

In Situ Spectroscopic Investigation into the Active Sites for Crotonaldehyde Hydrogenation at the Pt Nanoparticle–Co₃O₄ Interface

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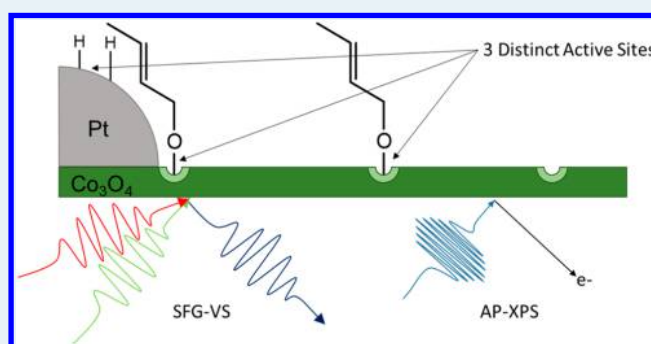
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S Supporting Information

ABSTRACT: The hydrogenation of crotonaldehyde by platinum nanoparticles supported on cobalt oxide was used as a reaction to probe the effect of the interface between the two materials on the activity and selectivity of the catalyst. Four potential products can be formed by this reaction: propylene, butyraldehyde, crotyl alcohol, and butanol. When Pt nanoparticles are supported on SiO₂, an inert support, only propylene and butyraldehyde are formed. However, when Pt is supported on cobalt oxide, the alcohols make up roughly 40% of the total activity, indicating that cobalt oxide plays a pivotal role in the reaction, much like other active supports such as TiO₂. To elucidate the mechanism of alcohol formation, in situ sum frequency generation vibrational spectroscopy (SFG) and ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) were utilized to probe the reactant adsorption and intermediate formation and the chemical state of the materials under working catalytic conditions. The SFG data indicate that crotonaldehyde adsorbs on the oxide surface, likely through the aldehyde oxygen as well as on the Pt surface through the alkene group. AP-XPS results show that the surface of the Co₃O₄ support becomes partially reduced under the reaction conditions and Pt exists in its metallic state. Taking these results together, we propose that the crotonaldehyde adsorbs at reduced oxide surface sites and that this adsorption mode is responsible for the production of alcohol products. A platinum nanoparticle density dependence study was also undertaken to change the abundance of interface sites and study their effect on the reaction. The selectivity between the two alcohol products was altered as a function of the Pt nanoparticle density: higher selectivity toward butanol and lower selectivity toward crotyl alcohol was obtained with increasing density, while propylene and butyraldehyde selectivities were constant with respect to density. On the basis of the data presented, we propose that butanol is preferentially formed at the metal–oxide interface, while crotyl alcohol is formed at oxide surface sites by reaction with spillover hydrogen.

KEYWORDS: hydrogenation, support effects, in situ characterization, cobalt oxide, sum frequency generation, ambient-pressure XPS



INTRODUCTION

Modification and control of catalytic properties by a seemingly inert support has been a focus of catalytic research for decades.^{1,2} A number of studies have shown that by changing the support one can change the activity and selectivity of a number of catalytic reactions including, but not limited to, alkane re-forming,³ hydrogenation of organic molecules,^{4,5} oxidation of carbon monoxide,⁶ and oxidation of methanol.⁷ In most of these cases, the oxide support does little to no chemistry on its own, but when it is combined with the active metal, the result is dramatically different from that with the metal alone. Several explanations have been offered in the literature⁸ to explain these effects, depending on the reaction and materials at hand, but few can be generalized to many reactions or material systems. In this work, we seek to establish a general mechanism for the selective hydrogenation of

aldehyde groups by Pt supported on reducible metal oxides. Previously the role of titanium dioxide as a support has been studied by our group,⁵ and here we expand that work to cobalt oxide (Co₃O₄).

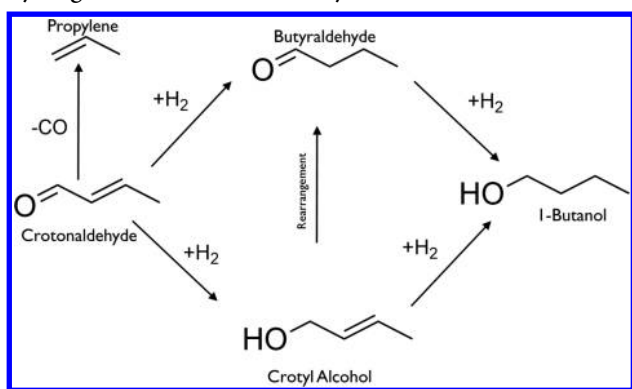
Crotonaldehyde hydrogenation is chosen here as a probe reaction, as it allows for a clear distinction between reaction pathways that have been shown to be sensitive to metal nanoparticle size⁹ as well as support material.^{10,11} As seen in Scheme 1, crotonaldehyde can hydrogenate into three products, butyraldehyde, crotyl alcohol, and butanol, or decarbonylate to make propylene. The most desired product of this reaction is crotyl alcohol, as it and other unsaturated

Received: June 9, 2016

Revised: September 14, 2016

Published: September 17, 2016

Scheme 1. Possible Reaction Pathways for the Hydrogenation of Crotonaldehyde



alcohols are valuable intermediates in the production of value-added fine chemicals and fragrances. As has been documented previously, platinum single-crystal surfaces¹² or platinum nanoparticles supported on SiO₂⁵ produce primarily propylene and butyraldehyde under the conditions used in this work. Through interaction with the support, in this case cobalt oxide, the aldehyde group can be activated and alcohols are formed. This type of interaction has been documented previously for TiO₂^{5,10,13} as the support, but some questions remain about the exact nature of the active site and the state of the active materials. Chief among these questions is the location of the active site for alcohol production. Three distinct possibilities exist: (1) alcohols are formed on the Pt surface which has been altered by an electronic interaction with the support, (2) alcohols are formed at the interface between platinum and the oxide, or (3) alcohols are formed on the oxide surface with atomic hydrogen that spills over from the metal surface following dissociation.

In this work we propose a direct adsorption of the reactant, crotonaldehyde, on the oxide surface, which is not active on its

own. The crotonaldehyde adsorbed on cobalt oxide can then react with spillover hydrogen from the platinum or additionally interact directly with the platinum surface at the interface through the carbon–carbon double bond. These two possibilities would in theory be responsible for the crotyl alcohol and butanol products, respectively. To arrive at this proposal, we undertook a study that allows us to vary the concentration of platinum nanoparticles on a flat cobalt oxide thin-film substrate, which in turn changes the relative abundance of interface versus oxide sites. The catalytic results show a clear dependence of the selectivities toward the two alcohols as a function of Pt NP density; as the density increases and thus there are more interface and fewer oxide sites, butanol formed more selectively at the expense of crotyl alcohol. This catalyst preparation also allows for study by sum frequency generation vibrational spectroscopy (SFG) and ambient pressure X-ray photoelectron spectroscopy (AP-XPS) experiments to be conducted. The development and use of in situ characterization techniques for catalysis and surface chemistry application has been a focus of research for the last two decades,¹⁴ and here we utilize two techniques that yield a fairly complete picture of the surface of our catalyst under reaction conditions. Using SFG we can study how the molecules adsorb on the surface of the metal and oxide, independent of one another and in combination, and correlate these surface intermediate species to the reaction performance. We found that the crotonaldehyde adsorbs strongly on the cobalt oxide surface under reaction conditions, likely through the aldehyde oxygen. With AP-XPS we can determine the composition and state of the catalyst surface under reactive conditions. Using this technique, we found that the Pt surface is fully reduced to its metallic state and the Co₃O₄ surface has been partially reduced, likely to Co(II), under the reaction conditions. By using our well-controlled catalyst preparation and these spectroscopic techniques, we get a full picture of the working catalyst.

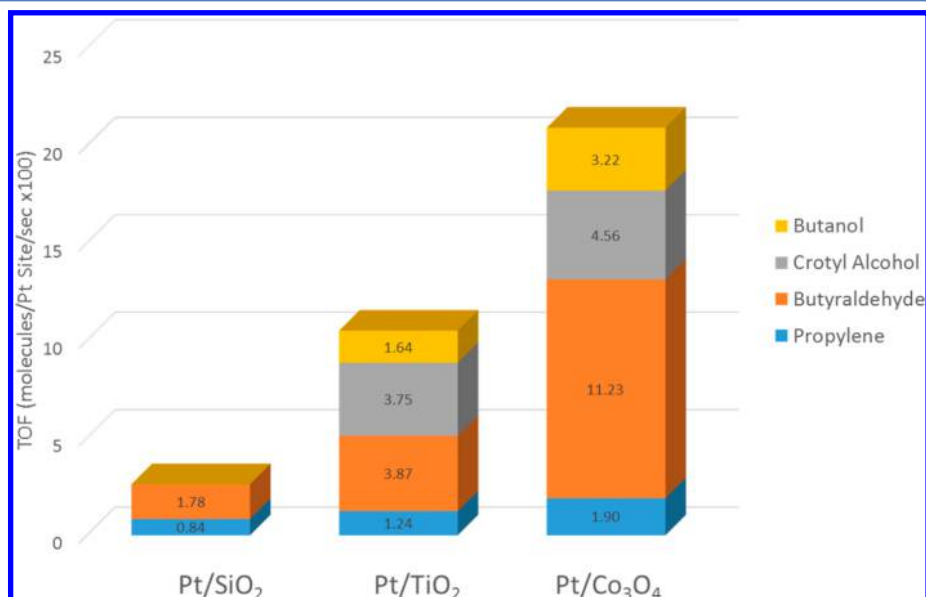


Figure 1. Comparison of the activity toward each product for crotonaldehyde hydrogenation on Pt supported on SiO₂, TiO₂, and Co₃O₄. SiO₂ plays no role in the catalytic reaction, and thus this point represents the activity of the Pt alone. Cobalt and titanium oxide both influence the reaction greatly by increasing the total activity and opening new reaction pathways toward the alcohol products. In all cases the Pt films were prepared with a roughly 27% coverage of the oxide surface, deposited at a surface pressure of 30 mN/m by the Langmuir–Blodgett method.

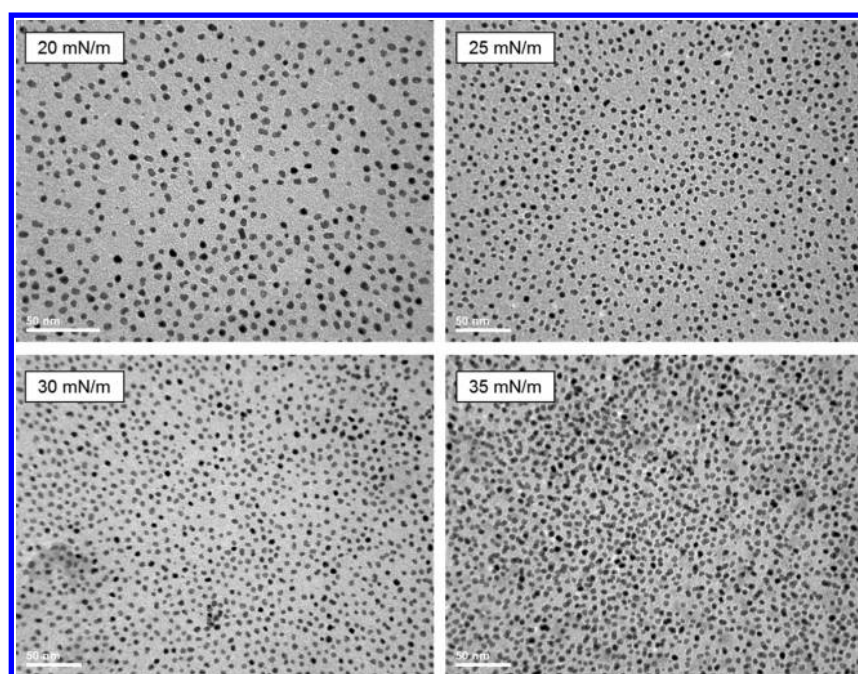


Figure 2. Transmission electron microscopy images obtained for each of the four density nanoparticle films studied for crotonaldehyde hydrogenation. The average particle diameter was determined to be 4.6 ± 0.4 nm. From these and 12 other images the percent coverage of the substrate by the nanoparticles was determined to be 17, 21, 27, and 32% for the Langmuir–Blodgett surfaces pressures of 20, 25, 30, and 35 mN/m, respectively.

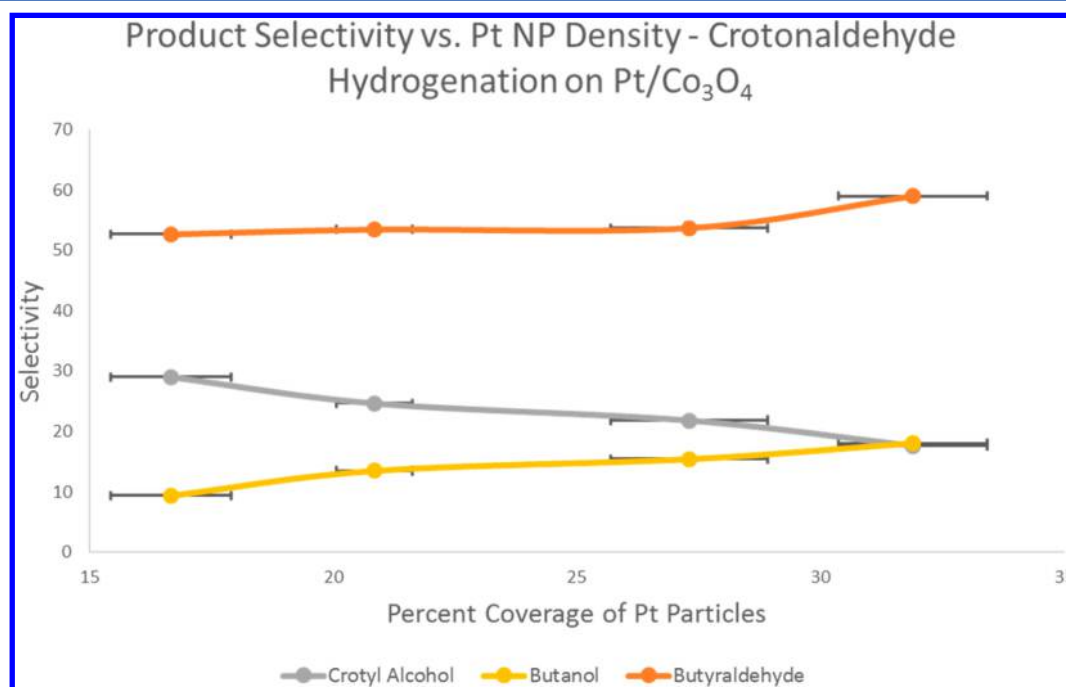


Figure 3. Selectivity toward the two alcohol products and butyraldehyde as a function of the Pt nanoparticle coverage on the cobalt oxide film. Here opposing trends for the crotyl alcohol and butanol are observed. As NP density is increased, the selectivity toward butanol increases at the expense of crotyl alcohol. Error bars represent the standard deviation obtained by quantifying multiple TEM images from different areas of the same sample.

RESULTS AND DISCUSSION

Catalytic Results. Figure 1 shows a comparison of the activity toward each of the four observed products for Pt on Co_3O_4 and previously reported data for Pt on SiO_2 and TiO_2 .⁵ As seen in the figure, Pt on SiO_2 produces exclusively butyraldehyde and propylene at 120 °C, results which closely mirror those from Pt single-crystal reaction studies.¹² This

indicates that SiO_2 plays no active role in the reaction. In contrast, the Pt supported on both TiO_2 and Co_3O_4 show dramatic increases in total activity in comparison to the Pt/ SiO_2 and for both a large part of that added activity is toward the alcohol products, which are not observed on Pt/ SiO_2 . The dramatic increase in activity, 3–4× increase for Pt/ TiO_2 and 8× increase for Pt/ Co_3O_4 , indicates that there are additional sites available for reaction on the cobalt and titanium oxide

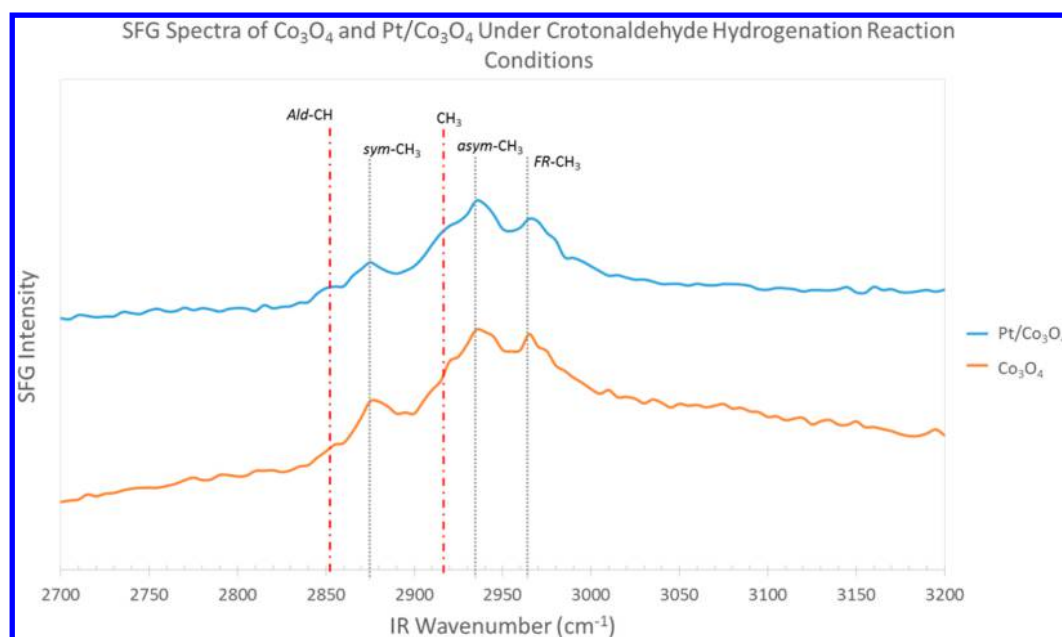


Figure 4. Sum frequency generation vibrational spectra of cobalt oxide with and without Pt nanoparticles under reaction conditions (1 Torr crotonaldehyde, 100 Torr H₂, 670 Torr He, 120 °C). The Pt film was deposited by the Langmuir–Blodgett method with a surface pressure of 30 mN/m, resulting in roughly 27% coverage of the support by Pt. The three features marked with the fine dotted line are assigned to a species adsorbed on the oxide surface via the aldehyde group. The two features marked with the heavier dotted line are assigned to crotonaldehyde adsorbed on Pt as a precursor to butyraldehyde.

supported catalysts and that these sites are active primarily for the formation of alcohols. The increased butyraldehyde formation on the Pt/Co₃O₄ and Pt/TiO₂ can be explained by the fact that a platinum-mediated rearrangement pathway exists for the conversion of crotyl alcohol to butyraldehyde. This rearrangement path was observed previously⁵ and was shown to be independent of the oxide. It is possible that this rearrangement could occur through the readsorption of previously formed crotyl alcohol molecules from the gas phase or by the migration and subsequent rearrangement of surface intermediates. However, we can not say conclusively which is the case from our work, since butyraldehyde is produced by a direct process as well as this indirect process.

In order to elucidate the role of each component, platinum and cobalt oxide, and the interface between the two, a study was subsequently undertaken in which the density of the platinum nanoparticle films was systematically varied. Catalysts were prepared with Langmuir–Blodgett films of platinum nanoparticles with surface pressures of 20, 25, 30, and 35 mN/m which yielded coverages of the substrate between 17 and 32%, as determined by transmission electron microscopy and summarized in Figure 2. A trend can be observed in the selectivity between the two alcohol products crotyl alcohol and butanol, as shown in Figure 3. As the density of the particle film is increased, a decrease in the crotyl alcohol selectivity and an increase in the butanol selectivity are observed. Across this range of particle densities the selectivity toward the other main product, butyraldehyde, increases slightly as well. This can be explained by the increase in Pt sites relative to oxide/interface sites as the density is increased. As described previously,⁵ we believe that butanol is produced by a concerted hydrogenation of both double bonds rather than by the sequential hydrogenation of one group, followed by desorption/readsorption and the hydrogenation of the other. Additionally, in the case of platinum supported on TiO₂ it was proposed that hydro-

genation of the aldehyde group was achieved through adsorption of the aldehyde oxygen on the oxide surface and hydrogenation by hydrogen spilling over from the platinum. We hold these ideas to be true for the case of cobalt oxide as well and propose that butanol production likely occurs very close to the Pt/Co₃O₄ interface, where the aldehyde group can interact with the oxide and the alkene group can interact with the Pt metal surface; thus, both bonds would be hydrogenated before desorption. We propose that the crotyl alcohol is likely produced by adsorption of the aldehyde group on the surface of the oxide, with platinum providing spillover hydrogen to reduce the aldehyde to an alcohol. With these proposed mechanisms we can make sense of the density-dependent selectivity. As the density of platinum increases, the amount of exposed oxide surface decreases and the amount of interface sites increases. We correlate a larger number of interface sites with a higher activity toward butanol and a decrease in exposed oxide surface to a decrease in crotyl alcohol production. This implies that there are at least three unique types of reaction sites on a Pt/Co₃O₄ catalyst, metal sites, oxide sites and interface sites, each of which can be correlated to a different reaction product.

Sum Frequency Generation Vibrational Spectroscopy.

Sum frequency generation vibrational spectroscopy, an in situ surface specific technique, is utilized here to understand how the reactant molecules interact with the catalyst surface under working catalytic conditions and correlate these interactions with the reaction results. Spectroscopic studies were done on cobalt oxide films with and without platinum nanoparticle films. This allowed us to decouple the support and metal signals to an extent and determine the extent to which the oxide alone interacts with the reactants. Figure 4 shows SFG spectra for cobalt oxide without Pt and Pt/Co₃O₄ under crotonaldehyde hydrogenation conditions at 120 °C. In the case of the oxide without platinum three peaks at 2875, 2940, and 2970 cm⁻¹ are assigned as the symmetric, asymmetric, and Fermi resonance

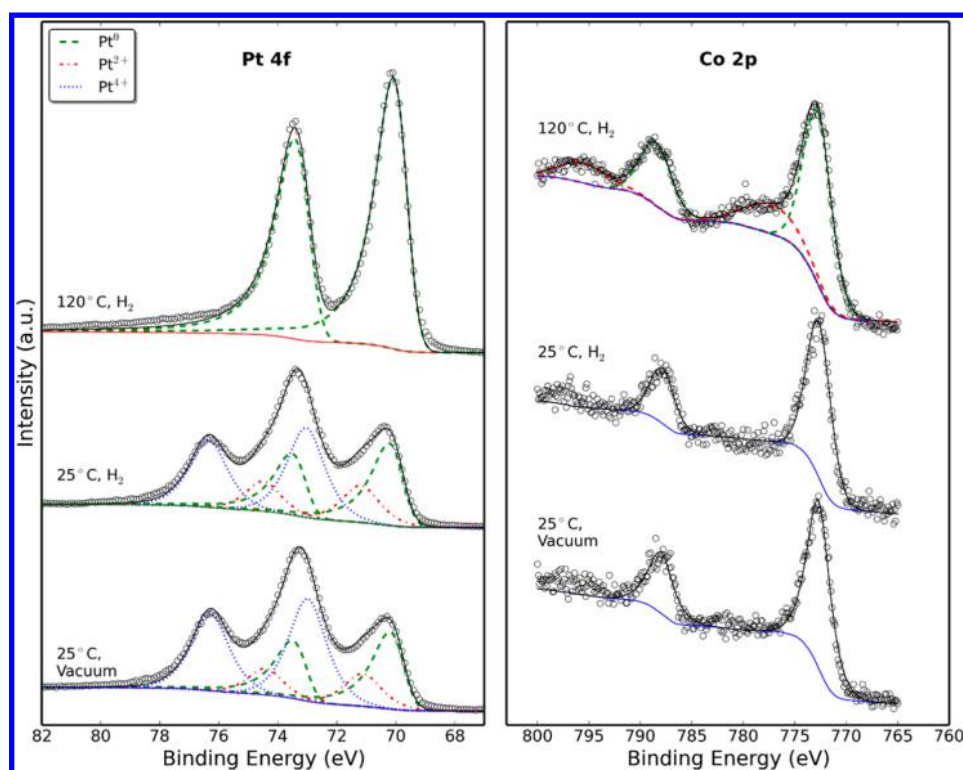


Figure 5. Ambient-pressure X-ray photoelectron spectra of the Pt 4f and Co 2p edges. The left panel shows the Pt 4f edge under three conditions. Immediately following the UV treatment the Pt is partially oxidized. When it is exposed to hydrogen at room temperature, the Pt remains oxidized; however, once it is heated to the reaction temperature of 120 °C the Pt is fully metallic. The right panel gives cobalt 2p spectra showing changes in the cobalt oxidation state at reaction temperature and in hydrogen versus immediately after UV treatment and hydrogen at room temperature. The appearance of satellites in the 120 °C in H₂ spectrum indicates that the surface of the Co₃O₄ support is partially reduced. The reduced surface is what is exposed during the reaction and likely has a role in the increased activity and selectivity.

peaks of the CH₃ group. These peak positions are largely unchanged relative to the gas-phase¹⁵ peaks, implying that there is no substantial interaction between the CH₃ group and the surface, as such an interaction would cause a shift in position. Furthermore, we assign the spectral features to these stretches, since we do not expect the molecule to have undergone any degree of hydrogenation on the Co₃O₄ surface without Pt, as there would be no source of atomic hydrogen; thus, no CH₂ stretches should be observed.

Adsorption and reaction of crotonaldehyde and hydrogen on platinum single crystals has been previously reported by Kliewer et al.¹² and the spectral assignments presented there have been shown to correlate well with the results for Pt nanoparticles on SiO₂.⁵ These results allowed us to assign two features observed in the Pt/Co₃O₄ spectrum at 2850 and 2920 cm⁻¹ to CH and CH₃(s) stretches of a crotonaldehyde molecule adsorbed on the Pt surface through the carbon-carbon double bond. This intermediate is believed to be the precursor to the formation of butyraldehyde, the major product for the Pt/SiO₂ catalyst and Pt single-crystal surface. It may appear that these features are present in the Co₃O₄ spectra as well, but they are quite close to the noise level of the spectrum and are clearly more intense in the Pt/Co₃O₄ spectrum. In the Pt/Co₃O₄ spectrum there are five identified features in total, three belonging to crotonaldehyde adsorbed on the oxide surface and two belonging to crotonaldehyde adsorbed on the platinum surface. However, this spectrum is dominated by the features assigned to the Co₃O₄ surface, with Pt adsorbed species giving rather small contributions comparatively. This would suggest that the cobalt oxide surface has an abundance of

sites available for adsorption of the crotonaldehyde. From this we can conclude that the cobalt oxide surface, while not active for the reaction on its own, can play a key role in controlling how the molecules interact with the catalyst surface and can provide additional reaction pathways that are not available to the Pt nanoparticles supported on inert supports. This is further supported by the fact that not only is the Pt/Co₃O₄ more selective toward the alcohol products but it is also far more active than the Pt/SiO₂ catalyst.

Ambient-Pressure X-ray Photoelectron and X-ray Absorption Spectroscopy. Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) was employed to determine the oxidation state of the platinum and cobalt constituents at various stages of pretreatment and under reaction conditions. These experiments were performed using catalysts prepared using the same methods as the catalytic and SFG studies but using a doped Si wafer to minimize the effect of charging. The samples were treated with UV irradiation for 3 h prior to being loaded into the XPS chamber. The results, summarized in Figure 5, show that immediately following UV treatment the surface of the platinum nanoparticles is substantially oxidized according to the fit of the Pt 4f edge. This is to be expected, as the UV lines used are known to produce ozone, which readily oxidizes and removes the organic capping agent, as well as the Pt surface. At room temperature hydrogen was introduced into the sample chamber following the vacuum spectra and the sample was then incrementally heated, taking spectra at various temperatures up to 240 °C. At room temperature in hydrogen the platinum surface remains predominantly oxidized. When it was heated to the reaction temperature of 120 °C in hydrogen,

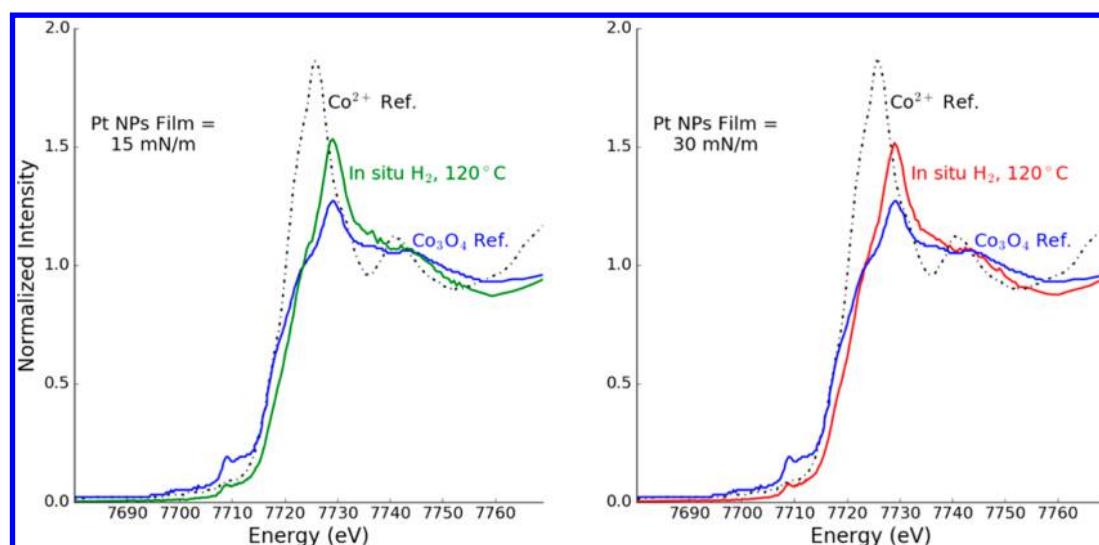


Figure 6. Near-edge X-ray absorption fine structure spectra for the cobalt K-edge for Pt nanoparticles of two film densities supported on cobalt oxide under reactive gas conditions in the fluorescence mode. The in situ spectra were taken at a catalyst temperature of 120 °C under a flow of hydrogen. This was done to mimic the reducing reaction gas mixture for crotonaldehyde hydrogenation. The in situ spectra show features closely resembling those of the spinel Co_3O_4 reference spectrum, specifically the pre-edge feature and the position of the white line, and are substantially different from the CoO reference spectrum. This goes to show that while the surface of the cobalt oxide is reduced to Co^{2+} , as shown by AP-XPS measurements, the bulk of the film remains predominantly in the Co_3O_4 structure.

the platinum became fully reduced to the metallic state and remained metallic as the temperature was increased further.

In Figure 5 the cobalt 2p edge is shown for two conditions: vacuum at 25 °C immediately after UV treatment and under hydrogen at 120 °C for a Pt/ Co_3O_4 catalyst. The major change here is the appearance of the satellite peaks near the oxide features under hydrogen. These satellites are indicative of CoO , while the as-prepared film is in the Co_3O_4 state. This is evidence that the oxide surface undergoes reduction under the reaction conditions. Considering this reduction occurs far below the bulk reduction temperature of cobalt oxide, it is likely due to the presence of atomic hydrogen spilling over from the Pt surface. Experiments were undertaken using in situ X-ray absorption spectroscopy in the fluorescence mode to measure the bulk cobalt oxide structure. The results (Figure 6) show that at 120 °C the bulk of the material remains in the spinel Co_3O_4 state, indicating that the reduction observed by AP-XPS is a surface effect. This is additional evidence that the oxide support can be active through a mechanism involving hydrogen spillover. Hydrogen spillover mechanisms have been shown previously, for example, in the case of carbon dioxide reduction.¹⁶

CONCLUSIONS

In summary we have established that Pt nanoparticles supported on Co_3O_4 give a dramatically enhanced activity and altered selectivity for crotonaldehyde hydrogenation in comparison to Pt supported on SiO_2 . The cobalt oxide support behaves similarly to another active support, TiO_2 , for this reaction, generating a large amount of the alcohol products. To understand the mechanism of the reaction, we employed in situ sum frequency generation vibrational spectroscopy and ambient-pressure X-ray photoelectron spectroscopy. The SFG results suggest that two species exist on the Pt/ Co_3O_4 surface: a Pt-bound precursor to butyraldehyde and a Co_3O_4 -bound precursor to the alcohols. The results obtained by AP-XPS show that under reaction relevant conditions, 120 °C and 100

mTorr H_2 , the Pt particles are fully reduced to the metallic state and the cobalt oxide surface is partially reduced, likely to Co^{2+} . This reduction of the oxide occurs at a temperature significantly lower than would be expected for the bulk oxide and suggests atomic hydrogen spills over onto the oxide to allow for this low-temperature reduction. This reduced surface contains sites for the adsorption and reaction of crotonaldehyde selectively to the alcohol products. By varying the density of the Pt nanoparticle film on the cobalt oxide support for reaction studies, we observed a trend in the selectivity between the two alcohol products, crotyl alcohol and butanol. As the density of the film increased, the butanol selectivity increased and the crotyl alcohol selectivity decreased. To explain this result, we propose a mechanism where butanol is formed at the interface between the Pt and Co_3O_4 such that the aldehyde group can interact with the oxide and the alkene group can interact with the Pt metal. We propose that crotyl alcohol is formed by adsorption at an oxide site through the aldehyde group, sufficiently far away from the Pt particle as to prevent interaction of the alkene with the metal. Crotyl alcohol is then formed by reaction with hydrogen spilling over from the Pt surface. These proposed mechanisms are in line with previous work on Pt/ TiO_2 ,^{4,5} and as such we believe this to be a general mechanism for activation of aldehyde groups by reducible oxide supports.

METHODS

Catalyst Preparation. The catalysts used for this study consisted of colloiddally synthesized platinum nanoparticles supported on cobalt oxide thin films prepared by atomic layer deposition (ALD).

Thin films were fabricated using an Oxford FlexAl-Plasma enhanced atomic layer deposition (ALD) apparatus in the Molecular Foundry at Lawrence Berkeley National Laboratory. Using bis(cyclopentadienyl)cobalt(II) as the gas-phase metal precursor, a substrate temperature of 300 °C, and alternating precursor and oxygen plasma cycles, thin films of spinel

(Co₃O₄)¹⁷ cobalt oxide were produced with a thickness of 30 nm for all applications.

Platinum nanoparticles with an average diameter of 4.6 nm were synthesized using the polyol method as described previously.¹⁸ In short, chloroplatinic acid hexahydrate and polyvinylpyrrolidone were dissolved in ethylene glycol in a 1:4 ratio by mass. The solution was then heated to 180 °C for 1 h under an argon atmosphere. The resulting dark brown solution was then mixed with acetone to precipitate the particles from solution. The particles were dissolved in ethanol and subsequently washed three times using ethanol and hexane.

The resulting particles were deposited onto two-dimensional substrates (silicon oxide wafers for catalytic tests and quartz windows for spectroscopic study which had been coated with the previously mentioned cobalt oxide films), using a Langmuir–Blodgett trough as described previously.⁵ Langmuir–Blodgett deposition allows for control of the nanoparticle density on the substrate by varying the surface pressure of a water surface coated with the nanoparticle solution maintained during deposition. Catalysts were prepared with surface pressures ranging between 20 and 35 mN/m, resulting in a 17–32% coverage of the substrate by platinum nanoparticles. Figure 2 shows transmission electron microscopy images of the four different density films. These images show a clear trend between LB pressure and particle coverage. Several images for each pressure were used to determine the percent coverages.

Following deposition of the nanoparticles the combined Pt/Co₃O₄ catalyst was treated with ozone-producing UV light, in a home-built treatment chamber consisting of two low-pressure mercury (Hg) lamps (Lights Sources Inc., Model No. GPH357T5VH/4P) which emit two lines: 184 and 254 nm. This serves to remove the PVP capping ligand from the particles and subsequently initiates contact between the metal particle and oxide. This contact has been previously reported as critical for the support to influence the reaction rate and selectivity.⁴ After this UV treatment the catalyst was ready for catalytic or spectroscopic measurement.

Measurement of Catalytic Performance. Catalyst reactivity and selectivity were measured using a stainless steel, batch mode, gas-phase reactor. The reactor consists of a 1 L chamber, boronitride resistive heater, thermocouple, metal bellow recirculation pump, and gas manifold for dosing reaction gases. For all crotonaldehyde hydrogenation reactions 1 Torr of crotonaldehyde, 100 Torr of hydrogen, and 669 Torr of helium were dosed into the reactor. Each reaction was run for 8 h, and the gas mixture was sampled approximately every 5 min and analyzed by a gas chromatograph equipped with a flame ionization detector and Cyclodex B capillary column. The catalysts temperature was 120 °C unless otherwise noted. Reaction rates were calculated by plotting the normalized GC peak area for each gas versus time. Total conversion was kept low (below 10%) over the 8 h reaction time in order for a steady-state approximation to be made. Reported rates were taken after initial deactivation, attributed to CO poisoning of the Pt surface.

To obtain a turnover frequency (TOF, product molecules produced per Pt site per second), the reaction rates were normalized to the number of Pt surface atoms, as determined from a measurement of the ethylene hydrogenation activity for each catalyst. Since ethylene hydrogenation is a structure-insensitive reaction, a known TOF¹⁹ can be used to calculate the number of Pt sites from a measured reaction rate.

Conditions for all ethylene hydrogenation reactions was 10 Torr ethylene, 100 Torr hydrogen, and 660 Torr He at 25 °C.

Sum Frequency Generation Vibrational Spectroscopy. Sum frequency generation vibrational spectroscopy (SFG-VS) is a nonlinear spectroscopic technique that allows for vibrational spectra to be collected specifically from surfaces and interfaces. Rather than probing the molecular dipole (infrared absorption) or polarizability (Raman spectroscopy), SFG probes the molecular hyperpolarizability. The hyperpolarizability (β) can be represented as the product of the molecular dipole (μ) and molecular polarizability (α):

$$\beta_{abc} = \mu_c \alpha_{ab}$$

By the rule of mutual exclusion we know that a molecule possessing centrosymmetry cannot have a vibrational mode with both a nonzero dipole moment and a nonzero polarizability; thus, SFG can only occur when centrosymmetry is broken, most importantly, at interfaces between phases. This property makes SFG exceedingly useful for selectively obtaining vibrational spectra from molecules adsorbed at a gas–solid interface. The SFG signal is generated when two beams, a visible beam with a fixed wavelength and an infrared beam with a tunable wavelength, are overlapped at the interface. The process can be thought of as a combined infrared absorption and anti-Stokes Raman scatter, yielding a photon whose frequency is the sum of the input beams. The signal intensity will increase when the wavelength of the infrared beam is resonant with a vibrational mode of a molecule at that interface, thus giving a spectrum of SFG intensity vs IR wavelength.

This was accomplished using an active/passive mode-locked Nd:YAG laser (Continuum Leopard D-20) which produces 20 ps pulses of 1064 nm light at a repetition rate of 20 Hz. The fundamental 1064 nm output was passed through an optical parametric generator/amplifier (Laservision) to give a second harmonic visible beam (VIS) of 532 nm and a mid-infrared beam (IR) tunable from 2700 to 3600 cm⁻¹. Spectroscopic experiments were performed in the total internal reflection geometry as shown in Figure S1 in the Supporting Information. The IR and VIS beams, each with 200 μ J power per pulse, were overlapped spatially and temporally at the surface of the catalyst deposited on a quartz window as described above, which was pressed against a quartz prism in order to direct the beams. An index-matching gel consisting of deuterated polystyrene and deuterated decalin was used to prevent reflection at the prism–window interface. The SF signal was collected using a PMT accompanied by a gated integrator to improve the signal quality. With use of a home-built cell the surface was heated and a recirculating mixture of the reaction gases was passed over the catalyst.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy, performed in vacuum and in ambient-pressure modes, allows for the characterization of composition of the catalyst surface and determination of surface oxidation states. Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) was performed at beamline 9.3.2 of the Advanced Light Source at Lawrence Berkeley National Laboratory. This beamline has a tunable X-ray source (240–900 eV) and a differentially pumped hemispherical analyzer that allows for the introduction of gas to the sample at pressures up to several Torr. Catalysts for XPS study were prepared in the same manner as those for catalytic tests; however, the wafer used was a highly p-doped wafer rather than one with a thermally grown silicon oxide, in order to reduce the charging of the surface. A thorough

description of the beamline can be found elsewhere.²⁰ Analysis and fitting of the XPS spectra was performed using CasaXPS.

Transmission Electron Microscopy. Microscopy experiments were performed using a JEOL 2100-F 200 kV field-emission analytical transmission electron microscope in the Molecular Foundry at Lawrence Berkeley National Laboratory. Image analysis was performed using ImageJ.

Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS). In situ NEXAFS spectroscopy was performed at the Advanced Light Source Beamline 10.3.2 at Lawrence Berkeley National Laboratory. Experiments were carried out using fluorescence yield detection in the QuickXAS mode using a home-built cell described previously.²¹ Dead-time correction, pre-edge removal, and post-edge normalization of the near-edge spectra (up to 250 eV past the absorption threshold at the Co K edge) were carried out with software developed at the beamline.²²

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b01640.

Schematic of the sum frequency generation vibrational spectroscopy in situ cell and a figure showing the activity toward the alcohol products as a function of particle density (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division, under Contract DE-AC02-05CH11231. Additional support for G.K. was provided by the Lam Research Graduate Student Fellowship. Work at the Molecular Foundry was done under proposal 3806. Work at the Advanced Light Source was done under proposals 06698 and 06735.

■ REFERENCES

- (1) Tauster, S.; Fung, S.; Baker, R.; Horsley, J. *Science* **1981**, *211*, 1121–1125.
- (2) Schwab, G. M.; Koller, K. *J. Am. Chem. Soc.* **1968**, *90*, 3078–3080.
- (3) An, K.; Alayoglu, S.; Musselwhite, N.; Na, K.; Somorjai, G. A. *J. Am. Chem. Soc.* **2014**, *136*, 6830–6833.
- (4) Baker, L. R.; Kennedy, G.; van Spronsen, M.; Hervier, A.; Cai, X.; Chen, S.; Wang, L.-W.; Somorjai, G. A. *J. Am. Chem. Soc.* **2012**, *134*, 14208–14216.
- (5) Kennedy, G.; Baker, L. R.; Somorjai, G. A. *Angew. Chem.* **2014**, *126*, 3473–3476.
- (6) An, K.; Alayoglu, S.; Musselwhite, N.; Plamthottam, S.; Melaet, G.; Lindeman, A. E.; Somorjai, G. A. *J. Am. Chem. Soc.* **2013**, *135*, 16689–16696.
- (7) Hervier, A.; Baker, L. R.; Komvopoulos, K.; Somorjai, G. A. *J. Phys. Chem. C* **2011**, *115*, 22960–22964.
- (8) Park, J. Y.; Baker, L. R.; Somorjai, G. A. *Chem. Rev.* **2015**, *115*, 2781–2817.
- (9) Grass, M.; Rioux, R.; Somorjai, G. *Catal. Lett.* **2009**, *128*, 1–8.

- (10) Englisch, M.; Jentys, A.; Lercher, J. A. *J. Catal.* **1997**, *166*, 25–35.
- (11) Vannice, M. A.; Sen, B. *J. Catal.* **1989**, *115*, 65–78.
- (12) Kliewer, C. J.; Bieri, M.; Somorjai, G. A. *J. Am. Chem. Soc.* **2009**, *131*, 9958–9966.
- (13) Dandekar, A.; Vannice, M. A. *J. Catal.* **1999**, *183*, 344–354.
- (14) Han, H.-L.; Melaet, G.; Alayoglu, S.; Somorjai, G. A. *ChemCatChem* **2015**, *7*, 3625–3638.
- (15) Jayaprakash, A.; Arjunan, V.; Jose, S. P.; Mohan, S. *Spectrochim. Acta, Part A* **2011**, *83*, 411–419.
- (16) Beaumont, S. K.; Alayoglu, S.; Specht, C.; Kruse, N.; Somorjai, G. A. *Nano Lett.* **2014**, *14*, 4792–4796.
- (17) Donders, M. E.; Knoops, H. C. M.; van, M. C. M.; Kessels, W. M. M.; Notten, P. H. L. *J. Electrochem. Soc.* **2011**, *158*, G92–96.
- (18) Rioux, R. M.; Song, H.; Hoefelmeyer, J. D.; Yang, P.; Somorjai, G. A. *J. Phys. Chem. B* **2005**, *109*, 2192–2202.
- (19) Kuhn, J. N.; Tsung, C.-K.; Huang, W.; Somorjai, G. A. *J. Catal.* **2009**, *265*, 209–215.
- (20) Grass, M. E.; Karlsson, P. G.; Aksoy, F.; Lundqvist, M.; Wannberg, B.; Mun, B. S.; Hussain, Z.; Liu, Z. *Rev. Sci. Instrum.* **2010**, *81*, 053106.
- (21) Alayoglu, S.; Beaumont, S. K.; Melaet, G.; Lindeman, A. E.; Musselwhite, N.; Brooks, C. J.; Marcus, M. A.; Guo, J.; Liu, Z.; Kruse, N.; Somorjai, G. A. *J. Phys. Chem. C* **2013**, *117*, 21803–21809.
- (22) Marcus, M. A.; MacDowell, A. A.; Celestre, R.; Manceau, A.; Miller, T.; Padmore, H. A.; Sublett, R. E. *J. Synchrotron Radiat.* **2004**, *11*, 239–247.