Ensemble Size Effects on Toluene Hydrogenation and Hydrogen Chemisorption by Supported Bimetallic Particle Catalysts

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Silica-supported bimetallic catalysts were prepared by decomposing the molecular clusters $Pt_2Au_4(C\equiv C^tBu)_8$ and $Pt_2Cu_4(C\equiv C^tBu)_8$. The resulting catalysts were characterized with hydrogen, oxygen, and carbon monoxide chemisorptions. These indicated that CO chemisorption is the preferred method for evaluating metal dispersion. Chemisorption results also suggested that different types of substrate binding sites may be present on the bimetallic particles and that a significant fraction of the available platinum atoms may not be capable of activating hydrogen. Catalytic activity was evaluated with the toluene hydrogenation reaction. The new catalysts were found to be relatively inactive for this reaction at 60 °C, despite having high platinum dispersions. Apparent activation energies for toluene hydrogenation were evaluated with Arrhenius plots. Although activities were low at 60 °C, the cluster-derived catalysts had smaller apparent activation energies than a traditionally prepared Pt/silica catalyst. Trends in hydrogen chemisorption and toluene hydrogenation are discussed in terms of possible electronic, particle size, and ensemble size effects.

Introduction

Supported noble metal catalysts are employed in a wide variety of economically and environmentally important catalytic processes such as the automotive catalytic converter and the refining of petroleum. Considerable efforts have gone toward preparing catalysts in which the metal is as finely dispersed on the support as possible. The economics behind this are straightforward. Because metals such as platinum, palladium, rhodium, and iridium are expensive, maximizing the exposed metal surface area minimizes the material investment in the catalyst. Further, when particle sizes become very small (<1 nm), the particle may begin to lose some of its metallic character[16] and new catalysts with unique morphologies and properties may arise. As particle sizes decrease to the point where particles contain only several atoms, traditional notions of the structure sensitivity or insensitivity of a reaction may also be altered. In this range, even minor differences in particle size can have significant effects on catalytic reactivity. These effects can go far beyond merely increasing or decreasing the fraction of metal surface area exposed.[16] The now well-documented studies of high aromatization activity by platinum supported on alkaline zeolites[9,25,31] is an excellent example of this phenomenon. In the best catalysts, the platinum is present as very small particles (as few as 5−12 atoms) within the cage structure of the zeolite.[25] Beyond the suggested role of inhibiting catalyst deactivation from coke deposition,[25] the electronic properties of the zeolite may be important in stabilizing the unique particle morphology that is responsible for the high aromatics selectivity.[31]

Recently, we reported on the preparation and characterization of supported bimetallic Pt−Au and Pt−Cu catalysts using the bimetallic molecular cluster precursors $Pt_2Au_4(C\equiv C^tBu)_8$ and

$Pt_2Cu_4(C\equiv C^tBu)_8$.[14,15] CO chemisorption experiments on the Pt−Au catalysts indicated platinum dispersions >85% and TEM particle size measurements showed particles generally between 1.5 nm (the detection limit of the instrument) and 3.5 nm in diameter. The Pt−Cu catalysts also had platinum dispersions >85% by CO chemisorption; however, the metal particles were too small to be imaged with TEM. In both the Pt−Au and Pt−Cu catalysts, the coinage metal was found to bind significant amounts of carbon monoxide. Catalysis studies with *n*-hexane conversion indicated that both catalysts were selective for C−C bond scission reactions and that skeletal rearrangements (cyclization, isomerization, and aromatization reactions) were slower on the cluster-derived catalysts than on a traditionally prepared Pt catalyst. Further, reactivity data also suggested that, under the hexane conversion reaction conditions, the cluster-derived catalysts had less surface hydrogen than wetness-impregnated Pt catalysts.

The emerging model of these new catalysts is that the catalyst surface is composed of very small and bimetallic particles. Because of the platinum-to-coinage metal ratio in these catalysts (1:2), it is expected that the surfaces of the particles have platinum ensembles with only a few (or possibly even isolated) platinum atoms surrounded by the coinage metal. For the cluster-derived Pt−Cu catalysts in particular, there appear to be few multi-platinum atom ensembles. The platinum−gold catalysts have slightly larger particles (1−3 nm) and are expected to have more multi-platinum ensembles (e.g., 2−5 platinum atoms in a contiguous arrangement or in close proximity) than the platinum−copper catalysts. Because the particles are bimetallic, larger platinum ensembles are, for the most part, rare or absent.

Because the previous catalysis studies suggested differences in hydrogen coverage, the current study examines hydrogen activation and chemisorption on the cluster-derived catalysts. The reactivity data is also extended to include toluene hydrogenation catalysis. Although this reaction is traditionally described as structure insensitive, it was chosen because recent results[1,3,16,46] suggest that this interpretation may not hold true

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for the smallest particles. The results with the Pt−Au and Pt−Cu catalysts described there indicate that both hydrogen activation and toluene hydrogenation become "structure sensitive" as Pt ensemble sizes decrease.

Experimental Section

Catalyst Preparation. The organometallic clusters Pt_2Au_4-$(C\equiv C^tBu)_8$ and $Pt_2Cu_4(C\equiv C^tBu)_8$ were prepared from [N-$(C_4H_9)_4]_2[Pt(C\equiv C^tBu)_4]$ and $Au(SC_4H_8)Cl$ or CuCl via literature procedures.[20] Hexachloroplatinic acid, $H_2PtCl_6\cdot 6H_2O$, was prepared from Pt metal (99.99%) according to literature procedure.[21] Cupric nitrate tetrahydrate $(Cu(NO_3)_2\cdot 4H_2O)$ was purchased from Aldrich. Davisil SiO_2 (35−60 mesh, BET surface area 360 m²/g, average pore diameter = 150 Å) was washed with high purity Millipore distilled and deionized water to remove the fine particles and dried in vacuo at 120 °C for 24 h prior to use. Conventional Pt catalysts were prepared by incipient wetness impregnation of platinic acid onto the dried silica support. The solution concentration was adjusted to give the 0.15-Pt catalyst: (0.15% Pt by weight). The bimetallic clusters Pt_2-$Cu_4(C\equiv C^tBu)_8$ and $Pt_2Au_4(C\equiv C^tBu)_8$ spontaneously adsorbed onto silica from hexanes solution.[14,15] The remaining solvent was decanted and the supported clusters were dried at 60 °C in vacuo to yield the 0.15-Pt_2Cu_4 (0.15% Pt, 0.10% Cu) and 0.15-Pt_2Au_4 (0.15% Pt, 0.30% Au) catalysts. Abbreviations indicate the atomic ratio of metals and are used only to refer to catalysts that have undergone the standard activation protocol (see below). The details of the general procedure have been previously reported for the support of phosphine-stabilized Pt and Pt−Au compounds[13,22] and were similarly employed in this study.

Catalyst Activation. Catalyst activation, chemisorption measurements, and catalytic investigations were carried out with the use of an RXM-100 catalyst characterization system purchased from Advanced Scientific Designs, Inc. All gases were UHP grade (99.999%) and were used without further purification. In a typical experiment, 40−350 mg of the supported catalyst precursors were loaded into a U-shaped quartz microreactor (i.d. = 11 mm), attached to the RXM-100 system, and heated in the presence of flowing gas as described below. With O_2 flowing at 10 mL/min, the temperature was ramped 10 °C/min to 300 °C, held for 2 h, and ramped 10 °C/min back to 30 °C. The sample was purged with He flowing at 100 mL/min for several minutes and the gas was switched to H_2 flowing at 20 mL/min. The temperature was then ramped 10 °C/min to 200 °C under flowing H_2 and held at 200 °C for 1 h. This is the standard activation protocol for all experiments.

Hydrogen Chemisorption and Hydrogen−Oxygen Titrations. All adsorption isotherms were measured at 21 (±2) °C over an equilibrium pressure range of 10−80 Torr using 350 mg of catalyst. All chemisorption calculations used Advanced Scientific Designs, Inc. software. In all the two isotherm chemisorption experiments, strong chemisorption was determined at 80 Torr by subtracting a reversible adsorption isotherm from the total adsorption isotherm. The chemisorption protocol was as follows. After the standard activation protocol, the sample temperature was ramped 10 °C/min to 100 °C, evacuated for 60 min, and cooled to 30 °C under vacuum. The furnace was then replaced with a water bath (21 °C) and a two-isotherm hydrogen chemisorption experiment was performed. This consisted of measuring a total hydrogen uptake isotherm, evacuation of the sample for 5 min, and measuring a reversible hydrogen uptake isotherm.

Next, the water bath was removed, the outside of the microreactor was dried with a towel, and the furnace was attached. The sample was then heated to 100 °C, pressurized
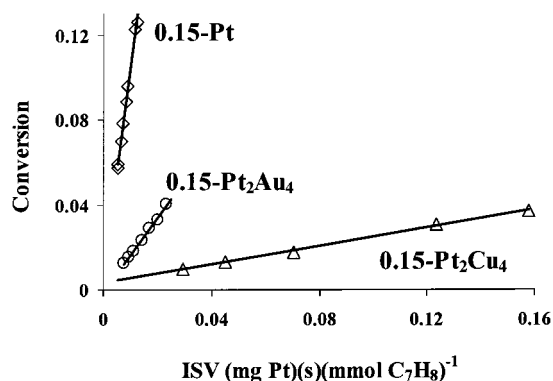

Figure 1. Typical toluene hydrogenation activity plots (conversion vs inverse space velocity) for the 0.15-Pt, 0.15-Pt_2Au_4, and 0.15-Pt_2-Cu_4 catalysts at 60 °C.

with 810−825 Torr H_2, and soaked at 100 °C for 2.0 h. The sample was then cooled to ambient temperature and the furnace was replaced with the water bath. The sample was then evacuated for 5 min at room temperature (the same evacuation time used to remove weakly bound hydrogen in the H_2 chemisorption experiment). A two-isotherm oxygen uptake experiment was then performed, evacuating the sample for 10 min between isotherms. Immediately following measurement of the second O_2 adsorption isotherm, the sample was evacuated for 10 min and a two isotherm CO chemisorption experiment was performed, evacuating the sample for 10 min between isotherms.

Toluene Hydrogenation Catalysis. After the reduction step in the standard activation protocol, the catalyst temperature was cooled 10 °C/min to 60 °C. A saturated toluene (Mallinckrodt, HPLC grade) in hydrogen gas stream was produced with a two-stage bubbler apparatus. The second stage was immersed in a room-temperature water bath (21 °C) giving a hydrogen:toluene ratio of 29:1 (partial pressure of toluene = 23 Torr). Reaction products were analyzed on stream via gas chromatography using a Hewlett−Packard 5890A gas chromatograph operated with an FID detector and a Hewlet−-Packard 3393A integrator. Toluene and methylcyclohexane were separated with a 15 m DB 1301 (film thickness = 1.0 μm) capillary column (J&W Scientific) operated at 35 °C with a head pressure of 15−20 psi.

Catalyst activities at 60 °C were determined from plots of conversion vs inverse space velocity (Figure 1) by calculating the slope of the linear portion of each plot. These plots were always linear below 15% conversion, and overnight catalysis runs showed that catalyst deactivation was less than 5% over 18 h. Because deactivation was not significant over the time scale of these experiments, several activity measurements were made with each sample (8−10 different flow rates, each repeated at least once). A minimum of 15 min was allowed between changing the flow rate of the feed and the first GC injection.

Apparent activation energies were determined by measuring toluene conversion over a range of temperatures, typically between 35 and 80 °C. The feed flow rate was adjusted as necessary to maintain conversions below 25% (most conversions were <15%); 10−15 min was allowed between adjusting the catalyst temperature and injecting a sample into the GC. In a typical experiment, three activity measurements per temperature were made over increasing temperatures (10 °C increments, e.g., 40, 50, 60 °C), followed by three activity measurements per temperature over decreasing temperatures between those made previously (i.e., 55, 45, 35 °C). Arrhenius plots were then prepared and apparent activation energies were calculated from the slope of the best fit line (least squares) through the data (Figure 2).
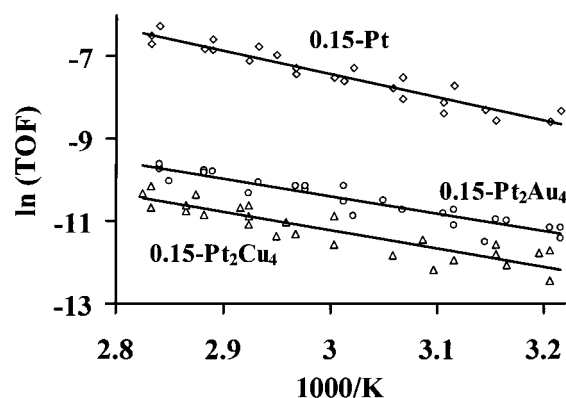
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Figure 2. Arrhenius plots for the 0.15-Pt, 0.15-Pt$_2$Au$_4$, and 0.15-Pt$_2$-Cu$_4$ catalysts.

TABLE 1: Gas Uptake Data for CO Chemisorptions and H$_2$−O$_2$ Titrations

	gas uptakes in μL per g-catalyst		
	0.15-Pt	0.15-Pt$_2$Au$_4$	0.15-Pt$_2$Cu$_4$
CO$_{tot}$[a]	90[c]	220[c]	313[d]
CO$_{str}$[a]	78[c]	150[c]	151[d]
total H$_2$	46	33	39
reversible H$_2$	20	8.1	23
irreversible O$_2$	33	48	130
total CO[b]	90	170	290
irreversible CO[b]	74	100	130

[a] CO chemisorption on freshly activated samples. [b] CO chemisorption after H$_2$−O$_2$ titration. [c] Data originally reported in ref 14. [d] Data originally reported in ref 15.

Results and Discussion

Chemisorption. The catalysts were characterized with hydrogen, oxygen, and carbon monoxide chemisorptions in order to measure hydrogen uptakes and compare the toluene hydrogenation results with those reported in the literature. Gas uptake values are compiled in Table 1, along with CO chemisorption data for fresh catalysts (from refs 14 and 15). The data are normalized to moles of the adsorbed species per mole of PtM$_2$ (M = Au, Cu, or absent) in Table 2. Hydrogen adsorption was measured with H$_2$ chemisorption (H_{tot}) and with an oxygen titration (H_{max}, vida infra). H_{max} was calculated by adding the weakly bound hydrogen (H_{wk} from the H$_2$ chemisorption experiment) to the strongly bound hydrogen measured via oxygen titration (H$_{titr}$) assuming the stoichiometry suggested by Menon et al.[36] and Boudart et al.:[33]

$$4Pt-H + 3O_2 \rightarrow 4Pt-O + 2H_2O$$
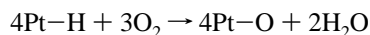
CO chemisorption experiments after the titration yielded CO uptakes similar to those on fresh catalysts, indicating that the titrant oxygen is readily removed via evacuation at room temperature.

For the monometallic 0.15-Pt catalyst, the gas adsorption data obtained with the various adsorbate gases are in good agreement and converge on a dispersion value of around 50%. As is shown in Table 2, the total hydrogen uptake measured by direct adsorption and via oxygen titration is very close to the CO chemisorption value for fresh catalysts and to CO chemisorption values after the titration. A Pt dispersion of 45−50% corresponds to an average Pt particle diameter of approximately 3.5−3.8 nm, a value that is consistent with TEM data in which the average observed particle diameter was 4.4 nm.[14]

Strong hydrogen chemisorption is often used to measure Pt dispersion; with our apparatus, however, the measured value

TABLE 2: Normalized CO Chemisorption and H$_2$−O$_2$ Titration Data[a]

	experiment	0.15-Pt	0.15-Pt$_2$Au$_4$	0.15-Pt$_2$Cu$_4$
d_{ave}[b]	TEM	4.4 nm[f]	2.4 nm[f]	<1 nm[g]
CO$_{tot}$[c]	CO chemisorption	0.52[f]	1.3[f]	1.8[g]
CO$_{str}$[c]	CO chemisorption	0.45[f]	0.88[f]	0.87[g]
H_{tot}	H$_2$ chemisorption	0.53	0.38	0.45
H_{wk}	H$_2$ chemisorption	0.24	0.09	0.27
H_{str}	H$_2$ chemisorption	0.29	0.27	0.18
H_{titr}[d]	O$_2$ titration	0.25	0.38	1.0[h]
H_{max}[e]	H$_2$ chemi & O$_2$ titr	0.49	0.47	1.3[h]
CO$_{tot}$	CO chemi after O$_2$ titr	0.52	1.0	1.7
CO$_{str}$	CO chemi after O$_2$ titr	0.43	0.60	0.78

[a] All chemisorption values normalized to mol adsorbate/mol PtM$_2$ (M = Au or Cu). [b] Average observed particle diameter from TEM. [c] CO chemisorption on freshly activated samples. [d] Calculated using the stoichiometry: $4Pt-H + 3O_2 \rightarrow 4Pt-O + 2H_2O$. [e] $H_{wk} + H_{titr}$. [f] Data originally reported in ref 14. [g] Data originally reported in ref 15. [h] Includes oxygen chemisorbed on copper. See text for details.

for H_{str} gives a significantly lower dispersion (29%, Table 2) than the other chemisorption methods and a much larger average particle diameter (6.2 nm) than is observed in TEM micrographs.[14] The designation of strongly bound hydrogen is an arbitrary one,[27] and depends on the specific treatments to the catalyst (e.g., evacuation temperature, time, and pressure). The lower H_{str} observed for this catalyst is likely due to the low evacuation pressures attained in our apparatus (ca. 1 × 10^{-7} Torr), which likely removes some of the "strongly" bound hydrogen. Because the total hydrogen chemisorption value is in good agreement with both CO chemisorption and TEM data, the total hydrogen uptake appears to be the best means of evaluating hydrogen chemisorption with this protocol, even if it might slightly overestimate Pt dispersion. Examining all the chemisorption and TEM data, the 0.15-Pt catalyst is best described as having Pt dispersion of around 50% and an average particle diameter somewhere around 4 nm.

The microscopy and chemisorption data for the cluster-derived catalysts are less straightforward. For both cluster-derived catalysts, energy dispersive spectroscopy (EDS) and infrared spectroscopy of adsorbed CO suggested the presence of bimetallic metal particles.[14,15] TEM particle size measurements (Table 2) of the Pt$_2$Au$_4$ catalyst yielded an average particle size of around 2.4 nm;[14] metal particles on the Pt$_2$Cu$_4$ catalyst were too small to be imaged with the instrument used and were estimated to be smaller than 1 nm in diameter.[15] Although correlations between TEM particle sizes and Pt dispersions are complicated for bimetallic particles, it is expected that as particle size decreases Pt dispersion should increase. CO chemisorption indicates that this is indeed the case as CO$_{str}$ is greater than 85% for both of the cluster-derived catalysts. The CO chemisorption protocol used in these experiments (adsorption isotherm, evacuation for 30 min, desorption isotherm) was chosen on the basis of control experiments with traditionally prepared bimetallic catalysts so that CO$_{str}$ estimates Pt dispersion.[14,15] This conclusion is also supported by DRIFTS experiments, which indicated that most of the CO desorbs from the coinage metals after flushing with He for 30 min,[12] while most of the Pt−CO remains on the catalyst surface.

Hydrogen chemisorption experiments, however, show an antipathetic trend with respect to particle size and hydrogen uptakes measured with the traditional two-isotherm experiment: despite having smaller particles, H_{tot} and H_{str} are lower for the cluster-derived catalysts than for the catalyst prepared from platinic acid. Because of the disparity between hydrogen and CO chemisorptions, hydrogen chemisorption was also

measured with oxygen titration (H_{max}). The titrations were performed in order to address the possibility that the hydrogen chemisorption experiment significantly under-measures the "true" amount of hydrogen adsorbing on the cluster-derived catalysts. Primarily, two factors were of concern: (1) that the evacuation conditions used in the chemisorption protocol (100 °C for 1 h) might leave some hydrogen on the surface, thus lowering the measured value of adsorbed hydrogen; and (2) that room temperature hydrogen adsorption on the cluster-derived catalysts may be kinetically slow.[27] For Pt, Rh, and Ir, Koningsberger, Prins, and co-workers have shown that slow hydrogen adsorption causes H/M ratios to be artificially low. Further, better correlations were found between H_{tot} (measured by preadsorbing hydrogen at an elevated temperature, cooling the sample to room temperature under hydrogen, and then measuring a desorption isotherm) and EXAFS particle size measurements than when the EXAFS measurements were correlated to strongly bound hydrogen.[27]

For the bimetallic catalysts, the reactivity of the coinage metal also needs to be considered in evaluating the titration data. The titration of strongly adsorbed hydrogen assumes that every surface Pt atom has an adsorbed H atom and that the adsorption stoichiometry is as suggested by Menon et al.[36] and Boudart et al.[33] (vida supra). However, if either naked Pt atoms or coinage metal atoms are present on the surface after hydrogen preadsorption, these atoms are be able to bind oxygen during the titration. Consequently, the measured value for strongly adsorbed hydrogen can only be greater than the "true" value for hydrogen adsorbed on Pt. Indeed, this is why the hydrogen adsorption measured with the titration is designated H_{max}—it likely does include oxygen adsorption on the coinage metal, particularly in the case of the Pt–Cu catalyst. H_{max}, then, represents an upper limit for the hydrogen chemisorption by Pt for each catalyst.

The titration value (H_{max}) suggests that the two-isotherm experiment does indeed slightly underestimate the total amount of hydrogen adsorbed on the Pt$_2$Au$_4$ catalyst. However, the differences between the two hydrogen adsorption experiments are small relative to the difference between hydrogen and CO adsorption (Table 2). For 0.15-Pt$_2$Au$_4$, hydrogen chemisorption is roughly one-third to one-half of the irreversible CO chemisorption on fresh samples. Further, CO chemisorptions performed on 0.15-Pt$_2$Au$_4$ samples immediately after the titrations indicated greater platinum availability than did the titrations. This confirms that the lower hydrogen adsorption is not an artifact of the experimental protocol, but is a property of the cluster-derived catalysts.

Qualitatively, the same general conclusions hold for the cluster-derived 0.15-Pt$_2$Cu$_4$ catalyst: the directly measured hydrogen chemisorption values are lower than CO chemisorption values on fresh catalysts. However, the chemisorption data for this catalyst is greatly complicated by the presence of Cu in the alloy. Quantitative interpretation of the titration results is especially difficult as reduced copper might be expected to bind some hydrogen and certainly is expected to bind oxygen. Consequently, the hydrogen chemisorbed on Pt is overestimated because the oxygen used in titrating adsorbed hydrogen (Pt–H → Pt–O) is only a fraction of the total measured oxygen uptake. With this in mind, H_{max} and H_{tot} indicate that hydrogen adsorption on Pt is less than the irreversible CO chemisorption on this catalyst. As with 0.15-Pt$_2$Au$_4$, CO chemisorption measurements after H$_2$–O$_2$ titrations on 0.15-Pt$_2$Cu$_4$ indicate that hydrogen chemisorption measurements do not accurately represent the dispersion of these catalysts. Because strong CO chemisorption is the only chemisorption method that shows

TABLE 3: Toluene Hydrogenation Activity at 60 °C

catalyst	rate at 60 °C[a]	"TOFs" ($s^{-1} \times 10^3$)			ref
		total Pt[b]	CO[c]	H[d]	
0.15-Pt	235	46	96	90	this work
0.15-Pt$_2$Au$_4$	42	8.1	9.2	19	this work
0.15-Pt$_2$Cu$_4$	8.7	1.7	2.0	4	this work
0.96% Pt/SiO$_2$[d]	132	26	-	27[g]	30
0.96% Pt/SiO$_2$[e]	162	32	-	33[g]	28
0.96% Pt/SiO$_2$[f]	354	69	-	72[g]	28

[a] Rate = μmol/(g Pt ·s). [b] Rate = mol/(s·mol Pt$_{tot}$). [c] Rate corrected for surface Pt measured via CO chemisorption in mol/(s·mol Pt$_{surf}$). [d] Rate corrected for surface Pt measured via H$_2$ adsorption in mol/(s·mol Pt$_{surf}$). For 0.15-Pt and 0.15-Pt$_2$Au$_4$, the average of H_{tot} and H_{max} was used; for 0.15-Pt$_2$Cu$_4$, only H_{tot} was used. [d] Toluene hydrogenation at 60 °C with P_{tol} = 50 Torr, P_{H_2} = 685 Torr. [e] Benzene hydrogenation at 60 °C with P_{bz} = 50 Torr, P_{H_2} = 685 Torr. [f] Benzene hydrogenation at 60 °C with P_{bz} = 35 Torr, P_{H_2} = 700 Torr. [g] TOF reported in original text for dispersion measured with irreversibly bound hydrogen.

increased gas uptake with decreasing particle size, CO$_{str}$ appears to be the most reliable measure of surface platinum for the cluster-derived catalysts.

The differences between the hydrogen and CO chemisorption results also indicate that the surface platinum atoms are not all (chemically) the same. Some are able to bind both CO and H$_2$ (under the conditions of the chemisorption experiments) while some only bind CO. Recent studies by Gates and co-workers using cluster-derived platinum–tungsten, platinum–molybdenum, and palladium–molybdenum catalysts have found similarly disparate results between hydrogen chemisorption measurements, carbon monoxide chemisorption, and EXAFS particle size measurements.[1,2,4,26] Studies with highly dispersed iridium clusters containing only 4–6 atoms also have similar gas adsorption properties.[3] It may also be possible that CO is able to restructure the bimetallic particles, drawing Pt atoms that are unavailable for hydrogen binding to the surface.[6] Such a restructuring has been shown to occur for Pt–Au alloys;[10] however, the observed restructuring was very slow and occurred over several days. Consequently, similar restructuring is unlikely on the time scale of the CO chemisorption experiment (15–20 min for each isotherm measurement); however, this possibility cannot be ruled out.

Toluene Hydrogenation Catalysis. Plots of conversion vs inverse space velocity (ISV) at 60 °C were prepared and used to determine catalyst activity. Typical activity plots for the 0.15-Pt, 0.15-Pt$_2$Au$_4$, and 0.15-Pt$_2$Cu$_4$ catalysts are shown in Figure 1; activity data at 60 °C for the catalysts are compiled in Table 3. The data clearly show that the cluster-derived catalysts (particularly 0.15-Pt$_2$Cu$_4$) are significantly less active than the catalyst prepared from platinic acid. Table 3 also includes toluene and benzene hydrogenation data for a 0.96% Pt/SiO$_2$ catalyst prepared from Pt(NH$_3$)$_4$Cl$_2$, reported by Lin and Vannice.[28,30] Activation energies were determined by measuring activity at various temperatures and preparing Arrhenius plots. These plots for the 0.15-Pt, 0.15-Pt$_2$Au$_4$, and 0.15-Pt$_2$Cu$_4$ catalysts are shown in Figure 2. The apparent activation energies (determined from the slopes of the lines in Figure 2, compiled in Table 4) for the cluster-derived catalysts are somewhat lower than the apparent activation energies of 0.15-Pt, despite the lower activity of the bimetallic catalysts at 60 °C.

The observed TOF for toluene hydrogenation by the 0.15-Pt catalyst (0.095 s^{-1}, Table 3) is in good agreement with data reported in a detailed kinetic and mechanistic study of benzene and toluene hydrogenation by supported platinum catalysts.[28–30] The TOF for toluene hydrogenation reported for a highly dispersed (95% by hydrogen chemisorption) 1% Pt/SiO$_2$ catalyst

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TABLE 4: Apparent Activation Energy Data from Arrhenius Plots[a]

catalyst	E_a (kcal/mol)
0.15-Pt	11.3 ± 1.6
0.15-Pt_2Au_4	8.6 ± 1.2
0.15-Pt_2Cu_4	8.9 ± 1.7
0.96% Pt/SiO_2[b]	10.3 ± 1.0

[a] Errors included with E_a values are the 95% confidence limits. [b] Activation energy reported with $P_{tol} = 50$ Torr, $P_{H_2} = 685$ Torr in ref 30.

(0.027 s^{-1})[30] is slightly lower than the value obtained in this study with the 0.15-Pt catalyst. Experiments reported by Lin and Vannice were performed with 50 Torr toluene and 680 Torr hydrogen while the present study used 22 and 740 Torr, respectively. For benzene hydrogenation, changing the reaction conditions from $P_{H_2} = 50$ Torr and $P_{Bz} = 685$ Torr to $P_{H_2} = 35$ Torr and $P_{Bz} = 700$ Torr more than doubled the turnover frequency of the catalyst from 0.033 (very similar to the toluene hydrogenation value of 0.027) to 0.072 s^{-1}. It is not surprising, then, that the TOFs reported here are slightly higher as they would be expected to follow the trend for benzene hydrogenation.[28] The activation energy determined for the 0.15-Pt catalyst (11.3 kcal/mol) is also in good agreement with the catalyst investigated by Lin and Vannice (10.3 kcal/mol) and with other reports discussed by Lin and Vannice.[29] Similar activation energies (12 ± 2 kcal/mol) for benzene, toluene, and xylene hydrogenation over Pt and Pd on several supports (e.g., TiO_2, Al_2O_3, and $SiO_2 \cdot Al_2O_3$) as well as the kinetic modeling studies[29] suggest that a common mechanism is involved.

Table 3 shows that the absolute rates of toluene hydrogenation by the cluster-derived catalysts are 6–30 times slower than the monometallic catalyst. The evaluation of turnover frequencies for these catalysts is complicated by the chemisorption data, which do not provide a clear picture of platinum dispersion and suggest inhomogeneity of the surface platinum. In Table 3 the toluene hydrogenation activity data is also corrected for dispersions measured with the various chemisorption gases; unfortunately, no clear trends present themselves. The different types of sites suggested by the chemisorption studies may or may not have the same activity for toluene hydrogenation, which makes evaluation of real TOFs (in terms of actual active sites) difficult at best. TOFs reported using the CO_{str} are the most reasonable, although these TOFs are actually surface averages that combine the activities of all surface Pt sites, regardless of whether they are able to perform the reaction or not. Using strong CO uptakes to determine catalyst TOF, the cluster-derived catalysts are 1–2 orders of magnitude slower than the 0.15-Pt catalyst or the Pt/SiO_2 catalyst reported by Lin and Vannice.[30]

The cluster-derived catalysts are not generally inactive; rather, they are relatively inactive for the toluene hydrogenation reaction. In catalyst testing with the hexane conversion reaction at 400 °C, the 0.15-Pt_2Au_4 and 0.15-Pt_2Cu_4 catalysts had similar or greater activities than 0.15-Pt.[14,15] Although toluene hydrogenation is generally considered to be a structure-insensitive reaction,[16] these results are not totally unexpected based on previous results from Gates and co-workers.[3,46,47,49] In these studies, several supported iridium catalysts were prepared and carefully characterized with EXAFS spectroscopy. Highly dispersed and uniform catalysts (Ir_4 and Ir_6 clusters supported on alumina and magnesia) were characterized and tested with toluene hydrogenation. The supported Ir_4 and Ir_6 clusters were ca. 2 orders of magnitude less active for toluene hydrogenation than were particles consisting of ca. 100 metal atoms. The authors also suggested that traditional models of this reaction's structure insensitivity may not be valid as particle sizes fall below 10 Å.[18,46,47]

Despite the lower activity at 60 °C, the apparent activation energies determined for the cluster-derived catalysts were lower than for the 0.15-Pt catalyst. They are slightly lower than the suggested range of activation energies (12 ± 2 kcal/mol) observed for benzene, toluene, and xylene hydrogenation on Pt and Pd surfaces and support acid sites.[29] Lin and Vannice have suggested that deactivation may be the cause of previous reports of lower activation energies; however, deactivation processes are not the cause of the observed lower activation energies reported here. All the activation energy determinations used both ascending and descending temperatures and all are plotted together. The catalysts were also tested for deactivation over time and showed only about a 5% decrease in activity after 18 h on stream at 60 °C.

A shift in mechanism could cause the small activation energies over the cluster-derived catalysts; however, this seems unlikely given that the previously proposed mechanism fits such a wide array of data from dissimilar catalysts (e.g., catalysis on the metal or at acid sites) using a variety of different aryl substrates.[28,29] Rather, it is important to stress that the "activation energies" are *apparent* activation energies determined from measured rates or average TOFs rather than rate constants. Differences in adsorption enthalpies can affect the observed activation energy and it is possible that adsorption barriers are different on the cluster-derived catalysts. Further, activation energies determined in this fashion include the inherent assumption that surface coverages of all species (e.g., hydrogen, toluene, or key intermediates such as cyclohexadiene)[29] do not change appreciably with reaction temperature. Changes in surface concentrations with temperature would also affect the observed rate at each temperature, but would not alter the intrinsic activation energy.

Electronic, Particle Size, and Ensemble Effects. The characterization and catalysis data for these catalysts indicate that, when the organometallic clusters are used as the catalyst precursors, small bimetallic particles are prepared on the support.[14,15] These supported bimetallic particles are much less active for toluene hydrogenation catalysis than traditionally prepared Pt catalysts, and hydrogen chemisorption is much less expected based on CO chemisorption and TEM experiments. Examination of these data in terms of possible electronic, particle size, and ensemble effects is appropriate for these catalysts and may help shed some light on the factors governing the observed trends in reactivity.

DRIFTS spectra of CO bound to these catalysts offer the possibility that the cluster-derived catalysts may have more electron rich surfaces than the traditionally prepared catalyst,[12,14,15,] which suggests that electronic effects might contribute to the trends observed in this study. In traditional electronic effects for these alloys, Au or Cu atoms might donate electron density to Pt atoms within the alloy or particle. Such traditional electronic donations are generally deemed to be exceptional for supported and bulk alloy systems and have been shown to be particularly unimportant for the Pt–Au[39,48] and Pt–Cu[43,44] systems. Further, any electronic differences between the bimetallic particles and the traditional catalyst essentially go in the wrong direction with respect to the differences in hydrogen chemisorption: the more electron-rich Pt atoms in the clusters bind less hydrogen (per surface Pt measured by CO_{str}) than do the Pt atoms in 0.15-Pt. Although they cannot be entirely ruled out, traditional alloy electronic effects are likely not the primary cause of the lower activity for hydrogen

adsorption and toluene hydrogenation, largely because it is difficult to rationalize how more electron-rich Pt atoms would be less able to bind and activate hydrogen.

Another possibility is that there is a significant particle size effect (which may include separate electronic distinctions between the cluster-derived and traditional catalysts). In applying a particle size effect to rationalize the data from the cluster-derived catalysts, one would have to accept that both hydrogen chemisorption and toluene hydrogenation exhibit antipathetic structure sensitivity. Gates and co-workers have reported that both H_2 chemisorption and toluene hydrogenation may indeed show this structure sensitivity as metal particle sizes fall below 10 Å.[1,2,4,26] Results with both of the cluster-derived catalysts show the same general trends as the results for supported iridium catalysts, which suggests that particle size effects may play a role in determining the activity characteristics of the cluster-derived catalysts, particularly for 0.15-Pt₂Cu₄.

Particle size effects cannot completely explain the data, however. On the 0.15-Pt₂Au₄ catalyst, particle sizes are not particularly small—especially in comparison to an Ir₄ or Ir₆ cluster. TEM micrographs of this catalyst were dominated by particles ranging from 1.5 to 3.5 nm in diameter.[14] In this particle size range, toluene hydrogenation is expected to be relatively structure *insensitive*.[8] The bimetallic particles prepared for this study, however, have the additional complexity of surface ensembles of an active metal (platinum) surrounded by an inactive metal (copper or gold). Unfortunately, it is not possible to experimentally evaluate surface ensemble sizes for the various catalysts; however, the relative number of multi-platinum ensembles can be qualitatively inferred from the particle sizes and composition in much the same fashion as has been done previously for Pt−Au alloys.[17,32,35,38−41,45] EDS data suggest that the atomic ratio of individual particles is similar to the atomic ratio of the clusters,[14,15] so the particles prepared are expected to have about twice as much Au or Cu as they do Pt. For the smallest particles, then, there would be very few surface Pt ensembles that contain 2, 3, or more Pt atoms in close proximity. As particle sizes increase, these surface multi-platinum ensembles are expected to increase in frequency; consequently, for the catalysts in this study, ensemble sizes are expected to follow the trend in particle sizes: 0.15-Pt > 0.15-Pt₂Au₄ > 0.15-Pt₂Cu₄.

Interpretation of the adsorption and toluene hydrogenation data with regards to platinum ensemble sizes, then, seems most appropriate as trends in both H_{str} and toluene hydrogenation follow the expected order for ensemble sizes. For the catalysts studied, particularly 0.15-Pt₂Au₄, the low activity for toluene hydrogenation suggests that there is a surface ensemble size below which the structure sensitivity for this reaction is expressed. Similar conclusions have been drawn for bulk platinum−gold and platinum−copper alloys in which very small platinum ensembles were prepared by diluting the active metal with a coinage metal.[7,11,19,37,42] The large differences between CO chemisorption and hydrogen adsorption measurements suggest that ensembles of platinum (perhaps two or more neighboring Pt atoms) are required for strong hydrogen adsorption, at least at pressures below 100 Torr. The lone platinum atoms surrounded by Au or Cu (which likely comprise much of the metal particle surfaces of the bimetallic catalysts) appear to be unable to bind and activate hydrogen at these pressures.

This is somewhat surprising considering the rich dihydrogen activation chemistry of ligand-stabilized platinum gold clusters, many of which have only a single Pt atom yet are very active H_2-D_2 equilibration catalysts.[5,22,34] However, the ligand-stabilized clusters may also help to gleen some insight onto hydrogen binding by supported catalysts. Platinum atoms are significantly more electron rich in phosphine-stabilized clusters than on an oxide support. For example, the CO adduct of the cluster [Pt(AuPPh₃)₈](NO₃)₂ has a characteristic C≡O stretch of 1945 cm⁻¹ in CH_2Cl_2 solution[5] and 1946 cm⁻¹ when supported intact on silica or alumina.[22] These values are roughly 100 cm⁻¹ lower in energy than what is common for supported platinum catalysts.[23,24] Despite having a more electron-rich Pt center, [Pt(AuPPh₃)₈](NO₃)₂ does not irreversibly bind H_2 in solution, in the solid state (crystalline samples), or when supported (intact) on silica or alumina.[5,22,34] Rather, the cluster [Pt(AuPPh₃)₈]²⁺ has been shown to rapidly and *reversibly* react with 0.8 mol equivalents of H_2 at 1 atm H_2 pressure and 25 °C.[5,34] It is not our intention to invoke cluster−surface analogy arguments between these two very different environments for Pt; however, the parallels in hydrogen activation are certainly interesting.

Summary

Supported bimetallic Pt−Au and Pt−Cu catalysts were prepared from organometallic cluster precursors. Hydrogen and carbon monoxide chemisorption studies indicated that the cluster-derived catalysts bind significantly less hydrogen than CO. Toluene hydrogenation catalysis was found to be much slower on the cluster-derived catalysts than on a traditionally prepared monometallic platinum catalyst; however, apparent activation energies for this reaction were somewhat lower on the cluster-derived catalysts. Both particle size effects and surface Pt ensemble effects may play a role in the reduced hydrogen binding and lower toluene hydrogenation activity.

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