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Effect of organic capping layers over monodisperse platinum nanoparticles upon activity for ethylene hydrogenation and carbon monoxide oxidation

John N. Kuhn [1], Chia-Kuang Tsung [1], Wenyu Huang, Gabor A. Somorjai *

Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720, United States
Chemical and Materials Sciences Divisions, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, United States

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ABSTRACT

The influence of oleylamine (OA), trimethyl tetradecyl ammonium bromide (TTAB), and polyvinlypyrrolidone (PVP) capping agents upon the catalytic properties of Pt/silica catalysts was evaluated. Pt nanoparticles that were 1.5 nm in size were synthesized by the same procedure (ethylene glycol reduction under basic conditions) with the various capping agents added afterward for stabilization. Before examining catalytic properties for ethylene hydrogenation and CO oxidation, the Pt NPs were deposited onto mesoporous silica (SBA-15) supports and characterized by transmission electron microscopy (TEM), H_2 chemisorption, and elemental analysis (ICP-MS). PVP- and TTAB-capped Pt yielded mass-normalized reaction rates that decreased with increasing pretreatment temperature, and this trend was attributed to the partial coverage of the Pt surface with decomposition products from the organic capping agent. Once normalized to the Pt surface area, similar intrinsic activities were obtained regardless of the pretreatment temperature, which indicated no influence on the nature of the active sites. Consequently, a chemical probe technique using intrinsic activity for ethylene hydrogenation was demonstrated as an acceptable method for estimating the metallic surface areas of Pt. Amine (OA) capping exhibited a detrimental influence on the catalytic properties as severe deactivation and low activity were observed for ethylene hydrogenation and CO oxidation, respectively. These results were consistent with amine groups being strong poisons for Pt surfaces, and revealed the need to consider the effects of capping agents on the catalytic properties.

1. Introduction

Colloidal synthesis and application of metal nanoparticles (NPs) are active areas of research [1,2]. Heterogeneous catalysis is a popular application because the size and shape control achievable through colloidal synthesis leads to well-defined structures, which permit unprecedented active site uniformity and, therefore, high catalytic activity and selectivity. However, commonly overlooked variables are the various synthetic additives used for control of the size and shape. Since capping agents manipulate the metals' growth behaviors during synthesis, the capping layer should also alter other – including catalytic – properties. The behavior may be similar to the altering of the catalytic properties by the reaction co-adsorbates. Researchers have suggested that the capping agent may be a major player in determining the catalytic properties of the metal, and the role could depend upon the reaction [3]. Moreover, during treatment protocols or under reaction conditions, decomposed products from the capping agents may adsorb onto the metal surface and alter the catalytic properties. Consequently, the effect of capping agent upon the catalytic properties is a worthwhile research endeavor, and it is important for the application of metal NPs prepared by colloidal synthesis.

For Suzuki reactions in aqueous solutions using Pd NPs, the activity and stability depended on whether Pd was capped by a linear polymer, a block polymer, or a dendrimer [4]. However, this study was performed in the liquid phase where capping agents would be expected to remain intact. Evaluation of polymer and dendrimer capping for gas phase catalysis demonstrated similar catalytic activities for a structure-insensitive reaction and, when Pt NPs were of similar sizes, for a structure-sensitive reaction [5]. The aim of this work is to provide a more extensive study comparing Pt NPs capped by common synthetic agents.

Here, we evaluated the influence of oleylamine (OA), trimethyl tetradecyl ammonium bromide (TTAB), and polyvinylpyrrolidone (PVP) capping agents upon the catalytic properties for ethylene hydrogenation and carbon monoxide oxidation over monodisperse Pt NPs supported on mesoporous silica. Our approach, which is depicted in Scheme 1, allowed for the use of different capping agents without altering the synthetic procedure. This approach is possible

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* Corresponding author. Address: Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720, United States. Fax: +1 510 643 9668.
E-mail address: somorjai@berkeley.edu (G.A. Somorjai).

[1] These authors contributed equally to this work.

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Scheme 1. Synthesis strategy for SBA-15-supported Pt NPs with different capping agents.

because the Pt NPs are stable without a capping agent at the highly basic conditions at which they are formed. A capping agent is necessary to prevent aggregation at neutral conditions, which are used for immobilization onto a support. The benefit of this approach is that, unlike most procedures, the capping agent is not used directly in the synthesis and, consequently, can be chosen.

2. Experimental

2.1. Synthesis of capped Pt nanoparticles

Capped Pt NPs were synthesized using established methods from the literature [6–9] with a slight modification to allow for use of different capping agents. Chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, 99.9% pure on metals basis), oleylamine (OA), and trimethyl tetradecyl ammonium bromide (TTAB), and polyvinlypyrrolidone (PVP) with a molecular weight of 29,000 were purchased from Sigma–Aldrich. NaOH was dissolved in ethylene glycol (12.5 mL, 0.5 M), and this solution was added to an ethylene glycol solution (12.5 mL) containing $H_2PtCl_6{\cdot}6H_2O$ (0.25 g, 0.48 mmol). Under a N_2 atmosphere, this combined solution was held at 433 K for 3 h. The resulting NPs were precipitated with 2 M HCl and were dispersed in a mixture containing both ethanol and the desired capping agent.

2.2. Synthesis of mesoporous silica

Mesoporous SBA-15 silica was prepared using the standard procedure [10]. At 308 K, Pluronic P123 (6.0 g, BASF) was dissolved in DI water (45 g) and 2 M HCl (180 g) while stirring. Tetraethylorthosilicate (12.8 g, Sigma–Aldrich, 98%) was added to the solution, and stirring was continued for 20 h at 40 °C. The mixture was then aged at 373 K for 1 day. After the resulting powder was obtained by filtration and purified via washing with ethanol and DI water, it was dried in air at 373 K and was finally calcined at 823 K for 6 h.

2.3. Deposition of Pt nanoparticles onto mesoporous silica

The Pt NPs were loaded onto mesoporous SBA-15 silica prior to catalytic and chemisorption studies. SBA-15 was added to the Pt NP colloidal solution, and the solution was sonicated (VWR ultrasonic cleaner, 75 T, 120 W, 45 kHz) for 3 h. The SBA-15 supported NPs were separated from the solution by centrifugation (Thermo Scientific IEC Centra® CL2). The supported Pt catalysts were obtained by decanting the solvent and then by washing to remove excess capping agent. The Pt/SBA-15 catalysts were washed with water, ethanol, and tetrahydrofuran, respectively, for the removal of TTAB, PVP, and OA. Finally, the Pt/SBA-15 catalysts were dried under ambient conditions and then at 100 °C.

2.4. Synthesis of standard Pt catalyst

For comparison, a standard Pt catalyst was prepared by supporting Pt onto SBA-15 by wetness impregnation (WI). $H_2PtCl_6{\cdot}6H_2O$ was dissolved in a large excess of a DI water/ethanol solution. After the desired mass of SBA-15 was added, this solution was sonicated. Finally, the excess solvent was removed by rotoevaporation. Finally, the Pt/SBA-15 catalyst was dried under ambient conditions and then at 100 °C.

2.5. Characterization

TEM images of the supported Pt NPs were acquired using a FEI Tecnai G2 S-Twin electron microscope at an accelerating voltage of 200 kV. Pt loadings of SBA-15-supported catalysts were confirmed by inductively coupled plasma mass spectrometry (ICP-MS) and/or by electron probe microanalysis (EPMA) on a Cameca SX-51 instrument. ICP-MS measurements were performed by Galbraith Laboratories, Inc. (Knoxville, TN). Physisorption and chemisorption isotherms were obtained using an Autosorb-I (Quantrachrome Instruments). Before measuring N_2 isotherms at 77 K, samples were degassed overnight at 473 K. Metal dispersions were determined by extrapolation of the total H_2 adsorption isotherm (measured at 30 °C) to zero pressure. Treatments prior to collecting adsorption isotherms were similar to those performed prior to the catalytic studies. For the capped Pt NPs, treatments consisted of heating at 10 °C min^{-1} in O_2 (50 mL min^{-1}) to the desired temperature. After exposure to O_2 for 60 min, the cell was purged with He (50 mL min^{-1}) for 30 min and followed by reduction in H_2 (50 mL min^{-1}) for 60 min. Finally, after raising the temperature 10 °C, the cell was evacuated for 90 min. A similar treatment was used for the WI-prepared sample, but only the reduction and evacuation steps were performed prior to chemisorption.

2.6. Catalytic testing

Catalytic rates under differential conditions for ethylene hydrogenation and carbon monoxide oxidation were performed over Pt/SBA-15 catalysts in a laboratory-scale flow reactor operated at atmospheric pressure. Gas flows (Praxair, UHP) were regulated using calibrated mass flow controllers. Temperature was controlled by a type-K thermocouple and a PID controller (Watlow 96). Catalysts were diluted with low surface area quartz sand (acid washed, DI water rinsed, and calcined before use), and were loaded into quartz reactors. C_2H_4 hydrogenation rates were obtained in 10 Torr C_2H_4 and 100 Torr H_2 with a balance of He. For ethylene hydrogenation, pretreatments were similar to those performed before chemisorption and consisted of oxidation for 1 h in 10% O_2/He (50 mL min^{-1}), He purging (50 mL min^{-1}) for 0.5 h, and reduction for 1 h in 10% H_2/He (50 mL min^{-1}) at various temperatures. CO oxidation rates were acquired in 40 Torr CO and 100 Torr O_2 with a balance of He. Similar results were obtained for CO oxidation when the catalysts were pretreated prior to the reaction (same conditions as stated for ethylene hydrogenation) or no pretreatment was performed. Gas compositions were analyzed with flame ionization detector (FID) and thermal conductivity detector (TCD) on a HP 5890 Series II gas chromatograph (GC). Under the conditions reported in this work, no conversion was obtained for either reaction when unsupported SBA-15 was used as the catalyst. Turnover frequencies (TOFs) were calculated by normalizing conversion to the number of available surface Pt atoms as measured by H_2

chemisorption or calculated based on size arguments. When low temperature pretreatments ($T = 100$ and 150 °C) were used for ethylene hydrogenation, the number of available surface Pt atoms was determined by size arguments (i.e., a 1.5 nm Pt NP contains 75% of its atoms at the surface).

3. Results

3.1. Catalyst details

The as-synthesized Pt NPs were 1.5 nm in diameter, which was very similar to results previously reported using this synthesis technique [6,8]. TEM images of the supported Pt NPs capped by OA (Fig. 1a) and PVP (Fig. 1c) showed no particle size increase after distribution throughout the mesoporous channels of SBA-15. Unlike the use of OA and PVP, the use of TTAB as the capping agent led to noticeable aggregation as the Pt NPs were between 3 and 4 nm (Fig. 1b). This conclusion was also supported by H_2 chemisorption results.

As presented in Table 1, the Pt dispersions (percentage of metal surface atoms out of total metal atoms assuming each surface atom adsorbed one H atom) of the PVP- and OA-capped NPs were approximately five times higher after 200 °C treatments than that of the TTAB-capped ones. However, these results must be viewed with caution because particle size was not the only factor influencing the dispersion. The capping agent or its remnants could be blocking sites. PVP, the most studied of these capping agents, decomposed to form carbonaceous materials, which covered a portion of the Pt surface [5,11,12]. Consequently, the effective particle size calculated from the metal dispersion will not reflect the true particle size. These factors are demonstrated when comparing the dispersions obtained after treatments at different temperatures. As exhibited by the catalyst prepared by wetness impregnation (WI), dispersion generally decreased as the treatment temperature increased. In contrast, OA- and TTAB-capped Pt NPs showed a higher dispersion after the higher temperature treatment than after the lower temperature one. For the PVP-capped Pt NPs, the decrease in the dispersion with increasing treatment temperature could be caused by aggregation (presumably as occurred for the WI catalyst) or increased site blocking by amorphous carbon.

Additionally, TTAB-coated Pt NPs were more difficult to be immobilized onto SBA-15. This result is evidenced by the measured Pt loadings of the supported catalysts (Table 1). The nominal Pt loading of each catalyst was 0.25% by mass. When OA and PVP were used as the capping agents, the majority of the Pt ended up in the final catalysts, meaning that it ‘survived’ the synthesis, loading, and purification steps. However, for TTAB-capped Pt, the yield of Pt was much lower in comparison.

As described in this section, capping agents directly (available metal surface due to site blocking) and indirectly (particle size increase by decreased stability) influenced the physiochemical properties of the Pt surface. The remaining portion of this paper focuses on highlighting the catalytic differences caused by these influencing factors (Sections 3.2 and 3.3), the origins of these factors (Section 4.1), a novel technique for characterization of these materials (Section 4.2), and our ongoing work on the role of synthetic additives in catalysis (Section 4.3).

3.2. Ethylene hydrogenation activity

Ethylene hydrogenation was selected as the initial test reaction because it is structure insensitive and occurs with high rates. Structure insensitivity or activity being independent from particle morphology means that the measured differences in rate are associated to the capping agents. High rates mean that the reaction is

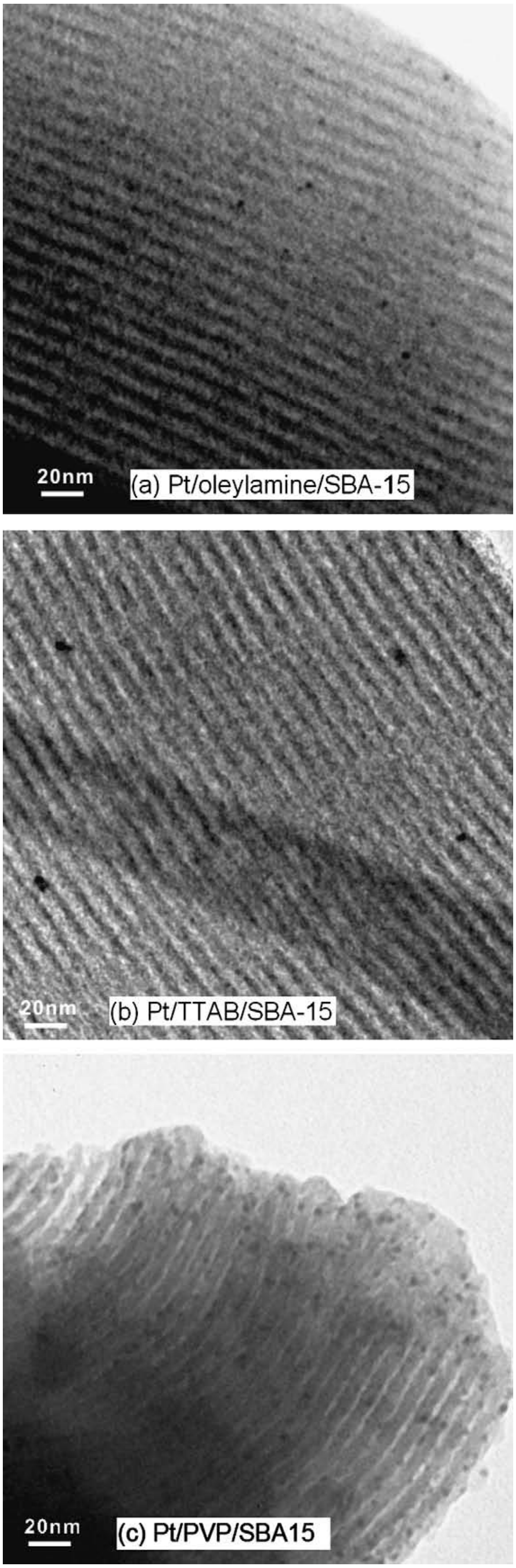

Fig. 1. TEM images of 1.5 nm Pt NPs capped with (a) oleylamine, (b) TTAB, and (c) PVP, and supported on SBA-15.

Table 1
Description and characterization of Pt/SBA-15 catalysts prepared with different capping agents.

Abbreviation	Capping agent	% Pt	Dispersion (%)[a]	
			T = 200 °C	*T* = 300 °C
PVP	Polyvinylpyrrolidone	0.20	34	41
OA	Oleylamine	0.20	39	51
TTAB	Trimethyl tetradecyl ammonium bromide	0.10	7	12
WI	Wetness impregnation	0.25	98	13

[a] Dispersion calculated from total H_2 isotherm measured at 30 °C following treatments at the denoted temperatures.

performed at low temperatures, and also that low temperature pretreatments are able to be evaluated. As shown, respectively, in Figs. 2–4 for PVP-, TTAB-, and OA-capped Pt NPs, the activity is reported at 20 °C as a reaction rate (millimoles of ethane formed per gram of Pt per second) and an intrinsic activity or turnover frequency (TOF defined as molecule of ethane formed per surface Pt atom per second). The catalyst prepared by WI is included for comparison (Fig. 5). All activation energies were approximately 10 kcal mol^{-1}, so only TOFs at 20 °C are reported here.

The results demonstrated that the catalytic properties were dependent on the capping agent. PVP-capped Pt had a TOF near 10 s^{-1} after treatments at 200 °C and below. After a 300 °C pretreatment, both the TOF and the mass-normalized rate were low. This result was consistent with products from PVP decomposition blocking the catalyst surface [11,12]. Compared to PVP-capped Pt, TTAB-capped Pt was much less active in terms of both TOF and its mass-normalized rate. The low rate was partially explained by its low dispersion, but other factors, as discussed in Section 4.1, must also contribute to its low rate and TOF. In contrast, OA-capped Pt yielded high activity as exhibited by initial TOFs between 20 and 30 s^{-1}.

In addition to initial catalytic activity, the capping agents also caused Pt to undergo different deactivation behaviors. No deactivation was observed over TTAB-capped Pt and the WI-prepared Pt, so the values shown in Figs. 3 and 5 also represent steady-state values. Although the PVP-capped Pt did exhibit deactivation, its rate was not severe (4.5 ± 1.7% per hour on stream) and was independent of treatment temperature. OA-capped Pt was stable after the 100 °C pretreatment. However, it demonstrated severe deactivation (>20% per hour) on stream after higher temperature treatments.

The traditionally prepared WI catalyst displayed TOFs near 5 s^{-1} regardless of the treatment temperature, which agreed superbly with the results acquired over model Pt surfaces. TOFs for Pt(1 1 1) [13], Pt(1 0 0)-(5 × 20) [14], and Pt(2 1 0) [15] were 4.5, 2.7, and 5.8 s^{-1}, respectively, after correcting (to 20 °C with reported activation energies or, if none given, assuming 10 kcal mol^{-1} and zero- and first-order dependence upon ethylene and hydrogen, respectively) to the conditions used in this paper. Similar results were also reported over Pt NP arrays and nanowires [16,17]. For supported Pt NPs, TOFs (after correcting to our standard conditions in the same way as described above) of 12–18 [18], 2–4 [19], 0.5 [8], 3 [9], and 9–11 [20] s^{-1} have been reported. Therefore, the WI-prepared Pt and PVP-capped Pt (when pretreated at 200 °C and below) displayed TOFs in the range described as typical. However, activities of TTAB- and OA-capped Pt were outside this range, and these results will be discussed in greater detail (Section 4).

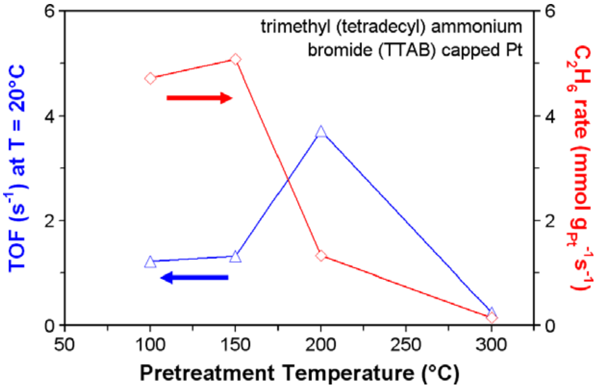

Fig. 3. Ethylene hydrogenation activity over SBA-15-supported 0.1% Pt with TTAB capping. Each pretreatment consisted of oxidation for 1 h in 10% O_2/He, He purging for 0.5 h, and reduction for 1 h in 10% H_2/He. Reaction conditions: 10 Torr ethylene/100 Torr H_2/balance He at 1 atm, *T* = 20 °C, no deactivation was observed.

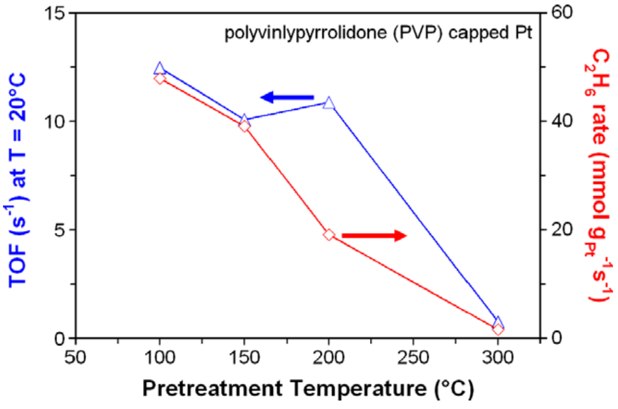

Fig. 2. Ethylene hydrogenation activity over SBA-15-supported 0.2% Pt with PVP capping. Each pretreatment consisted of oxidation for 1 hr in 10% O_2/He, He purging for 0.5 h, and reduction for 1 h in 10% H_2/He. Reaction conditions: 10 Torr ethylene/100 Torr H_2/balance He at 1 atm, *T* = 20 °C, initial activity with 4.5 ± 1.7% activity loss (independent of pretreatment temperature) per hour on stream.

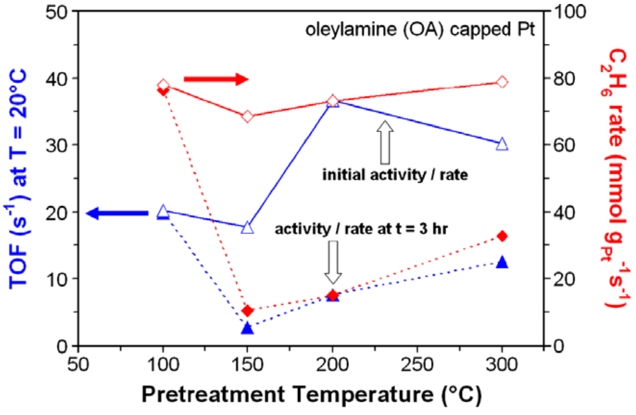

Fig. 4. Ethylene hydrogenation activity over SBA-15-supported 0.2% Pt with OA capping. Each pretreatment consisted of oxidation for 1 h in 10% O_2/He, He purging for 0.5 h, and reduction for 1 h in 10% H_2/He. Reaction conditions: 10 Torr ethylene/100 Torr H_2/balance He at 1 atm, *T* = 20 °C.

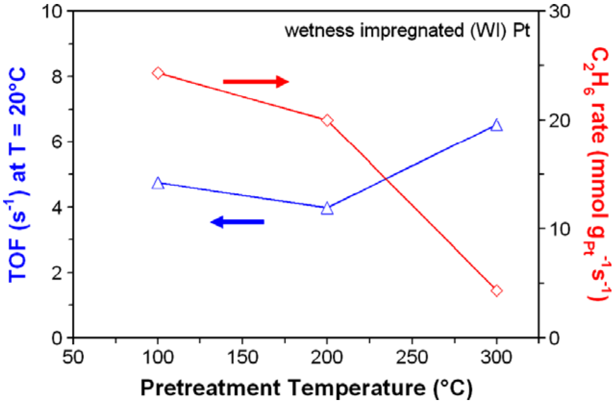

Fig. 5. Ethylene hydrogenation activity over 0.25% Pt/SBA-15 prepared by WI. Each pretreatment consisted of reduction for 1 h in 10% H_2/He. Reaction conditions: 10 Torr ethylene/100 Torr H_2/balance He at 1 atm, $T = 20$ °C, no deactivation was observed.

3.3. CO oxidation activity

The same four catalysts were also tested for carbon monoxide (CO) oxidation (Fig. 6), and the catalytic activity was again dependent upon the capping layer. PVP- and TTAB-capped Pt were more active than OA-capped Pt and WI-prepared Pt. Activation energies for all catalysts were between 21 and 26 kcal mol^{-1}, which suggested that no mechanistic changes occurred. Intrinsic activities were similar for PVP- and TTAB-capped Pt. OA-capped Pt had low activity, which was in agreement with the amine groups acting as a poisonous species. The WI-prepared Pt catalyst showed activity similar to that of the OA-capped Pt, but since the dispersion was much higher than that of the other catalysts, particle size effects (smaller Pt crystallites were demonstrated as less active than larger ones [21]) are presumably influencing the results. Over a Pt(1 1 1) single crystal [22], the TOF corrected to the present conditions yielded a value near 1 s^{-1}, so the capped Pt NPs exhibited a lower activity than the bulk Pt. The activity differences were interesting because the capping agents that yielded the more active catalysts for CO oxidation were different from those that yielded the more active catalysts for ethylene hydrogenation. These different trends demonstrated that, as suggested by the El-Sayed group [3], the optimal capping agent may depend upon the particular reaction.

4. Discussion

4.1. Origins of capping agent-induced catalytic differences

The main differences between the capping agents are their solubility in the solvents during washing, their structure, their binding strength to the Pt surface, and their thermal stability. The capping agents used in this paper are expected to show a wide range of behaviors in these properties. For example, PVP is a polymer that yields a structure that is very different from those yielded by other capping agents and its interaction with Pt is primarily through a charge transfer with a carbonyl. On the other hand, TTAB has weaker Coulombic interactions to Pt than water, which should result in a greater amount being removed during washing. OA is likely to be bound strongly to the Pt surface via the amine group, which is a known poison for precious metal catalysts.

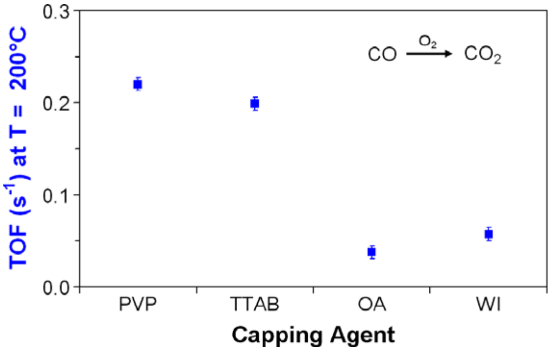

Fig. 6. Carbon monoxide oxidation over Pt/SBA-15 catalysts as a function of capping (see Table 1 for catalyst notation). Conditions: 40 Torr CO/100 Torr O_2/balance He at 1 atm, steady-state values.

Previous studies [11,12] on PVP-capped Pt demonstrated that thermal stability led to different Pt surface species in the temperature range used in this study. When heated in air, polymer crosslinking and densification began at 150–200 °C. Exposure to a higher temperature (300 °C) then led to the formation of amorphous carbon. Under reducing conditions, PVP degradation occurred above 170 °C. These molecular transformations of PVP were responsible for the continual decrease in the mass-normalized ethylene hydrogenation rate as the treatment temperature increased by decreasing the number of available Pt surface sites. Decomposed PVP covered the surface by either adsorbed pyrrolidone fragments or amorphous carbon. Even intact PVP covered more of the Pt surface after treatments due to crosslinking and densification, which led to a greater degree of carbonyl groups associating to Pt. Consequently, PVP transformations are only believed to cause changes in the available surface sites, but not to alter the intrinsic activity of an active site.

Due to the ionic nature of TTAB, it is more easily washed away than the other capping agents in their respective washing solutions. With less capping material available, it is not surprising that slight agglomeration occurred as was evidenced in the lower dispersion and larger particle size compared to the other capped Pt catalysts. Additionally, a spectroscopic study [23] indicated that ammonium cations, which remained after fragmentation of the hydrocarbon tail, covered the Pt surface at temperatures above 200 °C regardless of the gas environment (N_2, O_2, and 10% H_2/Ar studied). Using CO as a probe molecule, this work further demonstrated that the ammonium cation layer prevented CO adsorption (decreasing band intensity) although it did not alter the nature of the adsorbed species (constant band position). These two factors indicated that the reaction results from the present work were only influenced by the available Pt surface and not by a change in the intrinsic activity. For ethylene hydrogenation, the decreasing mass-normalized rate with increasing treatment temperature was consistent with the literature finding [23] demonstrating an increase in the ammonium cation surface coverage. For CO oxidation, the activities of the TTAB- and PVP-capped Pt surfaces were similar, which again highlights that these capping layers only alter the available Pt surface.

The OA-capped Pt demonstrated severe deactivation for ethylene hydrogenation and a low activity for CO oxidation. Since amine groups are known poisons for precious metal catalysts [24,25], these results are not surprising. This behavior serves as a reminder that the synthetic additives for morphology control of nanostructured catalysts must be chosen with the catalytic application in mind. For example, thiol-based synthetic additives would also likely poison the metal surfaces in a similar fashion as OA did in this instance. Additionally, shape-directing agents such as Fe [26] and Ag [27] are commonly used. In the case of Ag, it is a known poison for ethylene hydrogenation over precious metals [28] and it led to low activity for Pt unless it was properly removed [20,29]. Use of Br rather than of metal ions for shape control demonstrated a negligible effect on ethylene hydrogenation activity [30]. We present these examples in the light of our results using OA as a capping agent to stress the importance of keeping the application in mind while developing the synthetic approach for achieving the desired morphological control. Finally, whereas the current examples demonstrated decreased performance based on the synthetic approach, potential exists for boosting activity and/or selectivity with the judicious selection of the capping ligands. For example, Ag-decorated precious metal cubes may have a unique ability to selectively form ethylene during acetylene hydrogenation.

4.2. Estimation of metallic surface area by ethylene hydrogenation

Ethylene hydrogenation is a classical example of a structure-insensitive reaction [25,31]. The phenomenon that the intrinsic catalytic activity is not a function of the Pt surface for this catalytic reaction is quite interesting in itself, but is beyond the scope of the present work. Instead, we wish to exploit the phenomenon as a chemical probe. In particular, we aim to demonstrate ethylene hydrogenation as a chemical probe for estimating the available metallic Pt surface area and consequently the dispersion. This technique is used not to replace chemisorption as the primary technique, but rather to allow measurements under conditions that prevent chemisorption results (i.e., after low temperature treatments when capping layers are present) or prior to scaling up nanoparticle synthesis to the large sample amount needed for chemisorption.

To use this technique, a TOF value for ethylene hydrogenation must be established. Based on the literature for Pt single crystals [13–15], traditionally prepared supported Pt catalysts [18,19], supported Pt nanoparticles [9,20], Pt NP arrays [16,17], and Pt nanowires [16], an average TOF (after being corrected to the conditions reported in this paper in the same manner as described in Section 3.2) was 8.7 s^{-1}. Using this value as a normalization factor, dispersions were estimated from ethylene hydrogenation as a chemical probe technique (Table 2). The OA-capped Pt was not included due to its high level of deactivation.

For PVP-capped Pt, the dispersion estimation from ethylene hydrogenation demonstrated that the use of size arguments (dispersion of 75%) for calculating the dispersion after low temperature treatments (100 and 150 °C) was acceptable. In agreement with the TEM images showing large particles sizes for TTAB-capped Pt, size arguments did not appear as reliable as they did for PVP-capped Pt. After the 200 °C treatment for the PVP-capped Pt, good agreement was found between the two techniques as dispersions of 34% and 43% were obtained. This analysis may also shed light on the behavior of the PVP-capped Pt at a high temperature. Using chemisorption results (dispersion of 41%), the calculated TOF after the 300 °C treatment was 0.8 s^{-1}, which is much lower than expected. The decomposition products of PVP after the high temperature treatments were potentially able to either directly adsorb H_2 or uptake hydrogen from the Pt surface through a spillover mechanism. In either case, it led to a high H_2 adsorption amount, and to a low intrinsic activity when normalized by chemisorption results.

Therefore, due to the general agreement between the two techniques and the plausible explanation for the lone difference, we conclude that the capping layers did not influence the intrinsic activity and instead only influenced the metallic surface area. This phenomenon is not applicable to structure-sensitive reactions where the metallic surface area is related to the surface structure and consequently to the TOF. It could be used independently as an estimation of the fraction of the loaded metal that is catalytically available.

Table 2
Dispersion (%) estimates from ethylene hydrogenation ($R \times n$) rates[a] as compared to chemisorption (H_2) results as a function of pretreatment temperature.

Catalyst	T = 100 °C		T = 150 °C		T = 200 °C		T = 300 °C	
	H_2	$R\times n$	H_2	$R\times n$	H_2	$R\times n$	H_2	$R\times n$
PVP	n/a	108	n/a	88	34	43	41	4
TTAB	n/a	10	n/a	11	7	3	12	<1

[a] Dispersion calculated from ethylene hydrogenation was the measured TOF assuming 100% dispersion divided by the average TOF from the literature (8.7 s^{-1}) * 100%.

4.3. Ongoing research on influence of synthetic additives

Based on the current results and our desire to characterize interactions between adsorbed species on metal nanoparticles, we will continue to research the influence of synthetic additives. Currently, we are investigating dendrimers as a NP-templating and capping agent. [32] Our initial results demonstrated that dendrimer-encapsulated NPs behaved similarly as PVP-capped Pt [5]. However, we will extend that study by using G6OH (hydroxyl-terminated generation 6 PAMAM dendrimers) to synthesize metal clusters that are of the same size as the NPs in this study, and will give a more direct comparison of the role of the capping agent. Moreover, to study the clean metal NPs, a UV–ozone cleaning procedure was developed to remove the capping layers on two-dimensional films [33]. The method is advantageous because it does not involve thermal treatments, and has the potential to be applied to 3-dimensionally supported metal catalysts. Finally, as described in great detail in Section 4.1, the ability of synthetic additives to alter the catalytic properties of precious metals also demonstrates that there is potential for using these additives to improve the catalytic selectivity, and we will evaluate this area in our future work.

5. Conclusions

Pt NPs were synthesized by the same procedure with three different capping agents in order to study the influence of the capping layer on the catalytic activity. Prior to examining catalytic properties using ethylene hydrogenation and CO oxidation, the Pt NPs were supported onto mesoporous silica (SBA-15) and characterized by TEM, H_2 chemisorption, and elemental analysis. For polymer (PVP)- and ammonium (TTAB)-capped Pt, our results demonstrated that the capping agents influenced the available metal surface but not the intrinsic activity. Based on these results, ethylene hydrogenation was proposed as a chemical probe for estimating the metallic surface of Pt. Amine (OA) capping had a more involved influence on the Pt surface as it led to deactivation during ethylene hydrogenation and low CO oxidation activity. Since amine groups are strong poisons for precious metal catalysts, this demonstration is evidence of considering the application while developing the synthetic procedure.

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