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RESEARCH NOTE

Novel Sol-Gel-Based Pt Nanocluster Catalysts for Propane Dehydrogenation[1]

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We report the propane dehydrogenation behavior of catalysts prepared using two novel synthesis strategies that combine inverse micelle Pt nanocluster technology with silica and alumina sol-gel processing. Unlike some other sol-gel catalyst preparations, Pt particles in these catalysts are not encapsulated in the support structure and the entire Pt particle surface is accessible for reaction. Turnover frequencies for these catalysts are comparable to those obtained over Pt catalysts prepared by traditional techniques such as impregnation, yet the resistance to deactivation by carbon poisoning is much greater in our catalysts. The deactivation behavior is more typical of traditionally prepared PtSn catalysts than of pure Pt catalysts.

Key Words: **sol-gel; aerogel; xerogel; platinum; dehydrogenation; propane.**

INTRODUCTION

Sol-gel materials hold great promise as catalyst supports due to the wide range of physical properties achievable by varying processing conditions (1–5). The method of introduction of metal particles into sol-gel supports can strongly influence catalytic performance. One method for metal addition is demonstrated by numerous studies of metal catalysts prepared by addition of a metal salt or complex to silica and alumina sols prior to gelation. Conversion of the sols into xerogels or aerogels followed by reduction converts the metal precursor into metal particles. In an extensive series of papers Lopez *et al.* (6–17) demonstrate that Pt, Ru, and Pd particles resulting from their synthesis technique are at least partially buried, or encapsulated, in the silica support framework, and that the surfaces of the particles are partially covered by silicates. (Encapsulation refers to particles partially embedded in the support, while occlusion refers to particles trapped in closed pores and inaccessible to the gas phase.) As a result of encapsulation, the particles are highly resistant to sintering (12–14). As a result of coverage by silicates, selectivity for hydrogenation is typical of particles smaller than those known to be present (12, 13, 17). An important consequence of this last observation is that deactivation by carbon is much slower on sol-gel catalysts than on catalysts prepared by impregnation techniques (6, 7, 10, 12); the ensembles available at the metal surfaces in the sol-gel catalysts are too small to permit formation of coke precursors. Zou and Gonzales (18, 19) used a different sol-gel preparation resulting in Pt particles that are not encapsulated, partially covered by silicates, or occluded, as evidenced by agreement between particle sizes measured by transmission electron microscopy (TEM) and hydrogen chemisorption. Nevertheless, these materials show excellent resistance to poisoning by carbon deposition during reactions of *n*-hexane. This resistance is attributed to the high surface area of the materials (18–20) which can accommodate larger amounts of carbon than traditional supports, as well as to small particle sizes which inhibit coke formation (18). Surprisingly, a joint effort by Gonzales and Lopez seems to show no occlusion of Pt particles by either synthesis method (21), contradicting earlier work by the two groups (13, 14). Occlusion and/or encapsulation of Pt particles in sol-gel catalysts are evidently strongly dependent on synthesis parameters. Two other studies of sol-gel Pt catalysts (22, 23) show evidence of Pt particle occlusion, in agreement with Lopez.

Clearly, sol-gel catalyst preparations show great promise. Here and elsewhere (24, 25) we describe a new method for preparing sol-gel catalysts that not only results in sintering and deactivation resistant catalysts but also forms metal particles with a narrow size distribution and allows a high degree of particle size control. This method involves the synthesis of unsupported, monodisperse metal clusters

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through (i) surfactant-induced solubilization of metal salts in nonpolar solvents, (ii) chemical reduction of the metal salts to initiate nucleation and growth of the particles, and (iii) stabilization of the particles in solution by surfactant. Under proper conditions ultrasmall, monodispersed particles of controlled, tunable sizes result (26, 27). Unfortunately, practical utilization of these clusters as catalysts is limited by the surfactant surrounding the particles, and removal of the surfactant (by washing with solvent) generally results in severe aggregation of the metal clusters (28). By combining sol-gel and metal cluster technologies in a single synthesis, we have shown (24, 25) that it is possible to prevent agglomeration of the metal particles during surfactant removal and realize the advantages of metal cluster technologies in a supported catalyst material. The presence of the sol-gel matrix prevents or inhibits particle migration and coalescence upon surfactant removal. This synthesis method differs from earlier work (10–21) in that (i) the synthesis uses only nonpolar solvents, and (ii) metal particles are formed prior to gellation of the sol rather than by hydrogen reduction of an aerogel or xerogel containing a metal precursor. Note also that because the reduced metal particles are protected by surfactant, reaction with the support resulting in encapsulation may be avoided during gellation.

Because previously reported Pt sol-gel catalysts demonstrate resistance to carbon deposition, and carbon poisoning is a major cause of deactivation during dehydrogenation of small alkanes, we chose propane dehydrogenation to test the deactivation resistance of our catalysts. We describe the propane dehydrogenation activity, selectivity, and stability of Pt/SiO_2 and Pt/Al_2O_3 catalysts prepared by our novel synthesis method, and show that these materials exhibit high specific activities for propane dehydrogenation and deactivation rates far superior to those obtained with traditionally prepared Pt catalysts (29–32). In fact, our catalysts exhibit performance that is generally only obtained with Pt catalysts promoted by Sn to retard carbon poisoning (29, 30).

EXPERIMENTAL

Catalyst synthesis and characterization are described in detail elsewhere (24). Briefly, Pt/SiO_2 samples were prepared by adding didodecyldimethylammonium bromide (DDAB) to toluene to make a 5 wt% surfactant solution, followed by addition of $PtCl_2$ and tetraethylorthosilicate (TEOS) to result in concentrations of 0.005 and 0.4 M, respectively. Sufficient 2 M $LiBH_4$ in THF was then added to give a $Li^+ : Pt^{2+}$ molar ratio of 3 : 1 and cause reduction of the Pt. Finally, 40 wt% tetrabutylammonium hydroxide in water solution was added to give a water to TEOS molar ratio of 3 : 1 and the resulting emulsion was allowed to gel. The gel was aged at 323 K for 2 days and then washed with toluene to remove surfactant, unreacted metal salt, and excess $LiBH_4$. The gel was then split, with one half being dried in air in three 24-h stages at 313, 323, and 393 K, to form a xerogel. The other half was subjected to supercritical CO_2 extraction to form an aerogel.

Pt/Al_2O_3 catalysts were prepared in a similar manner, using a 1 : 1 molar ratio of aluminum tri-*sec*-butoxide and ethyl acetoacetate as the gel precursor and a precursor concentration of 0.8 M. Subsequent to $LiBH_4$ addition, an aqueous 4.3 M HNO_3 solution was added to induce gelation. Subsequent processing to form xerogels and aerogels was identical to that used for the Pt/SiO_2 samples.

An alternative synthesis method for Pt/SiO_2 involves separate synthesis of Pt clusters and a SiO_2 gel, followed by diffusion of Pt clusters into the gel. The clusters were synthesized by solubilizing 0.01 M $PtCl_2$ in 5 wt% DDAB in toluene, followed by reduction with $LiBH_4$ in THF to give a $Li^+ : Pt^{2+}$ ratio of 3 : 1. The SiO_2 gel was formed from a stock solution of 61 ml TEOS, 61 ml ethanol, 4.87 ml water, and 0.2 ml 1 M HCl, refluxed at 333 K for 1.5 h with stirring. This stock solution was mixed in a 10 : 1 ratio with 0.5 M NH_4OH to cause gelation, and the gel was aged a washed three times with excess ethanol at 323 K for several hours. The gel was next washed three times with excess toluene at 323 K and then immersed in excess Pt cluster solution three times, also at 323 K, to introduce Pt into the gel. Finally, a xerogel was formed by three staged drying cycles of 313, 323, and 393 K each overnight. This sample will be designated Pt/SiO_2^* to distinguish it from the other Pt/SiO_2 xerogel sample.

All samples were calcined in a tube furnace under air. A two stage temperature ramp was used. The samples were held at 523 K for 1 h and then the final temperature for 1 h. The final temperature for the Pt/SiO_2^* sample was 873 K while for the other samples a temperature of 723 K was used. These temperatures were chosen on the basis of thermogravimetric analysis reported earlier (24), which shows that weight loss due to volatilization of the sol-gel precursors is complete by these temperatures.

Metal contents of the catalysts were determined by atomic absorption. Platinum particles sizes and dispersions were determined with transmission electron microscopy and hydrogen chemisorption, as described elsewhere (24). BET measurements of surface area were obtained with a Quantachrome Autosorb-6. Results of these measurements are summarized in Table 1 and discussed in detail elsewhere (24).

All samples were initially obtained as monoliths. The Pt/SiO_2 and Pt/Al_2O_3 monoliths were carefully ground and sieved to obtain a −60/+80-mesh fraction for use in propane dehydrogenation tests. The Pt/SiO_2^* sample was tested using −80-mesh since careful grinding of the monolith did not result in a sufficient quantity of −60/+80-mesh material.

Activity measurements were made in a fixed bed flow reactor. In a typical reaction sequence, the catalyst is heated to the reaction temperature of 823 K in flowing nitrogen, whereupon nitrogen flow is stopped and rectant flow begun. Propane is fed through a calibrated mass flow controller and preheated in a 1/8-inch coiled stainless-steel tube at the reactor inlet. The preheated propane then enters a 3/8-inch stainless-steel tube containing the catalyst, supported on a fine-steel mesh at the bottom of the reactor. Depending on catalyst density, 0.3–0.6 g of catalyst is typically used to give a catalyst bed volume of 3.6 cc. Product gases are exhausted through the sample loop of a HP 5890 gas chromatograph equipped with a flame ionization detector and a 50-m fused silica capillary column (0.32 mm ID) with a Al_2O_3/Na_2SO_4 separation phase, where Cl–C4 hydrocarbons are analyzed. Gas sampling and analysis was performed at 20-min intervals. Oxygen regeneration and hydrogen reduction treatments were often used to achieve maximum catalyst activity. Reactor temperature is measured by three thermocouples externally attached to the top, middle, and bottom of the reactor, and one thermocouple located inside the reactor at the bottom of the catalyst bed.

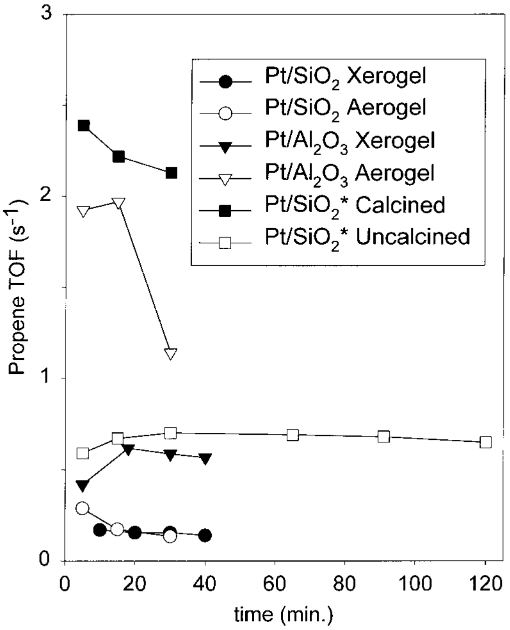

FIG. 1. TOF to propene on the various catalysts as a function of time. The reaction was run with a pure propane feed at a temperature of 823 K.

RESULTS AND DISCUSSION

The good agreement between particle sizes measured by TEM and hydrogen chemisorption (Table 1) indicates that neither particle occlusion nor encapsulation occurs, at least for the samples where both measurements were made. Thus, the Pt particles are not occluded or encapsulated by the support. Note, however, that with the exception of the Pt/SiO_2^* catalysts, the particle size is larger than the pore size, so the Pt particles must be located outside the pores on the external surfaces of the support particles. For further details on characterization, see Ref. (24).

Results of the propane dehydrogenation tests are given in Table 2 and Fig. 1. In general, no consistent activation behavior was observed among the various catalysts. In most cases, hydrogen reduction at the reaction temperature was found to be beneficial, but for one catalyst (Pt/Al_2O_3 aerogel) hydrogen reduction dramatically reduced propene selectivity to less than 10%. Also, the rate of deactivation of the catalysts varied, as did the efficacy of air oxidation to burn off carbon and regenerate the catalysts. Because of these variations among the catalysts, quantitative comparisons are difficult. The reported activities are the best that were achieved on each catalyst, and the prior histories of the catalysts vary as indicated in Table 2. In addition to variations in petreatment, variations in weight hourly space velocity (WHSV) and gas hourly space velocity (GHSV) occurred among the catalysts. The GHSV variations arise as a result of a loss of catalyst bed volume during the reactions, which prevents an *a priori* prediction of the true GHSV. The WHSV variations result from the bed volume changes and differences in density among the catalysts. In general, the initial bed volume was kept constant at ~3.6 cc,

TABLE 1

Physical Properties of Catalysts

Catalyst	Pt loading (wt%)	Particle diameter (nm) H_2 ads.	Particle diameter (nm) TEM[a]	BET surface area (m^2/g)		Average pore size (nm)	
				Initial	After reaction	Initial	After reaction
Pt/SiO_2 xerogel	0.32	4.5	4.5 (2–7)	739	645	1.5	1.3
Pt/SiO_2 aerogel	0.43		4.0 (2–6)	670	260	1.6	1.8
Pt/Al_2O_3 xerogel	0.5	4.9	3.5 (2–5)	468	439	1.1	1.2
Pt/Al_2O_3 aerogel	1.06		>50	336	228	6.9	8.4
Pt/SiO_2^* uncalcined	0.25		2.0 (2)	660	719	6.7	5.2
Pt/SiO_2^* calcined	0.3	2.5	3.5 (2–6)	826	697	6.4	6.4

[a] Values in parentheses show range of particle sizes observed.

TABLE 2

Propane Dehydrogenation Activity and Selectivity at 823 K

Sample	Sample history[a]	WHSV (h^{-1})	GHSV (h^{-1})	Total reaction time (min)	Propane conversion (%)[b]	Propane TOF (s^{-1})[c]	Propene selectivity (%)[d]
Pt/SiO$_2$ xerogel	None	7.0	7044	40	1.3–1.1	0.20–0.17	85
Pt/SiO$_2$ aerogel	Air 823 K, H$_2$ 823 K	6.7	7203	30	6.9–1.5	0.66–0.14	47–90
Pt/Al$_2$O$_3$ xerogel	Air 823 K, H$_2$ 823 K	5.7	8163	40	7.8–6.7	0.78–0.67	80–85
Pt/Al$_2$O$_3$ aerogel	Air 823 K	6.5	3725	30	5.4–2.8	2.4–1.2[e]	83–92
Pt/SiO$_2^*$ xerogel (uncalcined)	Air 823 K, H$_2$ 823 K	4.2	1612	120	15.7–12.3	0.93–0.73	63–90
Pt/SiO$_2^*$ xerogel (calcined 600°C)	H$_2$ 823 K	17.1	7600	30	9.4–7.9	2.7–2.3	86–94

[a] All samples were initially exposed to propane dehydrogenation conditions and then subjected to the treatment indicated before measuring the reported conversions and selectivities.

[b] Initial and final propane conversions are reported. Propane conversion always decreases with time.

[c] TOF based on average particle size from TEM and H$_2$ chemisorption. In cases where hydrogen uptake was not measured, dispersions were calculated from the TEM particle size by assuming hemispherical particles. Initial and final TOFs are reported.

[d] Initial and final propane selectivities are reported. Propene selectivities increase as conversion decreases. Methane is generally the major by-product with smaller amounts of ethane and ethylene.

[e] TOF calculation based on estimated Pt particle size of 50 nm.

provided a sufficient quantity of the −60/+80-mesh fraction was available. In order to compensate for the space velocity variations, both propane conversion/selectivity and propane turnover frequencies (TOF, calculated from measured dispersions, propane conversions, WHSVs, and Pt loadings) are reported. Because conversions are generally less than 10% and therefore far from equilibrium (equilibrium conversion is ∼30% at 823 K), the use of TOFs should compensate for space velocity differences and provide a valid measure of intrinsic activity.

Propane dehydrogenation was not studied over other Pt sol-gel catalysts reported in the literature (6–23), so direct comparison is not possible. Comparison with traditionally prepared catalysts (29–31), and with sol-gel catalysts tested for hydrogenation (13, 17), dehydrocyclization (10, 18, 20), isomerization (18, 20), and hydrogenolysis (18, 20, 23), is possible, however, and will be made as appropriate.

The propane conversion data in Table 2 show that the uncalcined Pt/SiO$_2^*$ xerogel results in the highest conversion of any of the Pt catalysts. Note, however, that the space velocity for this catalyst is substantially lower than for the other catalysts. Of the other catalysts, the calcined Pt/SiO$_2^*$ xerogel gives the highest conversions, although the performance of the Pt/Al$_2$O$_3$ aerogel is comparable if a linear correction for the difference in GHSV is made. Selectivities to propene are substantially better than the value of 60% reported by de Miguel *et al.* (29) at 853 K, but inferior to the values reported by Bariås *et al.* (30) at 792 K for alumina and silica-supported Pt and PtSn catalysts prepared by incipient wetness. This result is consistent with the intermediate temperature of 823 K used here.

On a TOF basis, the calcined Pt/SiO$_2^*$ xerogel and the Pt/Al$_2$O$_3$ aerogel have by far the highest activities. The anomolously low TOF measured over the Pt/SiO$_2$ xerogel is likely due to the fact this sample was never subjected to hydrogen reduction. As a result, surface oxides may have been present on the Pt particles that could not be reduced by propane during reaction. With the exception of this one catalyst, the initial TOFs agree within a factor of 4. Given the uncertainties inherent in measuring dispersion with very low metal loadings, the variation in TOF among the catalysts is not severe and we conclude that all of the catalysts have approximately the same intrinsic initial activity. The magnitudes of the initial TOFs are comparable to or higher than the initial value of ∼0.9 s^{-1} reported by Bariås *et al.* (30) for a traditionally prepared Pt/SiO$_2$ catalyst at 792 K. Using an activation energy of ∼58 kJ/mol, estimated from the temperature dependence reported by Bariås *et al.*, for Sn-promoted Pt/Al$_2$O$_3$ and the isobutane dehydrogenation work of Cortright and Dumesic (31), TOFs for our two best catalysts at 792 K can be estimated to be 1.7 and 1.9 s^{-1}, both superior to the traditionally prepared, unpromoted Pt/SiO$_2$ catalyst of Bariås *et al.* Comparison with initial TOFs for the unpromoted Pt/Al$_2$O$_3$ catalyst of Bariås *et al.* is not possible due to the rapid deactivation observed for that catalyst, which prevented accurate measurement of initial TOFs. The adjusted initial TOFs for our Pt/Al$_2$O$_3$ aerogel and Pt/SiO$_2^*$ xerogel catalysts are larger than those reported by Bariås *et al.* (30) for a Sn-promoted Pt/SiO$_2$ catalyst (1.2 s^{-1}), but lower than those reported for a Sn-promoted Pt/Al$_2$O$_3$ catalyst (3–4 s^{-1}).

Bariås *et al.* noted rapid deactivation over a period of ∼30 min, resulting in loss of more than 90% of the initial activity for both Pt/SiO_2 and Pt/Al_2O_3 catalysts. Other studies of traditionally prepared catalysts also show rapid deactivation of Pt catalysts during dehydrogenation (10, 31–33). In contrast, we find less than a 50% loss in activity for the Pt/Al_2O_3 aerogel, and only a 15% loss for the calcined Pt/SiO_2^* catalyst over a similar time period. In fact, except for the Pt/SiO_2 aerogel, all of our catalysts show higher resistance to deactivation than traditionally prepared catalysts (Table 2), reminiscent of results on other sol-gel prepared catalysts (6, 7, 10, 12, 18, 20). The extents of deactivation of our catalysts are comparable to those reported for traditionally prepared Sn-promoted Pt/Al_2O_3 and Pt/SiO_2 catalysts (30, 33), even though our catalysts contain no tin. The greater resistance of our sol-gel prepared catalysts to deactivation occurs despite the higher reaction temperature used in our study (823 K vs 773 K (33) and 792 K (30)). The deactivation resistance is not an artifact of low conversions (1–10%, see Table 2), since initial conversions of ∼3% can be calculated for both the Pt/SiO_2 and Pt/Al_2O_3 catalysts used by Bariås *et al.* Furthermore, the initial activities of our two best catalysts are comparable to those of the Sn-promoted Pt/Al_2O_3 and Pt/SiO_2 catalysts of Bariås *et al.* Thus, through the use of sol-gel techniques to prepare Pt clusters inside SiO_2 and Al_2O_3 xerogels and aerogels, we have obtained performance with unpromoted catalysts that is comparable to Sn-promoted Pt/Al_2O_3 and Pt/SiO_2 catalysts prepared by incipient wetness. Since deactivation in these catalysts is traditionally attributed to coke formation and addition of Sn inhibits coke formation (29, 30), it is probable that our sol-gel-derived catalysts also inhibit coke formation, as proposed by Lopez (6, 10, 12, 13) and Gonzales(18, 20). Since the metal particles in our catalysts are not always extremely small (Table 1) it seems unlikely that small particle size alone inhibits coke formation. It is likely that the high surface areas of our materials also contribute to the low rates of deactivation (18–20). Interestingly, of the catalysts studied here the two aerogel catalysts are the least resistant to deactivation. Balakrishnan and Gonzales (20) also observed a greater rate of deactivation for a silica aerogel catalyst relative to a xerogel, and attributed the difference to the presence of larger Pt particles in the aerogel catalyst. Larger Pt particles are more susceptible to carbon deposition because of the demanding site requirements for formation of coke precursors. A similar explanation could be advanced for the Pt/Al_2O_3 aerogel catalyst reported here since the Pt particles are very large (>50 nm). The high deactivation rate of the Pt/SiO_2 aerogel cannot be explained on this basis, however. Instead, we note that the aerogels are structurally less stable than the xerogels, losing a greater percentage of the initial surface area during reaction (Table 1). As a result, it is likely that a large fraction of the Pt particles in the aerogels become occluded during reaction and unable to contribute to catalytic activity. Since this loss in activity is largely reversible upon treatment in oxygen, the surface area loss is likely due to fouling of pore mouths by carbon buildup. In other words, the aerogels are less resistant to carbon deposition than the xerogels.

CONCLUSIONS

Using two novel synthesis strategies to make Pt nanoclusters on silica and alumina supports via a combination of inverse micelle technology and sol-gel processing, we have developed catalysts that take advantage of the precise Pt particle size control inherent in inverse micelle techniques while avoiding agglomeration problems arising from the removal of surfactant from the Pt particle surfaces. This synthesis strategy differs from previously reported sol-gel catalyst syntheses in that only nonpolar solvents are used and Pt is introduced to the gels in the form of prereduced surfactant-stabilized metal clusters, rather than as a metal salt or complex that must be reduced by hydrogen treatments subsequent to gelation. Unlike some other sol-gel preparations, the Pt particles in our catalysts are not encapsulated or occluded in the support. Our samples display relatively high catalytic activity and stability over time for propane dehydrogenation, indicating that the synthesis methods described here result in catalyst performance more typical of Sn-promoted Pt/Al_2O_3 or Pt/SiO_2 catalysts prepared by impregnation. This behavior indicates a high resistance to coke formation in our catalysts, much as observed for other sol-gel catalyst preparations.

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