makes high fidelity analysis of rates impossible.

For the selective hydrogenation of 1-butene both activity and selectivity are significant, although the latter is far more significant. The activity of the plasma generated PdAg/C catalysts is lower than that of the best alumina supported catalyst (Fig. 3). On the other hand, the selectivity of the

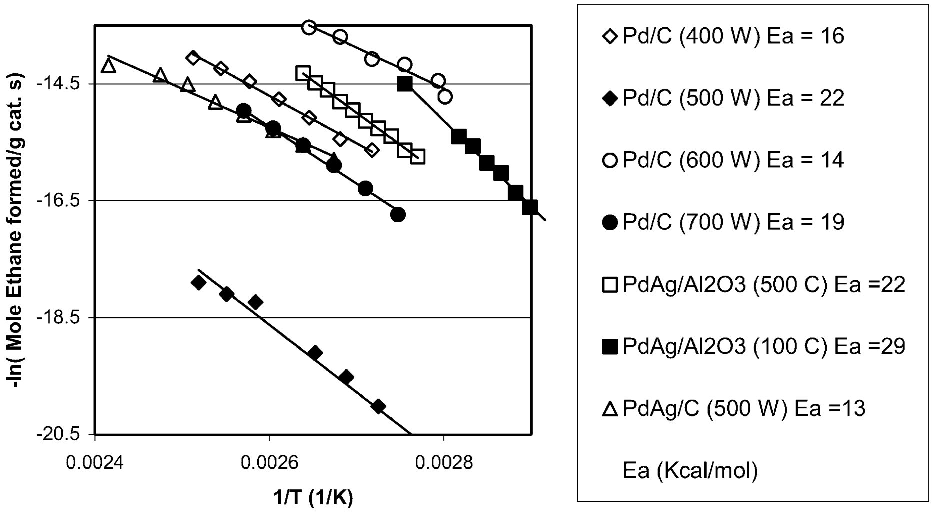

Fig. 2. A Boltzmann plot of differential rates of ethylene conversion as a function of temperature yields activation energies. Note, in the process of removing acetylene impurities from the ethylene stream there is inevitably a differential conversion of ethylene.

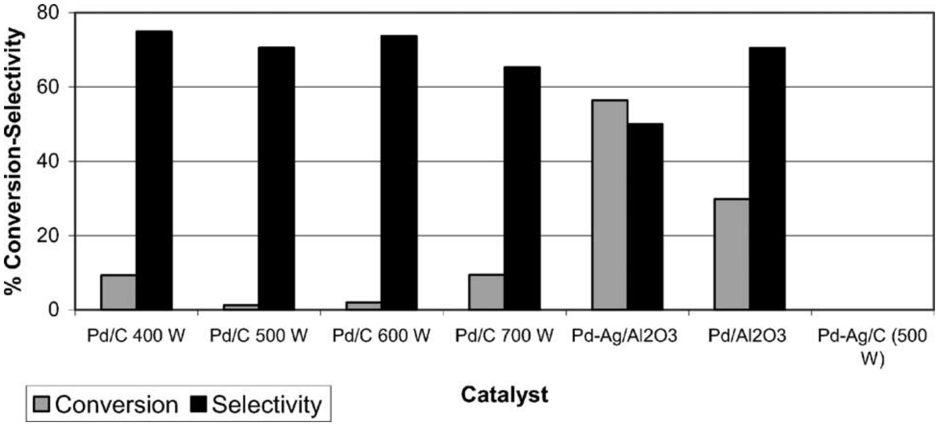

Fig. 3. Activity and selectivity measurements were collected at 30 °C and the same flow rates, and the same metal mass, for all catalysts. Note that the PdAg/C catalyst had no activity. Errors in selectivity values are estimated to be less than 3%.

plasma generated catalysts match that of catalysts prepared using incipient wetness.

A couple of surprises were found in the 1-butene isomerization study. First, the best catalysts, in terms of activity and selectivity were the PdAg/Al_2O_3 catalysts. Second, the plasma generated PdAg/C catalyst had absolutely no activity. This result was found repeatedly.

Other results showed that the power at which the Pd/C catalysts were produced has a significant impact on the activity of the plasma generated catalysts. Those Pd/C catalysts produced at 400 and 700 W had activity about 1/3 as high as the Pd/Al_2O_3 catalysts. Those two catalysts, and the other Pd/C catalysts, had selectivity as high as the alumina supported catalysts.

Studies of the plasma generated catalysts using both chemisorption and TEM show dispersions greater than 50% (Table 2). Fig. 4 shows the images taken from the Pd/C (600 W) catalyst. This sample contains small particles of Pd with an average diameter of 2.6 nm. In Fig. 5 the particle size distribution for Pd/C (600 W) catalyst obtained using Digital Micrograph^{TM} Version 3.6.1 is shown.

Efforts to measure Pd particle size using other techniques were consistent with both of these measures. For example, XRD data show no reflections due to metal particles. Only two broad lines, consistent with turbostratic carbon, were found in all of these catalysts. The absence of detectable Pd reflections is consistent with very small particles, and concomitantly very broad/weak XRD signals.

In contrast to the Pd/C catalysts the surface area of the PdAg/C catalyst was measured to be relatively low (dispersion $< 20\%$). These lower dispersion measurements are consistent with TEM images (Fig. 6), which show some particles of a complex ‘snake’ shape with moderate dispersion. It must be noted there are complications in interpretation of the results of CO adsorption on PdAg. For example, it is believed that CO only adsorbs on Pd [8]. The fact that any CO adsorption is measured may suggest that the surface of the particles is enriched in Pd. Yet this interpretation is not consistent with the finding that PdAg/C catalysts have no activity for the selective hydrogenation of 1-butene.

Although XRD studies clearly indicate the plasma treatment did not ‘graphitize’ the carbon, it did decrease the

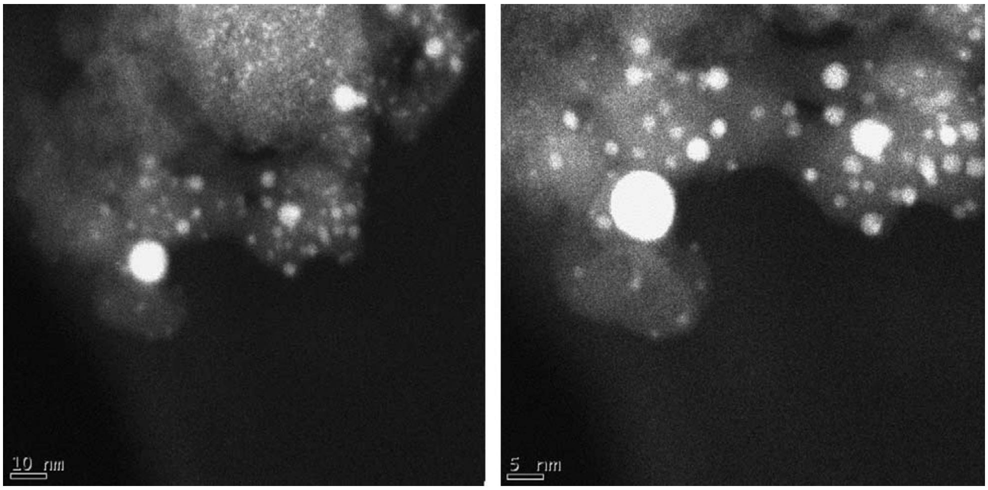

Fig. 4. TEM micrographs clearly show that the palladium particles are only a few nanometer across on the Pd/C (600 W) sample.

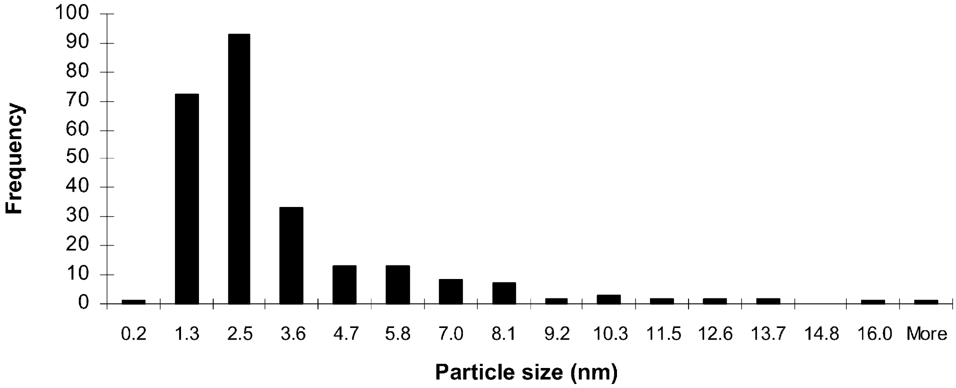

Fig. 5. Particle size distribution for Pd/C (600 W) obtained by TEM. Mean particle diameter is 2.6 nm.

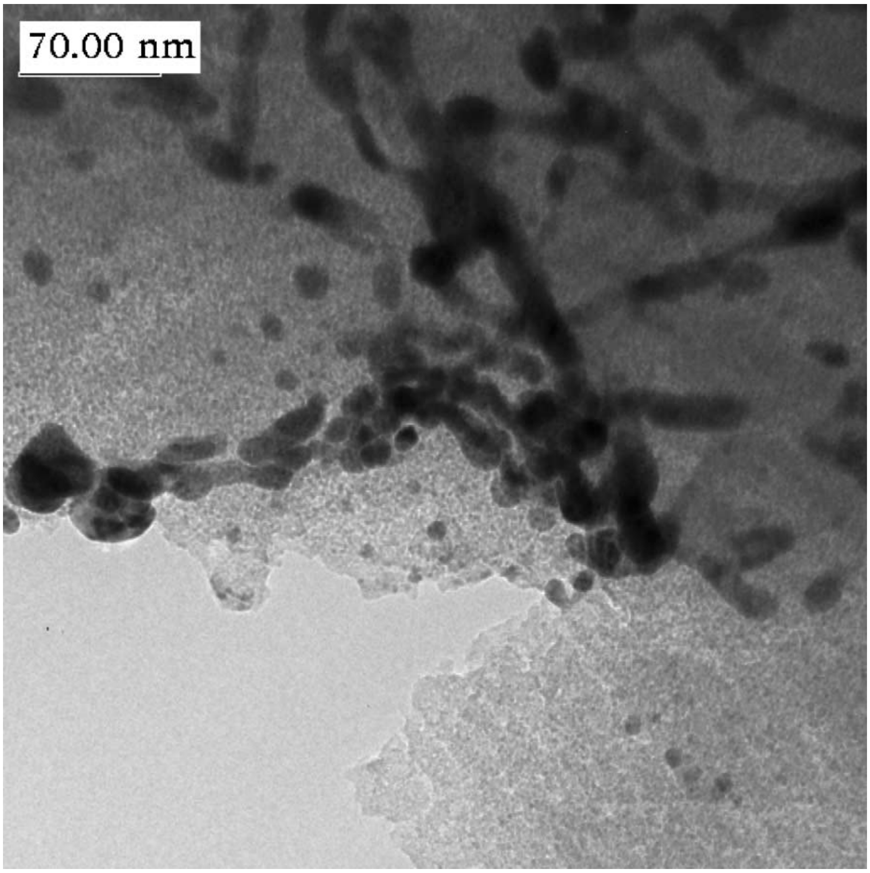

Fig. 6. TEM image taken from the PdAg/C (500 W) catalyst, which show particles of an ordinary shape as well as some with a complex 'snake' shape with moderate dispersion.

surface area of these carbons (Table 2). Some possible mechanisms for surface area reduction are discussed in the next section.

8. Discussion

Novel techniques to generate supported metal catalysts potentially can create novel structures and hence possibly improved catalytic properties. For example, the motivation for the in-depth study of the use of metal clusters to generate supported metal catalysts was the possibility that the technique was equivalent to using single atoms, or small atom clusters as the precursors. This might lead to the formation of catalysts of the ultimate dispersion with unique catalytic chemistry, particularly improved selectivity. It was found, unfortunately, after literally hundreds of studies [21], that the decomposition process was invariably accompanied by oxidation of the metal by surface hydroxyls. Subsequent reduction processes invariably resulted in sintering and the formation of reduced metal particles of a size readily prepared by conventional approaches such as incipient wetness. In sum, in most cases, there is apparently little advantage to the use of organometallic clusters for the generation of supported metal catalysts.

The use of the aerosol-through-plasma technique represents a novel, and virtually unstudied, means of generating metal catalysts. The first studies of plasma generated catalysts, performed on Pd/alumina catalysts, clearly indicated that unique catalysts can be created using the aerosol-through-plasma technique [1,2]. Unfortunately, this first study demonstrated that refractory oxide supports loose surface area, during the plasma processing. Invariably, this reduces the activity of the final catalyst product. The most likely mechanism is the 'burial' of metal in pores that are closed when the liquefied alumina 'freezes' in the afterglow region. Still, the selectivity of alumina supported catalysts generated with a plasma torch in many cases were as good in terms of selectivity and nearly as good, in terms of activity (per gram metal) as alumina supported catalysts made by incipient wetness with the same metal loading.

In this current study carbon was used as the support on the basis of the supposition it would not melt, and hence could not lead to metal 'burial' in pores during freezing. The data (Table 2) clearly show that burial did not take place as the dispersions were remarkably high. Also, all data show the catalytic performance of the catalysts was quite good. For both reactions studied plasma generated catalysts were as selective, or more selective, than catalysts of identical metal loading prepared using conventional techniques. Also, for both reactions the plasma generated catalysts had activities only slightly lower than those of the conventionally supported catalysts. In sum, this study clearly indicates that unique, and potentially valuable catalysts can be generated using this novel approach.

The data suggest the process of making active catalysts using the torch was not optimized. Indeed, the variation of a single parameter, power adsorbed by the plasma, significantly impacted the catalyst performance. Further study of plasma generated catalysts may lead to the discovery of optimal production conditions, that is production conditions that yield catalysts with superior activity and selectivity.

There are some aspects of the observed behavior that were so surprising they require additional commentary. In particular, the finding that PdAg/C catalysts had no activity for 1-butene isomerization is surprising, particularly in contrast to two other findings. First, PdAg/Al_2O_3 prepared by incipient wetness has the highest activity and the best selectivity of any of the catalysts studied for this reaction. Second, PdAg/C was very activity and selective for the selective hydrogenation of acetylene. At present it is not possible to provide a definitive explanation of this observation. Earlier studies do contain some potentially valuable clues. For example, several workers agree that palladium and silver can be phase segregated by the appropriate sequence of oxidation and reduction processes [7,8,22]. In fact, the dominant species on the surface can be either palladium or silver, as a function of the precise treatment sequence. Possibly the plasma generated PdAg/C catalysts are dominantly silver on the surface.

Also, Fig. 2 reveals an interested feature of the plasma generated catalysts: most of them have lower activation energy than the alumina supported catalysts. Activation energy modifications may reflect changes in the way CO in the feed adsorbs on the palladium particles. In a previous report [23], it was shown that the lower activation energies are obtained when linear CO adsorption is dominant over bridge type adsorption. IR spectra of adsorbed CO showed that the presence of Ag affects the bonding of CO, favoring linear CO over the bridged forms; this effect is even more pronounced after higher-temperature reduction in H_2.

Another interesting finding (Fig. 2) is that PdAg catalysts are generally less active than Pd only catalysts for ethylene hydrogenation. This could partially account for the fact that PdAg catalysts are more selective than Pd only catalysts. Indeed, the best catalyst for removing acetylene from an ethylene stream would have high rates of acetylene hydrogenation and low rates of ethylene hydrogenation.

Finally, there was some loss of surface area from the carbon during this treatment. It is possible that this loss of surface area reflects a removal of all oxygen groups and consequently the formation of a hydrophobic, inert substrate [24,25]. The impact of this on catalytic behavior could be pronounced [26]. It is also possible that during the high temperature treatment in the torch some limited and local reorganization of carbon atoms takes place, leading to the closure of some pores and the loss of some surface area. Although this is very speculative, it is consistent with the observation that significant surface area of the carbon is lost during plasma treatment.

Acknowledgements

We acknowledge support for this work from the Department of Energy, Office of Science, via grant DE-FG03-98ER14917. Electron microscopy was performed at the University of New Mexico (UNM), electron microscopy facility supported by the National Science Foundation and by the Department of Earth and Planetary Sciences at UNM via NAF grant CTS 98-71292. Additional support was obtained from the LDRD program (X1GH) at Los Alamos National Laboratories and the Ceramic and Composite Materials Center at the University of New Mexico.

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