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Catalytic conversion of olefins on supported cubic platinum nanoparticles: Selectivity of (1 0 0) versus (1 1 1) surfaces

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ABSTRACT

The surface chemistry and catalytic conversion of cis- and trans-2-butenes on platinum (1 0 0) facets were characterized via surface-science and catalytic experiments. Temperature-programed desorption studies on Pt(1 0 0) single crystals pointed to the higher hydrogenation probability of the trans isomer at the expense of a lower extent of C=C double-bond isomerization. To test these trends under catalytic conditions, shape selective catalysts were prepared by dispersing cubic platinum colloidal nanoparticles (which expose only (1 0 0) facets) onto a high-surface-area silica xerogel support. Infrared absorption spectroscopy and transmission electron microscopy were used to determine the conditions needed to remove the organic surfactants without loosing the original narrow size distribution and cubic shape of the original metal nanoparticles. Catalytic kinetic measurements with these materials corroborated the surface-science predictions, and pointed to a switch in isomerization selectivity from preferential cis-to-trans conversion with Pt(1 0 0) surfaces to the reverse trans-to-cis reaction with Pt(1 1 1) facets.

1. Introduction

As catalytic processes become more complex, the issue of selectivity continues to gain more significance. The need for selective catalytic processes arises from the need to minimize the amount of feedstocks consumed, bypass complex purification procedures for the products, and avoid releasing potentially polluting byproducts [1–3]. From a molecular standpoint, selectivity may be achieved by designing specific catalytic sites, perhaps emulating the way enzymes work. Controlling the shape of solid catalysts to produce such specific sites is in general difficult, but recent advances in self-assembly and nanotechnology offer novel approaches toward this goal. The use of catalysts with well-defined shapes has afforded high selectivities in many reactions [3–5].

Particularly promising are new reports on ways to control the shape of metal nanoparticles by using surfactants [6–8]. A multitude of shapes have been achieved by a variety of self-assembly synthetic approaches, including not only simple forms such as nanocubes, nanospheres and nanotetrahedra, but also nanostars, nanorods, nanofibers, nanowires, nanotubes, nanosheets, nanowheels, nanocages, and nanodendrites [9]. Some of these synthetic methodologies have been used in a few instances to prepare supported heterogeneous catalysts [10–13], but an additional challenge needs to be surmounted in such catalysis, the need to disperse the nanoparticles onto a high surface-area support and to pretreat the resulting solid in a way as to remove the organic material used during the nanoparticle synthesis without significantly affecting the shape of the metal clusters [2,8,14,15].

Our group has in recent years focused on the development of selective catalysts for the conversion of hydrocarbons by taking advantage of these new advancements [3,16–22]. Particularly critical to our work has been the identification of the potential effects of surface structure on the selectivity of mild reactions such as hydrogenations and C=C double-bond isomerizations, which have been previously assumed to be structure insensitive [23–26]. In that quest, we have recently shown that the (1 1 1) surfaces of platinum nanocrystals are particularly apt to promote the conversion of trans olefins to their more unstable cis isomers [27–31]. Subsequently, catalysts consisting of platinum tetrahedral nanoparticles, which only expose (1 1 1) facets, were developed and shown to indeed preferentially promote the desirable if thermodynamically unfavorable trans-to-cis conversion [32,33].

In this report we contrast the chemistry of the Pt(1 1 1)-based catalysts to new catalysts based on platinum with (1 0 0) surfaces. Initial surface-science experiments were carried out on Pt(1 0 0) single crystals to test the surface chemistry of cis- and trans-2-butene. Supported catalysts consisting of cubic-Pt nanoparticles were

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then produced and characterized, and their catalytic behavior toward the conversion of both 2-butenes was tested. Below we summarize the results from these studies, and provide a brief discussion on the contrasting catalytic behavior of cubic-versus tetrahedral-Pt nanoparticles.

2. Materials and methods

Temperature-programed desorption (TPD) experiments were carried out in an ultrahigh vacuum (UHV) system described in detail previously [34,35]. Briefly, a UTI 100C quadrupole mass spectrometer was employed for these experiments, retrofitted with a retractable nose cone terminated in a 5-mm-in-diameter aperture that can be placed within 1 mm of the surface of interest for the selective detection of molecules desorbing from the front face of the crystal. The mass spectrometer is interfaced to a personal computer capable of monitoring the time evolution of up to 15 different masses in a single TPD run. A constant heating rate, 10 K/s in the experiments reported here, is set by homemade electronics. The Pt(1 0 0) single crystal, a polished disk ∼1 cm in diameter and ∼1 mm in thickness, was mounted on a long-travel manipulator capable of cooling down to ∼90 K and resistively heating to 1100 K, and its temperature measured by a chromel–alumel thermocouple spot-welded to its side. The surface was routinely cleaned by cycles of oxidation and annealing in vacuum, and occasionally by Ar^+ sputtering. Gas exposures were performed by backfilling of the vacuum chamber, and are reported in Langmuirs (1 Langmuir = 10^{-6} Torr s), not corrected for differences in ion-gauge sensitivities. All gas dosing was done at temperatures below 100 K.

The cubic platinum nanoparticles were prepared by a procedure also reported in detail before [32] where an aqueous solution of K_2PtCl_4 and sodium polyacrylate (SPA, average MW ∼ 2100 amu) was reduced with hydrogen gas and let to rest until the growth of the nanoparticles was evident. The silica xerogel support was synthesized in-house by combining 30% aqueous ammonia and ammonium fluoride solutions with a 1:2 vol:vol ethanol:water mixture, stirring the resulting liquid into a separate ethanol solution of tetraethylorthosilicate (TEOS), and evaporating the solvent at 325 K until a white powder was obtained [36]. The silica xerogel powder was calcined to 675 K before use. To prepare the supported catalyst, the silica xerogel was added to a water-based colloidal solution of the cubic-Pt nanoparticles, and the mixture was sonicated and filtrated. The resulting wet powder was dried and calcined in air and oxidized and reduced three times in a quartz tube under flowing O_2 and H_2, respectively, all at the temperatures indicated in each specific case.

Characterization of the catalysts during the different stages of calcination and oxidation–reduction were carried out by transmission infrared (IR) absorption spectroscopy, using a cell for in situ spectra recording during gas exposures [37,38]. Additional characterization was performed by transmission electron microscopy (TEM), using a Philips TECNAI 12 instrument [39]. The kinetics of conversion of both cis- and trans-2-butenes with hydrogen were measured in a 150-ml close-loop recirculation reactor that can be evacuated with a mechanical pump to a base pressure of approximately 5×10^{-2} Torr, as measured by a thermocouple gauge and a capacitance manometer [40–42]. Samples (5 mg) of the catalysts were placed in a U-shaped quartz tube, a part of the reactor loop, and held in place by quartz wool plugs. Heating of the U tube was done with an Omega furnace equipped with an Omron temperature controller. The reactants (hydrogen, 2-butene, and argon) were introduced sequentially into the loop to the desired partial pressures (0.2, 10, and 590 Torr, respectively), and were mixed using a recirculation bellows pump. Aliquots (10-ml) of the gas sample were taken at 20-min intervals during the catalytic reactions and were analyzed by gas chromatography (GC) using a 23% SP-1700 on 80/100 Chromosorb PAW column (30 ft × 1/8 in. o.d., stainless steel; Supelco) and a flame ionization detector.

The cis-2-butene (>95% purity), trans-2-butene, (>95% purity), and deuterium (>99.5% atom purity) were all purchased from Matheson, and the hydrogen (>99.995% purity) and argon (99.998% purity) were obtained from Liquid Carbonic. Al gases were used as received.

3. Results

3.1. Temperature-programed desorption (TPD) on Pt(1 0 0)

The thermal chemistry of cis- and trans-2-butene on Pt(1 0 0) single-crystal surfaces was first characterized by TPD experiments under ultrahigh vacuum (UHV) conditions. The relevant results for the two isomers are reported in Figs. 1 and 2, respectively. Data from three sets of experiments are shown, carried out on clean (top traces) and hydrogen- (second traces from the top) and deuterium- (remaining traces) predosed surfaces. Desorption is reported for the butenes (left panels) and butanes (right) that are produced in these reactions. In the case of deuterium preadsorption, a maximum olefin isotope exchange of only two deuteriums was seen, presumably because of the preferential reactivity of the inner carbon atoms [27,28].

On clean Pt(1 0 0), only molecular 2-butene desorption was detected. However, the kinetics of that desorption appears to be somewhat complex, and results in the appearance of three TPD peaks with cis-2-butene, at 250, 265, and 310 K, and two with the trans isomer, at 252 and 282 K. Multiple TPD features with hydrocarbons is not unusual, in part because it is possible for the adsorbates to rearrange to different adsorption geometries as the surface coverage changes during temperature ramping [43]. Regardless, the total yield for cis-2-butene is larger than that for

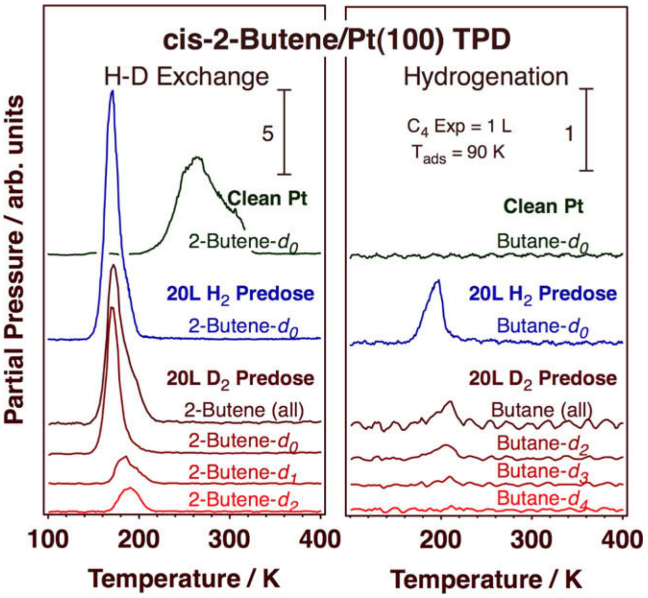

Fig. 1. Temperature-programed desorption (TPD) traces for 1.0 L of cis-2-butene adsorbed on a Pt(1 0 0) single-crystal surface under ultrahigh vacuum (UHV) conditions. Data are provided for the desorption of the relevant H–D exchange (left panel) and hydrogenation/deuteration (right) products. The results are reported from TPD experiments with cis-2-butene adsorbed on a clean surface (top traces), and on surfaces predosed with 20 L of either H_2 (second from top) or D_2 (remaining traces). Several observations are worth highlighting, including the significant lowering of the temperature of the cis-2-butene molecular desorption upon hydrogen/deuterium preadsorption, and the production of butanes and butenes with multiple deuterium substitutions.