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DRIFTS studies of carbon monoxide coverage on highly dispersed bimetallic Pt-Cu and Pt-Au catalysts

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Abstract

Silica supported platinum-gold and platinum-copper catalysts prepared from organometallic cluster precursors were characterized with diffuse reflectance Fourier-transform spectroscopy (DRIFTS) of adsorbed CO. Because of the effects that dipole coupling of adsorbed carbon monoxide molecules can have on the infrared spectrum, coverage studies were employed to evaluate the interactions between CO and the catalyst surfaces. DRIFTS spectra of the catalysts prepared from bimetallic molecular cluster precursors showed significantly lower C≡O stretching frequencies relative to a traditionally prepared platinum catalyst. The lowering of the C≡O stretching frequency may be the result of the formation of unique alloys and particle morphologies. In the case of the catalyst prepared from the platinum-copper cluster, two peaks were identified in the Pt–C≡O stretching region, one of which is postulated to be a bridging or semi-bridging mode between Pt and Cu. Infrared spectroscopy results are also discussed in relation to kinetic data from the *n*-hexane conversion reaction. Differences in catalyst activities and selectivities are concluded to be primarily due to geometric (i.e. structural or morphological) effects.

Keywords: Pt-Cu and Pt-Au catalysts; DRIFTS; Carbon monoxide; Bimetallic catalysts; Hexane conversion; Electronic effects; Geometric effects; Supported clusters

1. Introduction

Since the development of "platforming" processes in the late 1940s and the later discoveries that Pt catalyzes alkane skeletal rearrangement reactions, Pt-based catalysts have been extensively studied for many applications. Supported Pt catalysts, often with a second metal or other dopants added, are currently used as emissions control catalysts and are the mainstay for alkane conversion catalysts in the petrochemical industry [1–3]. Recent discoveries that very small Pt particles or clusters on basic supports selectively catalyze the formation of aromatics from alkanes [4,5] has also sparked a great deal of research in this general area.

Supported alloys comprised of an active group VIII metal and an "inactive" group IB metal have been examined as catalysts for a wide variety of industrially important reactions. A few examples of heterogeneous catalyst applications include the production of vinyl acetate (Pd-Au) [6,7], emissions control catalysts (Pt-Au) [8], and the dechlorination of chlorinated hydrocarbons (Pt-Cu) [9]. Metals such as platinum, palladium, and gold are expensive, so it is desirable to prepare supported catalysts that are as highly dispersed as possible to maximize the active metal surface area. Further, since the initial report of high selectivity for aromatics during hexane reforming by

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extremely small platinum clusters (∼20 atoms or fewer) in alkaline zeolites [4], the preparation and characterization of very small metal clusters has received significant attention in the recent literature [5,10–24]. The emerging picture from these studies is that unique morphologies/electronic properties of small platinum clusters are stabilized by the alkaline support and are responsible for the high aromatization selectivity [5,23,24]. Consequently, the preparation of supported metal particles or clusters with new and unique morphologies (particularly bimetallic particles) holds great promise for enhancing selectivities of known catalysts and discovering new catalyst properties.

The addition of a second metal greatly complicates the preparation and characterization of highly dispersed particles. Factors such as metal segregation and sintering, surface enrichment of the "inactive" metal, and compositional inhomogeneity of bimetallic particles make the preparation of highly dispersed and uniform bimetallic particles difficult with conventional impregnation methods. Although some techniques allow for a degree of control over metal particle sizes and distributions [25], particle composition and surface composition of metals may have wide ranging distributions in a given catalyst sample. Even when bulk surface compositions are relatively homogeneous, varying degrees of clustering of one metal on the surface can produce numerous types of active sites on particles throughout the catalyst [2]. The use of zeolitic supports has shown promise for the preparation of small bimetallic particles, particularly for the platinum-copper system [26–28]; however, the working model presented by Ahn and coworkers [28] is a cherry pit type catalyst in which small platinum clusters are covered with copper.

Recently, we reported on the preparation and characterization of supported bimetallic Pt-Au and Pt-Cu catalysts from the molecular cluster precursors $Pt_2Au_4(C{\equiv}C^tBu)_8$ and $Pt_2Cu_4(C{\equiv}C^tBu)_8$ [29,30]. 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. The Pt-Cu catalysts also had platinum dispersions >85% by CO chemisorption; however, 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 using *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 significantly slower on the cluster derived catalysts than on traditionally prepared (coimpregnated) Pt-Au and Pt-Cu catalysts. Reactivity data also suggested that, under the reaction conditions, the cluster derived catalysts had significantly less surface hydrogen than traditionally prepared Pt catalysts.

The emerging model of these new cluster derived catalysts is that the catalyst surface is composed of very small and bimetallic particles. Because of the ratio of platinum to coinage metal in these catalysts (1:2), it is expected that the surfaces of the metal particles are composed of small platinum ensembles surrounded by the coinage metal. For the cluster derived Pt-Cu catalysts in particular, these ensembles may contain very few platinum atoms and possibly isolated platinum atoms embedded in the copper. This manuscript involves a more detailed look at the electronic properties of these clusters using infrared spectroscopy of adsorbed CO over a wide range of surface coverages as a probe. The stretching frequency of carbon monoxide bound to a platinum catalyst surface is extremely sensitive to the electronic properties of platinum. This is largely due to the ability of carbon monoxide to accept electron density from the platinum 5d orbitals into the carbon monoxide π^* orbitals. The observed absorbance of the C≡O triple bond is also very sensitive to surface coverage [31] and dipole coupling between adsorbed carbon monoxide substrates has been shown to account for observed shifts of about 15–30 cm^{-1} in infrared spectra [2,31]. In order to evaluate the singleton C≡O stretching frequency, isotopic dilution studies with $^{13}C{\equiv}O$ or coverage studies must be employed to eliminate dipole coupling effects.

2. Methods

2.1. 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, respec-

tively, via literature procedures [32]. Hexachloroplatinic acid, $H_2PtCl_6{\cdot}6H_2O$, was prepared from Pt metal (99.99%) according to literature procedure [33]. Davisil SiO_2 (35–60 mesh, BET surface area = 360 m^2/g, average pore diameter = 150 Å) was washed with high purity millipore distilled and deionized water to remove the fine particles and dried under vacuum at 120°C for 24 h prior to use. Conventional Pt catalysts were prepared by incipient wetness impregnation of platinic acid precursors onto the dried silica support. Solution concentrations were adjusted to give the 1-Pt (1.0% Pt) catalyst. Catalyst abbreviations indicate platinum wt.% and the atomic ratio of metals in the bimetallic catalysts. The bimetallic clusters $Pt_2Cu_4(C{\equiv}C^tBu)_8$ and $Pt_2Au_4(C{\equiv}C^tBu)_8$ spontaneously adsorbed onto silica from hexanes solution. The excess solvent was decanted off and the supported clusters were dried en vacuo at 60°C to yield the 1-Pt_2Cu_4 (1.0% Pt, 0.67% Cu) and 1-Pt_2Au_4 (1.0% Pt, 2.0% Au) catalysts. The details of the general procedure have been previously reported for the support of phosphine stabilized Pt and Pt-Au compounds [34,35] and were similarly employed in this study.

2.2. Catalyst activation and sample preparation

Catalyst activation was carried out on an RXM-100 catalyst characterization system purchased from Advanced Scientific Designs, Inc. Hydrogen, nitrogen, and oxygen were all UHP grade (99.999%) gasses purchased from Linde and were used without further purification. Carbon monoxide was either purchased as a lecture cylinder from Aldrich or a UHP grade cylinder (Linde). In a typical experiment, 50 mg of the supported catalyst precursors were loaded into a U-shaped quartz microreactor (inside diameter = 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, the gas was switched to H_2 flowing at 20 ml/min, the temperature was ramped 10°C/min to 200°C held there for 1 h, and then ramped 10°C/min back to 30°C. This is the standard activation protocol for all experiments.

2.3. Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS)

DRIFTS studies were conducted with a Magna 750 FTIR system (Nicolet) using a DRIFTS cell (SpectraTech) equipped with an accessory that allows in situ treatments with different gasses at temperatures up to 900°C. A liquid nitrogen-cooled MCT detector was used for data collection and OMNIC software was used for data processing. The interferograms consisted of 512 scans and the spectra were collected with a 2 cm^{-1} resolution in the absorbance format using a KBr spectrum as the background. The silica supported precursors were always activated on the RXM-100 prior to DRIFTS experiments. The samples were finely ground with an agate mortar and pestle and placed into the DRIFTS cell where they were re-reduced at 200°C for 1 h with flowing hydrogen at ambient pressure.

After reduction, the samples were cooled under flowing nitrogen. The samples were then treated with carbon monoxide at room temperature by flowing CO through the cell for 1.5 min followed by flushing the cell with nitrogen for 3 min. The spectrum of CO bound to the catalyst surface was then collected at ambient temperature. In order to reduce CO coverage (θ) on the catalyst surface, spectra were recorded at elevated temperatures. After recording a spectrum at ambient temperature, the sample temperature was raised to 40°C and two to three spectra were recorded. Temperatures were increased in increments of 5–10°C with several spectra being recorded at each temperature. Maximum temperatures used were usually around 60°C for platinic acid derived catalysts and ca. 140°C for the cluster derived catalysts. After all the CO had been removed (generally 1.5–2 h) the sample was heated an additional 20°C for 10 min and cooled to the last temperature at which a spectrum was recorded. Spectra of the catalysts without CO were then recorded at all temperatures used previously. These spectra were subtracted from the spectra containing adsorbed CO in order to best observe the C≡O stretching frequency.

2.4. Hexane conversion catalysis

Hexane conversion catalysis experiments were originally reported in [29,30]. Briefly, a saturated hexane in hydrogen gas stream (hydrogen:hexane ratio =

16:1, partial pressure of hexane = 49 Torr) was produced with a two stage hexane bubbler apparatus. The gas mixture was fed directly into the RXM-100 reaction manifold and subsequently flowed over the catalyst bed. All catalysis was conducted at 400°C; typical hexane weight hourly space velocities were between 2 and 20 h^{-1}. Reaction products were analyzed on stream via gas chromatography with an FID detector. The products were classified into five categories: *cracking* (formation of C_1–C_5 hydrocarbons), *isomerization* (MP's = 2- and 3-methylpentane), *hexenes*, *methylcyclopentane* (*MCP*), and 1,6-*cyclization* (cyclohexane and benzene). Plots of conversion × selectivity versus inverse space velocity were prepared for each product class and used to determine activities.

3. Results

The infrared absorption spectra of several silica supported platinum-based catalysts were measured using DRIFTS. In order to reduce the effects of dipole–dipole coupling between adsorbed CO molecules, coverage studies were performed on the catalysts by slowly heating the samples in the DRIFTS cell. In order to insure that the coverage study did not affect metal particle dispersion or interactions between metals on the support, in some experiments CO was reintroduced to the catalyst after the coverage study had been completed. For all the catalysts, the spectrum obtained was identical (within experimental uncertainty) to the spectrum obtained from the initial adsorption of CO, indicating that the catalyst surfaces were unaffected by the treatments employed in the coverage study.

In order to compare the results of the cluster derived catalysts with previous results for platinum catalysts, the 1-Pt catalyst was prepared via insipient wetness impregnation of platinic acid. The infrared spectroscopy coverage studies for this catalyst are shown in Fig. 1. When the sample temperature was increased, the adsorption bands from linearly bound CO shift from an initial value of ca. 2076 cm^{-1} to lower energies. As the sample temperature was increased further and CO coverage approached zero (spectrum recorded at 60°C), the CO stretch shifted to a final value of 2065 cm^{-1}.

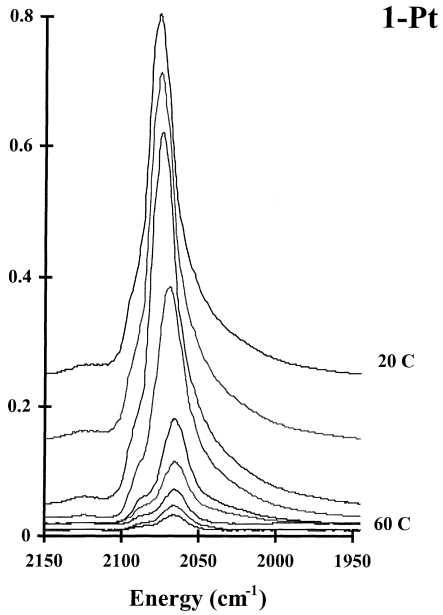

Fig. 1. DRIFTS carbon monoxide coverage study of the 1-Pt catalyst.

The IR spectroscopy coverage studies of the cluster derived 1-Pt_2Au_4 are shown in Fig. 2. The room temperature CO spectrum of this catalyst is clearly distinguished from the 1-Pt catalyst by the absorption band at 2124 cm^{-1}, assigned to CO weakly adsorbed to Au [36]. Comparable bands were absent in control experiments with monometallic Au and coimpregnated Pt-Au catalysts [29]. The band at 2124 cm^{-1} disappeared after purging with nitrogen for 10 min at 30°C. As samples of the 1-Pt_2Au_4 catalyst were heated, the absorption band resulting from CO bound to platinum shifted from an initial value of ca. 2065 cm^{-1} to a final value of 2049 cm^{-1} (spectrum recorded at 130°C). This value is almost 20 cm^{-1} red shifted relative to the low coverage peak from the platinic acid derived catalyst. The last few spectra for this catalyst (spectra with very low CO coverage) are replotted in Fig. 3 along with those for the 1-Pt and 1-Pt_2Cu_4 catalysts. Values of ν(C≡O) at high and low temperatures for all the catalysts are compiled in Table 1.

The infrared spectroscopy coverage studies of the cluster derived 1-Pt_2Cu_4 are shown in Figs. 4 and 5. As with the 1-Pt_2Au_4 catalyst, the room temperature CO spectrum contains a high energy absorption

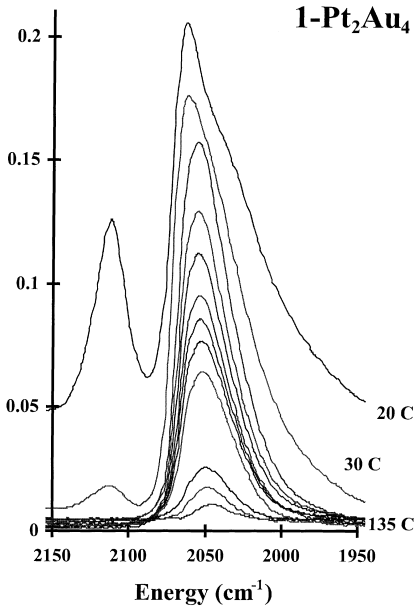

Fig. 2. DRIFTS carbon monoxide coverage study of the 1-Pt_2Au_4 catalyst.

band (ca. 2125 cm^{-1}) attributable to CO adsorbed on the coinage metal. The lower energy absorption band, however, was extremely broad and asymmetric. As samples of the 1-Pt_2Cu_4 catalyst were heated to 50°C,

Table 1
Characterization and catalysis data for activated catalysts

	1-Pt	1-Pt_2Au_4	1-Pt_2Cu_4
Low temperature Pt ν(C≡O)	2077	2063	~2050
High temperature Pt ν(C≡O)	2066	2049	2042
Cracking tof[a]	20[b]	23[b]	52[c]
1,6 Cyclization tof[a]	29[b]	8[b]	7.5[c]

[a] Activities in millimoles of hexane converted to product class per mole Pt per second.
[b] Data from [29].
[c] Data from [30].

the high energy absorption band disappeared and the low energy absorptions sharpened into a more symmetric peak centered around 2050 cm^{-1}. Upon further heating, this peak shifted to a final value of 2042 cm^{-1} (spectrum recorded at 155°C). This value is red shifted approximately 25 cm^{-1} from the low coverage peak from the platinic acid derived catalyst.

Fig. 5 shows how the general shape of the broad, asymmetric Pt–C≡O peak on the 1-Pt_2Cu_4 catalyst (at room temperature) is affected by the CO adsorption pressure. As the delivery pressure decreased from 20 to about 5 psi, this broad peak split into two clearly recognizable overlapping peaks. All three of the samples shown in Fig. 5 were examined with coverage studies as described above. Once the high energy peak

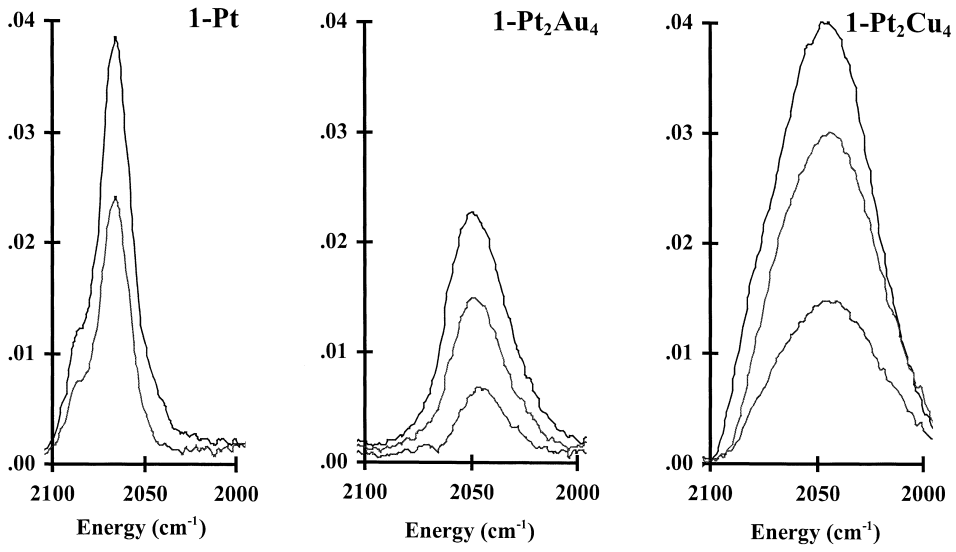

Fig. 3. High temperature (low CO coverage) DRIFTS spectra of the 1-Pt, 1-Pt_2Au_4 and 1-Pt_2Cu_4 catalysts.

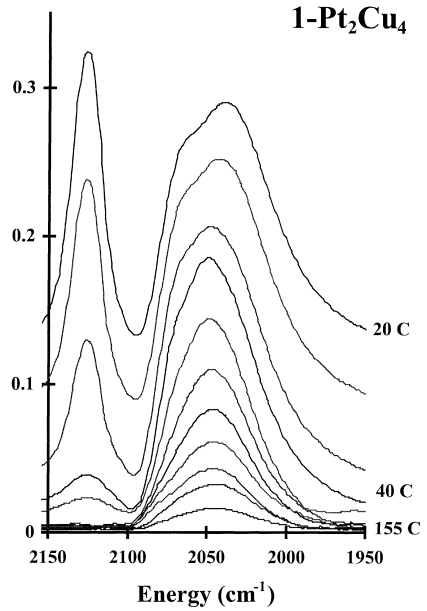

Fig. 4. DRIFTS carbon monoxide coverage study of the 1-Pt_2Cu_4 catalyst.

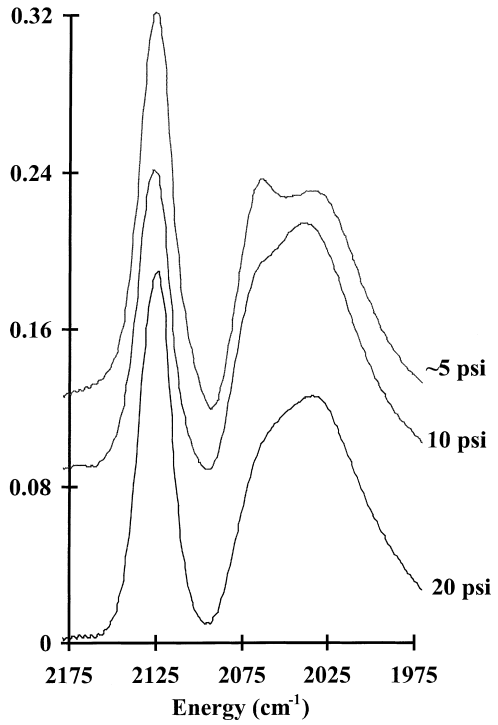

Fig. 5. Delivery pressure effects of CO adsorption on 1-Pt_2Cu_4.

disappeared (i.e. all of the carbon monoxide was removed from the copper) the spectrum of CO bound to platinum was always the same (within experimental uncertainty). Further, all three samples shown in Fig. 5 had the same value of ν(C≡O) ($2042 \pm 1\,cm^{-1}$) at the end of the coverage study.

4. Discussion

4.1. Catalyst characterization

Recently, we reported on the preparation and characterization of supported bimetallic Pt-Au and Pt-Cu catalysts from the bimetallic molecular cluster precursors $Pt_2Au_4(C{\equiv}C^tBu)_8$ [29] and $Pt_2Cu_4(C{\equiv}C^tBu)_8$ [30]. These catalysts, along with the platinic acid catalyst examined in the current study, were characterized with CO chemisorption and transmission electron microscopy (TEM) and underwent catalytic testing with the hexane conversion reaction. Briefly, 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 [29]. The Pt-Cu catalysts also had platinum dispersions ≥85% by CO chemisorption; however, particles were too small to be imaged with TEM [30]. In both the Pt-Au and Pt-Cu catalysts, the coinage metal was found to bind significant amounts of carbon monoxide.

The characterization results indicated that highly dispersed supported bimetallic particles were prepared when the molecular cluster were used as the catalyst precursors. These results are exciting, particularly for the platinum-gold system, because bulk Pt-Au alloys between 18 and 97% platinum are not thermodynamically stable [37,38]. Further, UHV studies on the Au (1 1 0) surface did not show CO adsorption down to 125 K [39] and previous studies with silica supported Pt-Au catalysts prepared from chloride salts did not show significant CO adsorption on Au [29,40,41] at ambient temperature.

Catalysis studies using *n*-hexane conversion showed that both cluster derived catalysts were selective for

C–C bond fission reactions [29,30] and that skeletal rearrangements (cyclizations, isomerizations, and aromatizations) were significantly slower on the cluster derived catalysts (relative to traditionally prepared Pt [29], Pt-Au [29], and Pt-Cu [30] catalysts). Reactivity data also suggested that the cluster derived catalysts had significantly less surface hydrogen than did traditionally prepared Pt catalysts under the reaction conditions (400°C, 700 Torr H_2). Preliminary infrared spectroscopy studies indicated a possible correlation between the stretching frequency of carbon monoxide adsorbed to the catalyst surface and some of the observed reactivity trends. In particular, catalyst activity for C–C bond fission reactions coincided with a reduction in the CO stretching frequency at room temperature (Table 1). The opposite trend occurs for 1,6 cyclization (aromatization) reactions. Because these correlations are somewhat in contrast to correlations observed between CO stretching frequency and reactivity for alkaline zeolite supported platinum catalysts [23], the DRIFTS studies reported here were undertaken in order to better evaluate the CO stretching frequency. These results shed light on the possible role of electronic and geometric or ensemble effects on the hexane conversion catalysis results.

4.2. Infrared spectra at ambient temperature

The DRIFTS spectra of the 1-Pt_2Au_4 (Fig. 2) and 1-Pt_2Cu_4 (Fig. 4) catalysts at ambient temperature have important distinctions from the impregnated platinum catalyst prepared for this study. All the catalysts have a large absorption band between 2080 and 2020 cm^{-1}, consistent with CO linearly bound to platinum [31,42]. Bands attributable to Pt-Pt bridge bonded CO were not observed, in agreement with other reports of silica supported platinum catalysts [36,43,44]. The large peak at 2124 cm^{-1} (Fig. 5) that is assigned to CO bound to Au on the 1-Pt_2Au_4 catalyst is exceptional and is consistent with large weak CO chemisorption values [29] for this catalyst. Previous infrared and CO chemisorption studies of silica supported Pt-Au catalysts (prepared via wetness impregnation of chloride salts) found no evidence for CO adsorption by Au at ambient temperatures [36,40,41]. Similarly, our own studies with coimpregnated Pt-Au catalysts having the same metal loadings as the cluster derived catalysts (Au:Pt = 2) did not provide evidence for Au–CO interactions [29]. Based on these results, it is unlikely that Au directly binds CO in the cluster derived catalysts. Rather, CO is probably initially bound to platinum and migrates or spills over to Au sites.

Schwank and coworkers have also examined Pt dispersion and metal particle sizes in silica supported Pt-Au catalysts. The catalyst most similar to our loadings was an insipient wetness coimpregnated catalyst prepared from hexachloroplatinic and auric acids (Au:Pt = 0.7). Despite TEM data indicating the presence of small particles (1–3 nm), carbon monoxide, hydrogen, and oxygen chemisorptions indicated relatively little surface platinum [36]. The authors concluded that this catalyst had extensive surface enrichment in Au. Our own studies with coimpregnated Pt-Au catalysts (Au:Pt = 2) indicated Pt dispersions comparable to monometallic Pt catalysts; however, extensive phase separation had occured and there was little evidence for Pt-Au interactions. The CO chemisorption and infrared studies on the new cluster derived Pt_2Au_4 catalysts, on the other hand, indicate the vast majority of the deposited Pt is available ($\geq$85%) and that bimetallic surface ensembles dominate the catalyst surface [29].

DRIFT spectra of the 1-Pt_2Cu_4 catalyst, particularly the variance in ambient temperature spectra with dosing pressure (Fig. 5), support the conclusion that bimetallic ensembles are present on this catalyst as well. At higher delivery pressures, the Pt–C≡O peak is very broad and asymmetric; when a lower delivery pressure was used, the DRIFT spectrum clearly shows two overlapping peaks (top spectrum of Fig. 5). These spectral differences in the Pt–C≡O region are only observed while CO is adsorbed on copper; the shape of the Pt–C≡O peak does not change significantly or sharpen until essentially all of the carbon monoxide is removed from the Cu sites. Once the CO is removed from Cu, the peak for CO bound to platinum is largely symmetrical, although it remains broad. This suggests that the interaction causing the low energy absorption (shoulder) only occurs when all (or most) of the platinum sites are covered and CO binds to copper.

A similar phenomenon was reported for alumina supported Pt-Cu alloys upon increasing CO coverage in a ^{13}CO dilution experiment. As the Cu–C≡O band started to develop at high coverage (of ^{12}CO), the Pt–C≡O band frequency began to decrease [45]. The

observation reported here is comparable; however, we observe the clear appearance of two distinct peaks in the top spectrum of Fig. 2. The higher energy band (ca. 2065 cm^{-1}) observed at high coverage is likely due to linearly bound CO on Pt. The lower energy stretch is speculated to be a bridging or semi-bridging mode between Pt and Cu; differences in the spectra are attributable to differences in the relative populations of the two adsorption sites. Physical characterization data indicates that very small and bimetallic particles are prepared from the $Pt_2Cu_4(C{\equiv}C^tBu)_8$ cluster [30]; these would necessarily have a large fraction of low coordination surface atoms [46]. In order to increase the coordination number of the surface atoms (particularly surface copper atoms), it may be possible for some of the linearly bound Pt–C≡O to shift to a bridging or semi-bridging mode between platinum and copper. Further, small monometallic particles have been shown to undergo contraction of the lattice parameters relative to bulk values [46]. Although this phenomenon has not been examined for the 1-Pt_2Cu_4 catalyst, a similar contraction might be expected to increase the likelihood of producing such bridging or semi-bridging modes.

The large high energy absorption band (2125 cm^{-1}) observed for the cluster derived Pt-Cu catalyst results from CO bound to Cu. If this were a pure Cu catalyst, the position of this band would be more consistent with Cu^+ (or perhaps Cu^{2+}), rather than Cu^0 [47]. At the same time, this band disappears at relatively low temperatures (<50°C), which is more consistent with reduced Cu^0. CO chemisorption experiments indicated that that weakly bound CO could also be removed at room temperature; the resulting values for strongly bound CO (strongly bound CO ≈ Pt dispersion) were consistent with TEM studies [30,48]. Discussions at the 16th North American Meeting of the Catalysis Society suggested that the high ν(C≡O) value might be due to trace oxygen contamination after reduction in the DRIFTS cell. Although we do not believe that this is necessarily the cause, we can not exclude it with apodictic certainty. Previous studies on silica and alumina supported Pt-Cu alloys by Ponec and coworkers [45,49] report infrared spectra that are essentially the same as ours. They consistently observed ν(C≡O) values between 2120 and 2130 cm^{-1} for CO bound to *reduced* copper in the alloys. Toolenaar et al. [45] go on to attribute the high value of ν(C≡O) to the same dipole coupling and dilution effects that lower the CO stretching frequency on platinum. Our results are completely consistent with both the study dealing with variance in Pt:Cu ratio [49] and with the ^{13}CO dilution experiments [45]. We will not comment further on the state of the Cu in this catalyst other than to reiterate that the characterization and reactivity data [30] indicate that very small and bimetallic particles are prepared from the molecular cluster.

4.3. Carbon monoxide coverage studies

Dipole–dipole coupling is well-known to cause significant shifts in the observed stretching frequency for carbon monoxide bound to metal surfaces. This coupling is a "through space" interaction that occurs between dipoles vibrating at roughly the same frequency [31,42,45,49]; the effects are reduced drastically as the distance between dipoles increases [45,49]. Hence, as interactions between the vibrating dipoles are decreased either via greater distance (i.e. lower coverage) or via dilution with a dipole vibrating at a different frequency (e.g. isotopic dilution with ^{13}CO or dilution with ^{12}CO on a different metal), effects of dipole coupling on the infrared absorption spectrum decrease. For carbon monoxide on platinum surfaces, dipole–dipole coupling interactions are well known to cause an increase in the observed stretching frequency of 15–30 cm^{-1} over the uncoupled frequency [2,31,42,45,49]. The effects of coverage on the infrared spectrum of CO bound to Cu are less pronounced, often causing a decrease in the observed stretching frequency of a few wavenumbers [45].

For all the catalysts investigated, as the sample temperature was raised, surface coverage decreased, and the observed C≡O stretching frequency for platinum bound CO shifted to lower frequencies. This behavior is consistent with decreasing dipole–dipole coupling between adsorbed carbon monoxide substrates on the catalyst surface. The high temperature CO stretches for the 1-Pt_2Au_4 and 1-Pt_2Cu_4 catalysts suggest the possibility of electronic differences between the cluster derived catalysts and the monometallic 1-Pt catalyst. The ν(C≡O) values found for the cluster derived catalysts are red shifted 20–30 cm^{-1} relative to the corresponding low coverage value for 1-Pt. It may be possible that the surfaces of the cluster derived catalysts are more electron-rich than the

surfaces present in the traditionally prepared catalysts. A more electron-rich surface platinum atom would have greater ability to back donate electron density into the antibonding orbitals of carbon monoxide, thus weakening the C≡O bond and lowering its vibration frequency. This possibility is qualitatively supported by the higher temperatures required to desorb carbon monoxide, which indicate that carbon monoxide is more strongly bound to the cluster derived catalysts than the platinic acid catalyst.

The CO coverage experiments cannot attribute the differences in DRIFT spectra to electronic effects, however. The dipole–dipole coupling effects between adsorbate molecules may not be removed completely when CO is desorbed from the 1-Pt catalyst. Single crystal studies of CO bound to Pt have shown that on a more open single crystal plane, CO tends to cluster, even at low coverage [50]. If this were the case, the observed ν(C≡O) for the 1-Pt catalyst at low coverage would still include some dipole coupling effects and would not correspond to the singleton (uncoupled) frequency of CO bound to the platinum. The presence of residual chlorine in the 1-Pt catalyst may also contribute to the differences between the cluster derived and the traditionally prepared catalyst, as residual chlorine would be expected to cause a blue shift on the 1-Pt catalyst [31,42]. Either or both of these would be manifested as an observed red shift for the cluster derived catalysts (relative to 1-Pt) and comparisons between 1-Pt and the cluster derived catalysts would be obscured. These possibilities cannot be discounted and may partially contribute to the observed red shift of the cluster derived catalysts at low coverage.

A variety of alloy systems similar to the Pt-Au and Pt-Cu systems (weakly exothermic alloys, e.g. Ni-Cu [51], Pd-Ag [52], Pd-Au [53], Rh-Cu [54]) have been previously examined with infrared spectroscopy. For these systems, the $\Delta\nu$ shifts reported from high coverage to low were all between 15 and 30 cm^{-1} [45]. This has been suggested to be the expected range of varying dipole–dipole coupling effects that should be attributed to a traditional geometric effect [45]. The shifts observed for the cluster derived catalysts (relative to the 1-Pt catalyst at high coverage) are on the order of 30–40 cm^{-1}. This observed shift is on the high end of what might be expected for geometric effects; however, considering the diversity in morphologies and particle sizes of the catalysts involved as well as the possible effects of CO clustering and residual chlorine, the observed shifts are reasonable without invoking traditional electronic effects.

We believe that the differences in ν(C≡O) observed for carbon monoxide bound to the catalysts prepared from bimetallic precursors are at least partially due a "morphological–electronic effect" of using the organometallic clusters as precursors. By "morphological–electronic effect" it should be clearly stated that there is absolutely no intention of evoking images of traditional alloy electronic effects whereby 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 [55,56] and Pt-Cu [45,49] systems. Rather, the term "morphological–electronic effect" is meant to describe that, when using the organometallic clusters as the metal source, a unique particle morphology is prepared that has surface electronic properties distinct from what is prepared from platinic acid.

The electronic properties of these small bimetallic particles apparently provide for greater electron density on surface platinum atoms and allow for greater backbonding into the antibonding C≡O π^* orbitals. Given the aforementioned studies with bulk and supported Pt-Au and Pt-Cu alloys, a formal electronic donation from Au or Cu to Pt is unlikely. However, it is well-known that different Pt single crystal surfaces can have different characteristic C≡O stretches for carbon monoxide bound to the metal surface [31,42]. It follows that, if a unique particle morphology is prepared, this morphology is likely to have a C≡O stretch different than that for the relatively large and inhomogeneous particles of the 1-Pt catalyst [29]. This "morphological–electronic effect" may be the result of several factors, such as particle size, lattice parameters, surface composition, and surface morphology. Particle size may play a particularly important role in determining the electronic properties of these catalysts. Indeed, as the fraction of surface platinum atoms approaches unity (as is the case for the cluster derived catalysts) particle size, electronic properties, and morphologies are closely intertwined and are ultimately inseparable [46]. Similar arguments as to the preparation of unique particle morphologies and electronic properties are at the heart of recent discussions

and investigations of the high aromatization activity of highly dispersed platinum on alkaline zeolites [23,24].

4.4. Electronic versus geometric effects on hexane conversion catalysis

Hexane conversion catalysis studies with the cluster derived catalysts showed higher selectivities for light hydrocarbon production and lower selectivities for benzene production than platinic acid derived catalysts [29,30]. Further, analysis of the light hydrocarbon distributions suggested that the mechanisms of C–C bond fission were different on cluster derived and traditional catalysts. The platinic acid-based catalysts produced large amounts of methane, presumably via a terminal bond fission (hydrogenolysis) reaction mechanism [29]. The cluster derived catalysts, however, showed light hydrocarbon distributions that favored internal C–C bond fission.

Hydrogenolysis reactions are known to require strong bonding between the metal and hydrocarbon and the strength of the resulting metal–carbon bond is a critical factor in determining the rate of hydrogenolytic C–C bond fission [1]. In this case, carbon monoxide stretching frequencies are a measure of the strength of a particular metal–carbon bond, with lower ν(C≡O) corresponding to stronger metal carbon bonds. Consequently, if hydrogenolysis-type mechanisms dominate the cracking activity of these catalysts, one would expect increased cracking activity to correlate with lower CO stretching frequencies. Comparing these two parameters using ambient temperature CO stretching frequencies (in which dipole–dipole coupling is still a large factor) suggests a loose correlation may exist (Table 1). However, using the IR data taken at elevated temperatures as a more accurate measure of ν(C≡O) (hence a more accurate measure of the metal–carbon bond strength), it is clear that there is little or no correlation between ν(C≡O) and cracking activity. This is consistent with the conclusion that the cluster derived catalysts perform C–C bond fission reactions via a mechanism different than hydrogenolytic cracking. Because hydrogenolysis reactions are know to require large platinum ensembles (on non-alkaline supports) [1], the lack of correlation is also consistent with the conclusion that these catalysts consist of very small bimetallic particles and do not have large platinum ensembles. This is also supported by the slower rate of benzene formation over the cluster derived catalysts, as 1,6 cyclization requires successive dehydrogenations and (on non-alkaline supports) occurs on multi-platinum ensembles [57].

Although the two cluster derived catalysts have reasonably similar CO stretching frequencies, their cracking activities differ by a factor of 2. The cracking activity of the Pt-Cu catalyst is also more than double that for the Pt catalyst — a catalyst that likely includes residual chlorine, which would be expected to enhance C–C bond fission reactions [58]. The increase in activity for C–C bond fission on traditional Pt-Cu alloys has been well documented [59–63]. One study in particular attempted to establish the role of Cu in hydrogenolysis reactions for several Cu containing alloys [64]. The authors suggested that Cu does indeed play a role in increasing rates of hydrogenolysis, possibly by participating in the binding of hydrocarbon intermediates via a "mixed ensemble". This investigation also suggested that "the individuality of the (active) transition metal atoms is possibly preserved in the alloys" [64]. Results with the cluster derived catalysts are consistent with this observation as light hydrocarbon distributions for the Pt_2Au_4 and Pt_2Cu_4 catalysts were nearly identical [30]. Further, the DRIFTS spectra of CO bound to the Pt-Cu catalyst offers possible spectroscopic evidence for such a "mixed ensemble" binding motif. The low energy absorption band postulated to be a bridging or semi-bridging mode between Pt and Cu, along with the data from supported alloys, suggests that such mixed ensembles may play a role in the reactivity of the Pt_2Cu_4 catalysts.

5. Summary

DRIFT spectroscopy of adsorbed carbon monoxide was used to further characterize bimetallic Pt-Au and Pt-Cu catalysts prepared from bimetallic molecular precursors. DRIFT spectra of catalysts prepared from $Pt_2Au_4(C{\equiv}C^tBu)_8$ and $Pt_2Cu_4(C{\equiv}C^tBu)_8$ supported previous evidence for the presence of bimetallic particles, as both cluster derived catalysts had significant binding of CO by the coinage metal. For the Pt-Cu catalyst, he shape of the Pt–C≡O peak was found to vary with CO delivery pressure. Both cluster derived catalysts had low coverage ν(C≡O) values that were red shifted 15–20 cm^{-1} relative to the value of a plat-

inum catalyst prepared from hexachloroplatinic acid. The spectroscopic results support several observations from previous catalysis results. There was no apparent correlation between between the low coverage C≡O stretching frequency and activity for C–C bond fission reactions during hexane conversion catalysis, which supported the conclusion that the cluster derived catalysts do not perform cracking reactions via a terminal carbon abstraction (hydrogenolysis) type mechanism. The role of Pt-Cu mixed ensembles in cracking reactions was also supported by spectroscopic evidence of a possible Pt-Cu bridging mode for carbon monoxide on the Pt_2Cu_4 catalyst.

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