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Structure-Sensitivity of propylene hydrogenation over cluster-derived bimetallic Pt-Au catalysts

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A series of Pt and Pt-Au catalysts supported on TiO_2 has been studied using C_3H_6 hydrogenation as a probe reaction to determine the composition of the active catalytic surface. The catalysts were characterized by H_2 chemisorption and TEM analysis to determine concentrations of surface Pt sites for TOF calculations and metal particle size distributions, respectively. Similar TOF values for C_3H_8 formation (approximately 30 sec^{-1}) were observed for a monometallic Pt/TiO_2 and a bimetallic $Pt–Au/TiO_2$ sample prepared by impregnation from individual salt precursors. In contrast, the TOF for C_3H_8 formation over a Pt_2Au_4/TiO_2 sample prepared from an organometallic Pt_2Au_4 cluster precursor was decreased to 0.07 sec^{-1}, suggesting strong structure sensitivity for the hydrogenation reaction over this catalyst. Characterization results indicate that Pt on the surface of the Pt_2Au_4/TiO_2 catalyst is heavily diluted by Au atoms. In combination with the kinetic results, this suggests that the highly diluted surface ensembles of Pt are too small to effectively catalyze C_3H_6 hydrogenation, although electronic effects induced by the presence of Au adjacent to Pt sites can not be excluded.

KEY WORDS: propylene hydrogenation; bimetallic Pt–Au catalysts; structure-sensitivity.

1. Introduction

Supported bimetallic catalysts have been used in large-scale applications such as naphtha reforming [1], automobile exhaust control [2], and direct methanol fuel cells [3], because they exhibit higher activities and longer lifetimes than their monometallic counterparts. However, limited control is available over the morphology and distribution of the bimetallic components in most of these systems, since they are typically prepared by either co-impregnation of individual metal salt precursors onto the catalyst support or by successive steps of metal salt addition [4]. In many cases, it is very difficult to ensure formation of only bimetallic particles; rather, formation of monometallic particles can and does occur [5]. Thus, it is also difficult to characterize such catalytic systems, and to correlate catalyst performance with catalyst composition.

One alternative method for the preparation of true bimetallic catalysts involves the use of heteroatomic and polynuclear organometallic compounds as catalyst precursors. In recent years, our group has examined supported Pt–Au catalysts prepared from a bimetallic $[Pt_2Au_4(C \equiv CBu^t)_8]$ cluster precursor that contains easily removable acetylide ligands [6–8]. When conventional co-impregnation methods are used to prepare bimetallic Pt–Au catalysts, phase separation of the two metals and inhomogeneous composition of the resulting bimetallic particles are expected due to the large miscibility gap in the bulk phase between Pt and Au (between 18 and 97 wt.% Pt) [9]. However, a combination of catalytic and characterization measurements has shown that when the bimetallic $[Pt_2Au_4(C \equiv CBu^t)_8]$ cluster is used as the precursor, the SiO_2-supported catalysts obtained contain bimetallic Pt–Au nanoparticles, in which the presence of Au has substantially reduced the Pt ensemble size and has affected the activity and selectivity for the reduction of NO by C_3H_6 [8]. However, no definitive conclusions could be reached regarding the sizes of the Pt ensembles formed in these systems in the presence of the Au component.

While the results of our previous work indicate the existence of bimetallic Pt–Au catalyst particles, the distribution of Au and Pt on the surface of such particles is not known. One method to address this problem is to examine a catalytic reaction that occurs only on one of the two metals. The hydrogenation of simple olefins is such a reaction. There is extensive evidence for example, regarding the catalytic activity of Pt for the hydrogenation of propylene [10–17], while Au catalysts show no activity for this reaction [18]. Therefore, in this communication, we report results for the hydrogenation of propylene to propane as a probe reaction to investigate the surface of bimetallic Pt–Au catalysts. More specifically, we have measured the turnover frequency for the formation of propane on Pt/TiO_2, $Pt–Au/TiO_2$ prepared from individual salt precursors and Pt_2Au_4/TiO_2 prepared from an organometallic cluster precursor. These results along with those obtained from H_2 chemisorption and TEM measurements were used to demonstrate that

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surprisingly the C_3H_6 hydrogenation reaction becomes structure-sensitive over the Pt_2Au_4/TiO_2 catalyst.

2. Experimental

2.1. Catalyst Preparation

The catalysts examined in this paper were prepared via incipient wetness impregnation of the TiO_2 (AKZO Nobel TiO_2; BET surface area 182 m^2/g) support with aqueous solutions of hydrogen hexachloroplatinum hydrate ($H_2PtCl_6 \cdot 6H_2O$ – Aldrich Chem. Co.) and/or hydrogen tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$ – Aldrich Chem. Co.). Bimetallic (Pt–Au) catalysts were prepared with both precursors added together in the same solution (“co-impregnation”). Prior to impregnation, the support was calcined overnight at 500 °C. Following impregnation, all samples were dried at 120 °C for 2 h to remove the residual moisture, and then reduced in flowing H_2 for 2 h at 300 °C.

Cluster-derived Pt_2Au_4 catalysts were also prepared by wet impregnation. A hexane solution of the $Pt_2Au_4(C \equiv C^tBu)_8$ cluster precursor was used in this case. Following impregnation, the cluster-derived catalysts were dried in vacuum for 2 h at room temperature, and reduced in H_2 at 300 °C for 4 h.

Similar metal loadings were obtained for all catalysts by appropriate adjustment of the concentrations of the precursors in the impregnating solutions. In particular, all Pt-containing catalysts have approximately 1 wt.% Pt and all Au-containing catalysts approximately 2 wt.% Au. The metal loadings of all catalysts used in this study were confirmed by elemental analysis via Inductive Couple Plasma (ICP) spectroscopy performed by Galbraith Laboratories Inc. (see table 1 below for details). A reference 2 wt.% Pt/SiO_2 catalyst provided by Engelhard Corporation was also used for comparison purposes.

2.2. Catalyst Evaluation

Propylene hydrogenation was carried out in a tubular, stainless steel reactor containing approximately 0.01–0.08 g of catalyst diluted in approximately 1 g of quartz chips in the mid-section of the tube. A thermocouple embedded in the catalyst bed was used to monitor and control catalyst temperature. Before reaction, each catalyst sample was loaded into the reactor and heated *in situ* in flowing H_2 at 300 °C for 1 h. The temperature of the sample was then lowered to 40 °C and the reaction was started by introducing the reactants to the catalyst. The typical feed composition was 10% C_3H_6, 20% H_2, and 70% He. Respective flow rates and GHSV’s are shown in table 2 for all the catalysts tested. Variations in GHSV’s were necessary in order to keep conversions as close to differential as possible for the calculation of turnover frequencies. Catalyst performance was automatically monitored over specific time intervals for the duration of catalyst evaluation by on-line, gas sample injection into a Hewlett-Packard 5890 Series Gas Chromatograph. Products were separated using a 30 m Poraplot Q capillary GC column and reactor effluents could be analyzed by either thermal conductivity or flame ionization detection.

Table 1
Reaction conditions used during hydrogenation of C_3H_6

Catalyst	Flow Rate (ml STP/min)	GHSV (h^{-1})
Pt/TiO_2	210	310,000
$Pt–Au/TiO_2$	750	146,000
Pt_2Au_4/TiO_2	26	45,900

2.3. Catalyst Characterization

Transmission electron microscopy (TEM) measurements were carried out with a Phillips CM12 microscope at Eastman Chemical Company Research Laboratories. Average particle sizes were determined by measuring at least 100 particles from three different pictures. Hydrogen chemisorption analyses were conducted at 30 °C using standard methodologies with a static, volumetric system employing Baratron capacitance manometers for precision pressure measurements ($\pm 0.5 \times 10^{-5}$ kPa).

3. Results and discussion

3.1. Catalyst characterization

Both hydrogen chemisorption and electron microscopic measurements were used to determine active Pt site concentrations and particle size distributions, respectively. Table 1 summarizes the H_2 chemisorption data for all the catalysts used in this study. For monometallic Pt catalysts, hydrogen chemisorption is the preferred method of measuring Pt site concentrations from which the average Pt particle size and dispersion can be calculated. For bimetallic catalysts, hydrogen chemisorption can be also used to measure Pt surface site concentrations, since Au is not active for dissociative H_2 chemisorption at ambient conditions [4,19]. However, chemisorption can not be used in this case to calculate the average bimetallic particle size since hydrogen uptake provides an estimate only for the Pt component of the bimetallic particles.

In these cases, TEM was used to obtain the particle size distributions. This information, combined with the total metal loading, was used to calculate the total number of metal surface sites and the average particle sizes (table 3). Bulk, metal parameters weighted for the atomic ratio of each component were utilized in these calculations [20,21]. Because Pt and Au are adjacent atoms in the Periodic Table and both crystallize in an fcc structure, the use of linear combinations for the calculation of structural parameters for a “weighted bimetallic

Table 2
Structural characteristics of different Pt and Pt–Au catalysts obtained from H_2 chemisorption and TEM measurements

Catalyst	Au loading (%)	Pt loading (%)	Total metal loading (%)	TEM Measurements[a]		H_2 Chemisorption	
				Total surface sites/g_{cat}	Average particle diameter (nm)	Total Pt surface sites/g_{cat}	Dispersion (%)
Pt/TiO_2	–	0.72	0.72	–	–	5.4×10^{18}	24.1
$Pt–Au/TiO_2$	1.68	0.89	2.57	5.3×10^{18}	17.1	2.4×10^{18}	N/A
Pt_2Au_4/TiO_2	1.76	0.77	2.53	5.5×10^{19}	1.7	7.0×10^{18}	N/A
Pt/SiO_2	–	2.14	2.14	–	–	8.1×10^{18}	12.0

[a] Results of calculations based on the following solid state parameters: Unit cell dimension (Å): Pt 3.92, Au 4.08, Pt–Au: 4.03; Atomic volume ($Å^3$): Pt 15.1, Au 17.0, Pt–Au: 16.3; Atomic weight (g/mol): Pt 195.1, Au 197.0, Pt–Au: 196.3; Cross-sectional area of surface atoms ($Å^2$): Pt 8.0, Au 8.7, Pt–Au: 8.47.

Table 3
Kinetic results for the hydrogenation of C_3H_6 over Pt and Pt-Au catalysts (Reaction conditions: 40 °C, 10% C_3H_6, 20% H_2, 70% He)[a]

Catalyst	GHSV (h^{-1})	Initial Rate (μmoles C_3H_8 /min/g_{cat})	Pt surface sites per g_{cat}	Initial TOF (sec^{-1})
Pt/TiO_2	310,000	18,490	5.4×10^{18}	35
$Pt–Au/TiO_2$	146,000	6514	2.4×10^{18}	27
Pt_2 Au_4 /TiO_2	45,900	48	7.02×10^{18}	0.07
2%Pt/SiO_2 [1]	380,000	9317	8.1×10^{18}	12

[a]Reference catalyst supplied by Engelhard Corporation.

particle" is a reasonable approximation. For the bimetallic Pt–Au catalyst prepared by co-impregnation ($Pt–Au/TiO_2$), the total Pt surface site concentration determined from hydrogen chemisorption (table 1), represents approximately 45% of the total metal surface sites calculated from TEM data. The TEM measurements further indicate a bimodal particle size distribution with some large particles of approximately 15–20 nm in diameter present (determined by energy dispersive x-ray analysis to be monometallic Au), as well as some much smaller particles of 2–4 nm in diameter of unknown composition. Surface Pt sites apparently are abundant on these smaller particles, but is not clear whether these particles are monometallic (only Pt) or have a small bimetallic character as well (i.e., containing some Au).

For the cluster-derived Pt_2Au_4/TiO_2 catalyst the particle size distribution is uniform and only small particles (i.e., <3 nm) are observed. Results of our earlier work with this type of catalyst suggest a strong bimetallic Pt–Au character [8]. The hydrogen chemisorption data in table 1 represent the concentration of surface Pt sites ($7.0\times10^{18}/g_{cat}$, corresponding to a Pt dispersion of approximately 29%), while the TEM data yield an estimate of the total surface site concentration ($5.3\times10^{19}/g_{cat}$). Thus, the surface of these bimetallic particles appears to be composed primarily of Au atoms, and only 13% is occupied by Pt. In such a heavily "diluted" surface, it is expected that the catalytic activity, for structure-sensitive reactions catalyzed by Pt would be substantially modified.

Finally we should point out that the Pt site concentration on the Pt_2Au_4 cluster-derived catalyst obtained by the hydrogen chemisorption measurements represents a minimum estimate. Chandler et al. [22] have shown that in similar Pt_2Au_4 cluster-derived catalysts, the amount of chemisorbed hydrogen is decreased in the presence of Au, and as a result, the Pt dispersion on these catalysts can be underestimated. Similar observations have also been reported for other bimetallic systems [23–25].

3.2. C_3H_6 Hydrogenation

Kinetic results obtained at 40 ° for the hydrogenation of C_3H_6 over monometallic Pt and bimetallic Pt–Au catalysts are summarized in table 3. Because of a slow deactivation observed with some of these catalysts, initial rates of formation of propane have been used in this study. A comparison of the turn over frequencies (TOF) obtained for C_3H_8 formation, reveals a similar catalytic activity for both the monometallic Pt/TiO_2 and the co-impregnated $Pt–Au/TiO_2$ catalysts. A slightly lower TOF was observed with the Pt/SiO_2 catalyst, but the difference is within a factor of 3. These TOF values suggest that the Pt sites in all these catalysts are similar in terms of C_3H_6 hydrogenation reactivity, indicative of the structure-insensitive nature of this reaction. In contrast, the TOF for C_3H_8 formation over the Pt_2Au_4/TiO_2 sample is 2–3 orders of magnitude lower than those of the other samples in table 3.

Simple olefin hydrogenations are considered to be structure-insensitive reactions using the definition proposed by Boudart [26], since their measured activities are independent of the catalyst particle size and morphology for metallic catalyst particles greater than 2 nm.

Structure sensitivity is typically observed for more demanding reactions (such as paraffin hydrogenolysis as detailed by Sinfelt and coworkers [27] and Burch [28]), typically involving C–C and/or C–O bond breaking steps. There is some evidence however, that olefin hydrogenations may exhibit structure sensitivity for very small particle sizes (i.e., clusters), or for those cases where the metal surface is modified by the presence of a second metallic component. For example, Masson and coworkers [29,30] have reported that the rate of ethylene hydrogenation over a series of Pt/SiO_2 and Pt/Al_2O_3 catalysts was dependent on the size of the supported Pt particles. The Pt particles in this case were deposited on the supports using a vapor phase condensation method which permitted the preparation of Pt structures ranging in size from adsorbed single adatoms to particles up to 3 nm in diameter by varying the condensation time during Pt deposition. The reaction was found to be structure-insensitive for particles larger than 1.1–1.5 nm. A maximum turnover frequency was obtained for 0.6 nm particles. Below this particle size, the TOF decreased rapidly with particle size. In fact, with the SiO_2-supported system, where very small particles were obtained [30], no reaction was observed with particles/clusters containing less than 3 Pt atoms, leading these authors to suggest that this is the minimum number of Pt atoms required to catalyze the ethylene hydrogenation reaction.

Similar results were also obtained during the hydrogenation of ethylene over Ni supported on silica [31]. Once again, no measurable activity for the ethylene hydrogenation reaction was observed over Ni particles smaller than 5 Å and the authors speculated that a minimum size of the Ni ensemble is required to catalyze the reaction (on the order of 3–6 atoms). These results are consistent with the stoichiometry proposed by Bond [32], which indicates that four contiguous Pt sites are required for facile olefin hydrogenation; two sites for the formation of the 1, 2-di-σ adsorbed propylene and two sites for the dissociative adsorption of hydrogen. This argument was advanced further by Zaera [14] and Anderson [15] for propylene adsorption on Pt (111) single crystal surfaces.

In contrast, Biloen et al. [33] have reported that the reverse reaction (i.e., propane dehydrogenation) can also become structure sensitive at very low active ensemble sizes, but not as severely affected. In this case, although Au dilution of the active Pt ensembles can slow down the reaction rate by a factor of 5–7, the authors concluded that the dehydrogenation can take place even on a single Pt atom. However, one has to consider the differences in the catalyst structural requirements for the forward and reverse reactions. More specifically, while hydrogen and propylene adsorption and activation have to take place on adjacent sites in the case of the hydrogenation – as pointed out in the Bond stoichiometry – the dissociative adsorption of propane, which represents the first step of the dehydrogenation process, can take place on a single Pt atom with the hydrogen formed possibly "spilling over" to a non-Pt adjacent site. Biloen et al. proposed that the subsequent β-hydrogen elimination is the rate determining step for dehydrogenation. Once again, this step can take place on the same Pt site and one can envision the produced hydrogen "spilling over" to a non-Pt site.

In view of these previous results, we believe that the hydrogenation of C_3H_6 over the Pt_2Au_4/TiO_2 catalyst examined may also represent a test case for the lower limit of the size of the Pt ensemble needed for this reaction to occur, due to the very high dilution of the Pt sites on the surface of the bimetallic particles (approximately 85% of the surface of such particles is occupied by Au, based on the data in table 2). Consequently, the results in this study suggest that either Au has diluted the Pt_2Au_4 surface into Pt ensembles containing less than four atoms and/or Au has modified the electronic properties of the Pt sites such that C_3H_6 hydrogenation is strongly suppressed. While we can not exclude the possibility of any electronic effects, the previous results discussed in detail above for the C_2H_4 hydrogenation reaction render support to the active ensemble hypothesis, and suggest that Pt ensembles containing less than 4 atoms are the most abundant Pt surface structures on the cluster-derived Pt_2Au_4/TiO_2 catalyst.

4. Conclusions

H_2 chemisorption and TEM analysis have been used to determine the active Pt site concentration and particle size distributions, respectively, of the three catalysts used in this study: Pt/TiO_2, $Pt–Au/TiO_2$ prepared from individual salt precursors and Pt_2Au_4/TiO_2 prepared from an organometallic cluster precursor. Segregation of Pt and Au is observed for the $Pt–Au/TiO_2$ catalyst; however, it is not possible to exclude the existence of a small fraction of bimetallic Pt–Au particles in this catalyst. Analysis of the H_2 chemisorption and TEM measurements for the Pt_2Au_4/TiO_2 catalyst indicates that Pt on the surface of this catalyst is heavily diluted by Au, with approximately 85% of the surface of the metal particles occupied by Au atoms.

Similar TOF values for C_3H_8 formation were obtained for the Pt/TiO_2 and the $Pt–Au/TiO_2$ catalysts. In contrast, the TOF value for C_3H_8 formation obtained for the Pt_2Au_4/TiO_2 catalyst is 2–3 orders of magnitude lower indicating a strong structure-sensitivity for the C_3H_6 hydrogenation reaction over this catalyst. These kinetic results suggest that the highly diluted surface of the Pt_2Au_4/TiO_2 catalyst may have restricted the size of the Pt ensembles to less than 4 Pt atoms, which is below the lower limit required to efficiently catalyze the hydrogenation of C_3H_6.

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