Heterogeneous Catalysis

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Selective Amplification of C=O Bond Hydrogenation on Pt/TiO_2: Catalytic Reaction and Sum-Frequency Generation Vibrational Spectroscopy Studies of Crotonaldehyde Hydrogenation**

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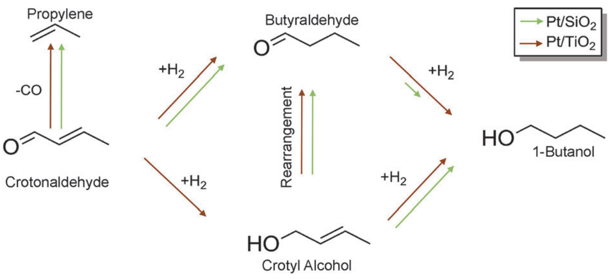
Abstract: *The hydrogenation of crotonaldehyde in the presence of supported platinum nanoparticles was used to determine how the interaction between the metal particles and their support can control catalytic performance. Using gas-phase catalytic reaction studies and in situ sum-frequency generation vibrational spectroscopy (SFG) to study Pt/TiO_2 and Pt/SiO_2 catalysts, a unique reaction pathway was identified for Pt/TiO_2, which selectively produces alcohol products. The catalytic and spectroscopic data obtained for the Pt/SiO_2 catalyst shows that SiO_2 has no active role in this reaction. SFG spectra obtained for the Pt/TiO_2 catalyst indicate the presence of a crotyl-oxy surface intermediate. By adsorption through the aldehyde oxygen atom to an O-vacancy site on the TiO_2 surface, the C=O bond of crotonaldehyde is activated, by charge transfer, for hydrogenation. This intermediate reacts with spillover H provided by the Pt to produce crotyl alcohol.*

Enhancement of a metal catalyst's reactivity and selectivity by a seemingly inert metal oxide support has been documented in the literature for numerous gas-phase reactions, such as methanol oxidation,[1] CO oxidation,[2] partial hydrogenation of organic molecules,[3–6] CO and CO_2 hydrogenation,[7] and hydroformylation,[8] on a variety of metals and supporting oxide systems. In some cases, by combining a metal with a metal oxide support the activity of the resulting system can far surpass what would be expected from a simple combination of the two materials. Among a number of explanations for these enhancements, depending on the reaction and catalyst materials utilized, the proposed mechanism of particular interest to this work involves a direct interaction between a reactant molecule and the oxide support, and the spillover of a second reactant from the metal.[9,10] In a reducing atmosphere at elevated temperatures, and in the presence of Pt, metal oxides undergo changes in the surface oxidation state by the formation of O vacancies. For example, Ti^{4+} is reduced to Ti^{3+}.[11,12] These electron-rich sites interact with adsorbate molecules and activate them toward a certain reaction pathway.[4] Studies of various metal oxide films deposited on metal surfaces have shown that the oxide plays a key role in activating C=O bonds.[7,13] The activity of catalysts for C=O bond hydrogenation in these studies scaled with the Lewis acidity of the oxide, thus indicating the critical role charge transfer plays in the catalytic process. The implication of charge transfer between the support and adsorbate draws a comparison to acid-base catalysis in which the generation of charged intermediates is the crucial step in determining the activity and selectivity of a reaction.[14,15] In this study it is proposed that intermediates are generated at O-vacancy sites on the TiO_2 surface of Pt/TiO_2 catalysts and that these intermediates are active for the hydrogenation of the C=O group in crotonaldehyde.

Crotonaldehyde hydrogenation (Scheme 1) and hydrogenation of other unsaturated aldehydes have been studied extensively because these reactions have three distinct, competing reaction pathways: decarbonylation to produce CO and propylene, hydrogenation of the C=C bond to yield the saturated aldehyde, and the hydrogenation of the C=O bond to yield the unsaturated alcohol.[5,16–18] Selective hydrogenation of the carbonyl bond in such systems without hydrogenation of the C=C bond is of great interest since unsaturated alcohols are useful chemical intermediates for pharmaceuticals and fragrances. However, even though the hydrogenation of the C=O bond has a 40 $kJ\,mol^{-1}$ lower activation barrier,[19] selectively producing the unsaturated alcohol at high rates can be a challenge since hydrogenation of the C=C bond is thermodynamically favored by 35 $kJ\,mol^{-1}$.[20] Previous work by Kliewer et al.[19] on croton-



Scheme 1. Reaction scheme showing all product pathways observed in the course of reaction studies. Two sets of arrows represent the activity for each pathway for Pt/SiO_2 and Pt/TiO_2. Equal sized arrows indicate no influence of support. Different length arrows represent relative difference between supports for that pathway.

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> aldehyde hydrogenation using platinum (111) and (100) single crystals shows that the dominant pathways at the temperature used in the present work are C=C bond hydrogenation to form butyraldehyde, and decarbonylation to form propylene, regardless of the crystal face. Based on these results, a C=O bond activating support could drastically alter the activity and selectivity of crotonaldehyde hydrogenation on Pt.

In this study Pt nanoparticle films, deposited onto SiO_2 and TiO_2 substrates, serve as model catalysts for the hydrogenation of crotonaldehyde (Figure 1). This reaction is well suited to probe how the SiO_2 and TiO_2 supports impact, or do not impact, the selectivity and activity for the various products. By coupling catalytic reaction studies with sum-frequency generation (SFG) vibrational spectroscopy, a highly surface-sensitive technique, we gain information at the molecular level about the surface species present on our catalysts under the reaction conditions,[21–23] and can correlate those species to the products formed with each catalyst. All turnover frequencies (TOFs) reported here are normalized to the number of Pt surface sites, as determined by ethylene hydrogenation, to account for any differences in catalyst size and metal loading. Full experimental details are given in Supporting Information.

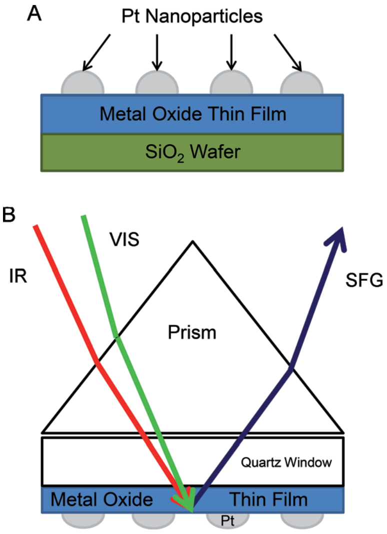

Figure 1. Schematic of samples prepared for catalytic tests (A) and SFG studies (B). The metal oxide films are deposited on the substrate (SiO_2 wafer or Quartz window) by electron beam evaporation. Pt nanoparticles are deposited onto the supporting material by Langmuir–Blodgett deposition. All samples are subsequently treated with UV irradiation in air to remove the capping ligands from the Pt nanoparticles.

A Pt/SiO_2 catalyst is used as a reference state under the assumption that SiO_2 has no active role in the catalysis. Inspection of our kinetic results and comparison to previous work, in which crotonaldehyde hydrogenation was carried out on Pt single crystals, give strong evidence that this assumption is valid. Catalytic tests were carried out in a batch-mode gas-phase reactor, and the crotonaldehyde conversion was kept below 15%. Figure 2 shows the TOF for the formation of each observed product for Pt/SiO_2 at 120°C. Only two products are produced by this catalyst under these reaction conditions: the decarbonylation product propylene (32% of total products), and the C=C bond hydrogenation product butyraldehyde (68% of total products). Neither of the C=O hydrogenation products, 1-butanol and crotyl alcohol, are detected. These results are similar to those obtained by Kliewer et al.[19] when using Pt (111) and (100) single crystals: propylene and butyraldehyde were also the two dominant products at 120°C along with the combined alcohol products making up less than 5% of all products on both crystal faces. It is therefore confirmed that SiO_2 has no impact on the catalytic reactions occurring on the Pt nanoparticle surface.

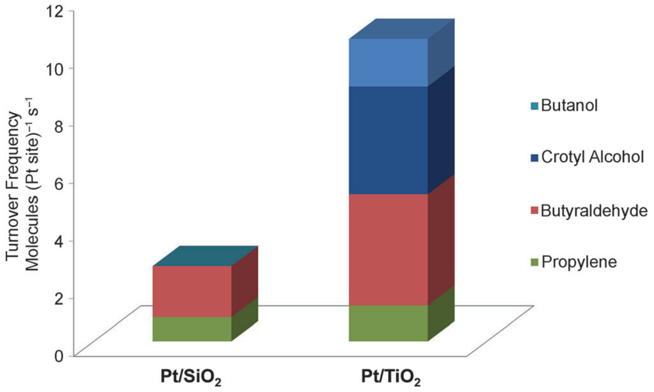

Figure 2. TOFs for the four observed products are reported for both Pt/SiO_2 and Pt/TiO_2 catalysts. Similar rates of propylene production are observed for both catalysts. Butanol and crotyl alcohol production is only observed on Pt/TiO_2 catalysts.

In contrast, the Pt/TiO_2 catalyst shows dramatically different performance (Figure 2). Under the same reaction conditions for crotonaldehyde hydrogenation, the Pt/TiO_2 catalysts showed a three- to fourfold increase in total activity, mainly from high rates of crotyl alcohol and butanol formation. The combined TOF toward the alcohol products is greater than that for either the propylene or butyraldehyde. The selectivity for the alcohol products is zero for Pt/SiO_2, but is 52% for Pt/TiO_2. Most importantly this change in selectivity is not a result of the loss of activity toward the other pathways, but is due to additional activity, thus indicating the presence of a new catalytic active site when Pt and TiO_2 are brought into atomic contact, a site which selectively produces alcohol products. The production of butanol is believed to be from a concerted reaction of both the C=O and C=C bonds of species adsorbed at the interface between TiO_2 and Pt, the alternative being that butanol is formed as a secondary product from the hydrogenation of butyraldehyde or crotyl alcohol. In our case butanol is observed very early on and the rate of its formation does not depend on the concentration of either of the primary products, thus supporting a concerted mechanism on Pt/TiO_2. Additionally if one were to assume a pseudo-first-order rate equation for the formation of the primary products (butyraldehyde and crotyl alcohol) from crotonaldehyde and for the formation of butanol from these primary products (as determined in Figure 2 in the Supporting Information), the amount of butanol produced as a secondary product would be below the detection limit of our apparatus. This data gives additional support to the conclusion that butanol is formed by a concerted process. Further catalytic tests were performed using the primary products (crotyl alcohol and butyraldehyde) as reactants and are presented in the Supporting Information. These tests help to further elucidate the mechanism we propose.

To better understand the mechanism by which TiO_2 enhances the rate of C=O bond hydrogenation SFG vibrational spectroscopy is employed to determine surface reaction intermediates. Figure 3 shows the SFG spectra for Pt/SiO_2 and Pt/TiO_2 under hydrogenation reaction conditions for crotonaldehyde. The proposed adsorption geometries and reaction intermediates are also shown. The Pt/SiO_2 spectrum shows two features at 2860 and 2915 cm^{-1}, which are consistent with previous work from Kliewer et al. on Pt single-crystal surfaces.[19] The peak at 2915 cm^{-1} is assigned to a CH_3 stretch and the peak at 2860 cm^{-1} is assigned to an aldehyde CH stretch. It has been shown previously that aldehyde stretches, usually near 2800 cm^{-1}, can be shifted into this range when adsorbed onto a surface.[24] This assignment is in agreement with the proposed η_2 adsorption mode, which is believed to be the intermediate responsible for the formation of butyraldehyde. The clear similarities between the SFG spectra taken on the Pt/SiO_2 and Pt (111) single crystal further support the claim that the SiO_2 support plays no active role in the hydrogenation of crotonaldehyde on Pt.

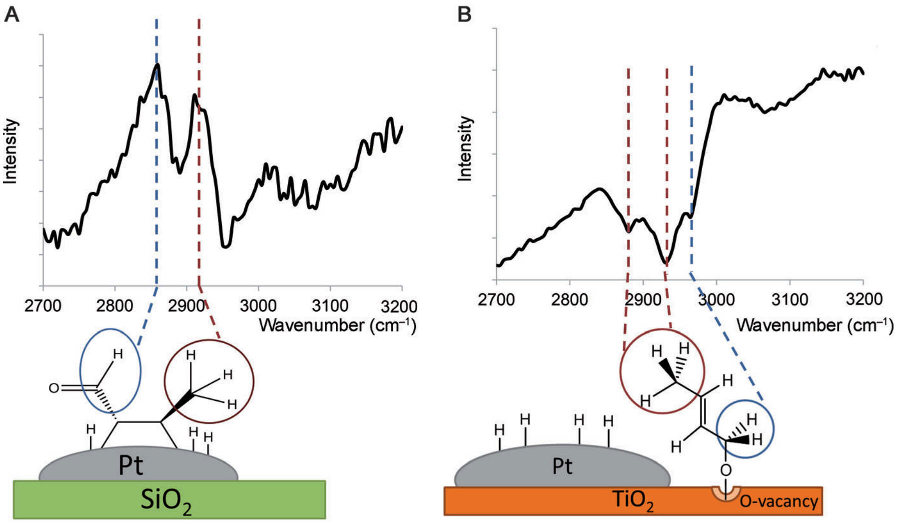

Figure 3. SFG spectra for A) Pt/SiO_2 and B) Pt/TiO_2 under reaction conditions of 1 Torr crotonaldehyde, 100 Torr hydrogen, and 669 Torr argon at a catalyst temperature of 120 °C. Assignment of these spectra, explained in the text, yields the accompanying surface intermediates.

The spectrum of Pt/TiO_2 (Figure 3B) shows several intense negative features at 2880, 2930, and 2965 cm^{-1}. Both the strength and sign of these peaks are due to the increased nonresonant component of the signal from Pt/TiO_2 in the presence of hydrogen. Hydrogen spillover from Pt to TiO_2 serves to reduce the surface of the TiO_2 to TiO_{2-x}, and in turn makes it more metallic. Additionally, this surface reduction increases the number of O-vacancy sites. The nonresonant component of the SFG spectra is largely the result of free-carrier motion at the surface of a sample. As more O vacancies are formed on the TiO_2 surface the free-carrier concentration increases, as evidenced by increased surface conductivity,[25] and subsequently the nonresonant component of the sum-frequency signal is larger. This increased signal serves as a marker for the chemical and electronic structure of the oxide surface and supports our hypothesis that O vacancies are the active catalytic sites. The increased nonresonant contribution can serve to elevate the baseline level in SFG spectra and also enhance the intensity of resonant features because of the relationship between the nonresonant and resonant components of $\chi^{(2)}$ and the SFG intensity. The resonant features observed are out of phase with this nonresonant background and thus appear as negative peaks.

The reported spectrum in Figure 3B is remarkably similar to the same region in the gas-phase IR spectrum for crotyl alcohol, and is indicative of a crotyl-oxy intermediate bound to the TiO_2 surface through the aldehyde oxygen atom. The features at 2880 and 2930 cm^{-1} are assigned to the CH_3 symmetric and asymmetric stretching modes, respectively.[26] The stretch at 2965 cm^{-1} is assigned to the CH_2 asymmetric stretching mode of the O-bound carbon atom.[27] Comparison of the Pt/TiO_2 spectrum with that of TiO_2 alone (see Figure 3 in the Supporting Information) shows that the aldehyde stretch disappears and a CH_2 stretch appears in the presence of Pt, thus indicating hydrogenation of the carbonyl carbon atom by H spillover from the Pt to the TiO_2. The result of this initial hydrogenation step is a crotyl-oxy surface intermediate (Figure 3B), which is the precursor to the crotyl alcohol product.

As stated previously, it is believed that the Ti^{3+} atoms at O-vacancy sites bind strongly to the aldehyde oxygen atom and activate the aldehyde carbon atom for hydrogenation by a charge-transfer process, thus drawing an analogy to acid-base catalysis. The charge-transfer process described previously,[4] wherein the excess electron at the Ti^{3+} site forms a covalent Ti−O bond with the aldehyde oxygen atom, results in a charge on the aldehyde carbon atom as the C=O bond becomes a C−O σ bond. This charged carbon atom is highly reactive and quickly reacts with the atomic hydrogen present on the surface. In the previous case of furfural, the adsorption of the aldehyde group at this Ti^{3+} site resulted in an energy decrease of the system by 1.35 eV as determined by DFT calculations. Addition of the hydrogen at the carbonyl carbon atom lowered the energy of the system by an additional 0.2 eV. The adsorption and initial single hydrogen addition are believed to be very fast and result in a fairly stable surface species, which we observe by SFG vibrational spectroscopy. The subsequent hydrogen addition at the aldehyde oxygen atom to form an O–H bond and adsorption of a new reactant molecule at this site would likely provide the energy required to desorb the molecule as a product. In light of this and the reaction data previously presented, which clearly demonstrate that the change in selectivity of the Pt/TiO_2 catalyst is due to additional activity toward the alcohol products relative to that of Pt/SiO_2, we are confident that the SFG spectrum observed for Pt/TiO_2 is that of a reactive surface species.

It has been shown for crotonaldehyde hydrogenation that the support for Pt particles has a substantial impact on the selectivity and activity of a catalyst. Pt particles on SiO_2 show few, if any, differences in both their catalytic selectivity and observed surface intermediates when compared to Pt single crystals, thus confirming that SiO_2 plays no active role in the catalytic reaction. When Pt nanoparticles are supported on TiO_2, substantial changes in the catalytic activity and selectivity are observed along with accompanying changes to the SFG spectrum. The Pt/TiO_2 catalyst has nearly four times the activity of that of Pt/SiO_2 and is over 50% selective toward the alcohol products. SFG vibrational spectroscopy was utilized to probe the molecular species present on the surface of these catalysts under the reaction conditions. The spectrum observed for Pt/SiO_2 is remarkably similar to that obtained for a Pt (111) single crystal under the same reaction conditions, and leads to the same assignment of a species which is an intermediate for the formation of butyraldehyde. Analysis of the SFG spectra for TiO_2 with Pt leads to the conclusion that crotonaldehyde binds to the TiO_2 surface through O-vacancy sites, thus activating the molecule for hydrogen addition at the aldehyde carbon atom. A crotyl-oxy species is observed on the TiO_2 surface, and is the intermediate for the formation of crotyl alcohol.

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