



The molecular mechanism of the poisoning of platinum and rhodium catalyzed ethylene hydrogenation by carbon monoxide

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

CO poisoning of ethylene hydrogenation was studied on platinum and rhodium single crystals as well as on platinum nanoparticles deposited on alumina in the mTorr and Torr pressure regimes. Reaction studies using gas chromatography on Pt(1 1 1) show that CO poisons the reaction, and the measured activation energy in the presence of CO (20.2 kcal/mol) is higher than without CO (9.6 kcal/mol). STM studies on Rh(1 1 1) show that in the absence of CO, hydrogen and ethylidyne species that are present on the surface in large concentrations diffuse rapidly on the surface and thus, cannot be imaged. When CO is introduced, ordered structures appear on the surface. Based on these results, a model is proposed for CO poisoning on single crystals in which CO adsorbs on vacant hollow sites, preventing the diffusion of ethylidyne. With the immobile adsorbates filling the surface, ethylene from the gas phase has no room to adsorb, and ethylene hydrogenation is prevented. Similarly, CO on platinum nanoparticles reduces the reaction rate of ethylene hydrogenation. Unlike on Pt(1 1 1), however, CO does not change the activation energy significantly. This indicates that platinum at the oxide–metal interface sites remains active as CO is rapidly hydrogenated and removed from these sites.

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1. Introduction

The metal catalyzed hydrogenation of ethylene was discovered by Sabatier (for a review see [1]), and it was an important part of his Nobel Prize winning research. This was the first catalytic reaction for which a mechanism was proposed in 1934 by Polanyi and Horiuti [2], which postulated hydrogen molecule dissociation on the metal surface and the sequential

hydrogenation of ethylene to C₂H₅ and then to C₂H₆. Since the late 1970s our laboratory was engaged in molecular studies of the mechanism of this reaction on platinum and rhodium crystal surfaces, and a detailed picture of many of the elementary reaction steps has emerged. Using low-energy electron diffraction (LEED) and sum frequency generation (SFG)-surface vibrational spectroscopy, the structure of adsorbates has been determined [3–7]. Three species: π -bonded ethylene (C₂H₄), di- σ -bonded ethylene (C₂H₄), and ethylidyne (C₂H₃), have been identified on the surface under reaction conditions (Fig. 1). The latter two species are bound to the metal surfaces strongly

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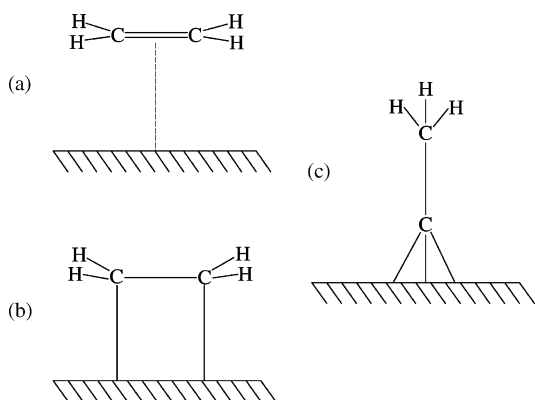


Fig. 1. The three surface structures formed by adsorbed ethylene on Pt(111) and Rh(111): (a) π -bonded ethylene; (b) di- σ -bonded ethylene; (c) ethylidyne.

enough to be stable even in vacuum. π -Bonded ethylene is weakly bound and present on the surface only at high-pressures of hydrogen and ethylene under the reaction conditions. Scanning tunneling microscopy (STM) studies [8] and modeling [9] indicate that the ethylidyne species are mobile on the surface at 300 K shuttling between three-fold fcc and hcp sites with an activation energy of 0.1 eV. Ethylidyne also restructures the Pt(111) and Rh(111) surfaces as it forms, as has been detected by LEED surface crystallography studies. These structures are shown in Fig. 2 [10]. This restructuring is also confirmed by density functional theory studies [11].

A mechanism for ethylene hydrogenation involving several elementary reaction steps can be proposed based on experimental observations, as displayed in Fig. 3. In this mechanism, hydrogen molecules adsorb dissociatively on an ethylidyne-covered metal surface. Ethylidyne diffusion between fcc and hcp three-fold hollow sites opens up holes in the ethylidyne overlayer where π -bonded ethylene weakly adsorbs on the metal. The ethylene is then stepwise hydrogenated through an ethyl intermediate to ethane. Isotope exchange experiments indicate that ethylidyne is a spectator [12]. π -Bonded ethylene hydrogenation turnover accounts for most of the ethane that forms. Its concentration is only 4% of a monolayer. This mechanism was elucidated from experiments on Pt, and chemical reaction studies have shown that ethylidyne formation and stepwise hydrogenation of π -bonded ethylene are also mechanistically probable on Rh [13].

We discovered that CO, when introduced in the reaction chamber during ethylene hydrogenation, poisons the catalytic reaction. In this paper we discuss the experimental evidence for this poisoning effect and propose mechanisms that explain this interesting effect based on our studies of reaction rates using metal single crystals and metal nanoparticles on alumina. SFG and STM permit us to monitor the metal surfaces under reaction conditions.

2. Experimental

2.1. Reaction rate studies on a Pt(111) single crystal by a gas chromatography

The experimental apparatus is comprised of an ultra-high vacuum (UHV) chamber with a base pressure of 4×10^{-10} Torr and a high-pressure (HP) cell. The HP cell, where high-pressure catalysis studies were carried out, was connected to the UHV chamber through a gate valve. A gas chromatograph (GC, Hewlett-Packard 6890) was connected to the HP cell through a recirculation loop.

The Pt(111) crystal was cleaned by sputtering with Ar^+ ions (1 keV), heating it at 1100 K in the presence of 5×10^{-7} Torr O_2 for 2 min, and then annealing it at 1100 K in UHV for 2 min [14]. After a few cycles of cleaning, the Pt(111) crystal was transferred to the HP cell for GC experiments. The cleanliness of the Pt(111) surface was routinely checked by Auger electron spectroscopy (AES). A detailed description of the UHV-HP system can be found elsewhere [15].

Gases were pre-mixed before being introduced to in the HP cell. The mixture of gases for ethylene hydrogenation without CO includes 10 Torr C_2H_4 , 100 Torr H_2 , and Ar added to make total of 760 Torr. To study the poisoning effects of CO on ethylene hydrogenation, 1 Torr CO was added to the mixture before introduction. The mixture of gases was always recirculated during the GC measurements.

2.2. Scanning tunneling microscopy studies at high-pressure

All STM experiments were performed in a high-pressure, high-temperature system combining a UHV surface analysis/preparation chamber with a

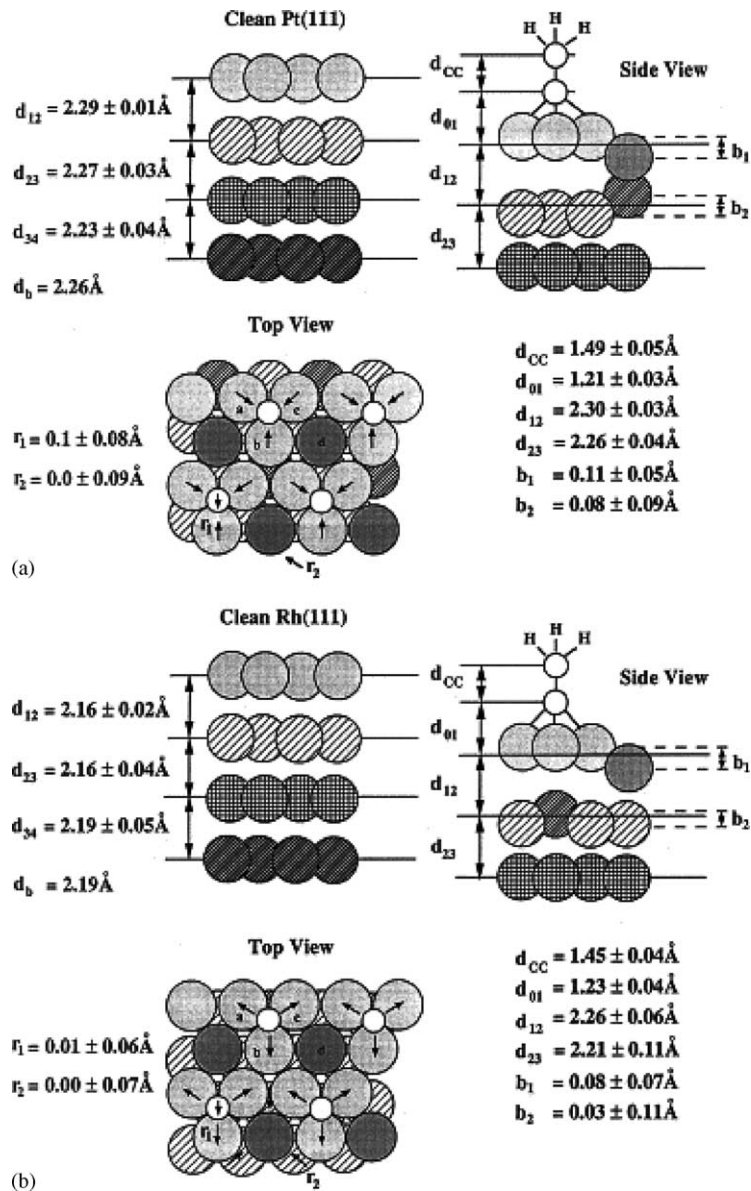


Fig. 2. (a) Structure of chemisorbed ethylidyne on Pt(111); (b) structure of chemisorbed ethylidyne on Rh(111) [10].

variable pressure (10^{-10} to 10^3 Torr) and temperature (300–675 K) STM. The base pressure of the system was 5×10^{-10} Torr, with the background made up primarily of H_2 , CO, and water. The STM chamber can be isolated by three gate valves and filled with any gas mixture. The composition of the gas can be monitored using a mass spectrometer. More specific

capabilities of the instrument have been described in detail elsewhere [16].

The Rh(111) sample was prepared by sputtering with 400 eV oxygen ions for 10 min followed by annealing in vacuum at 973 K for 2 min. Just before the sample was exposed to the reaction gases, it was flashed again briefly to 973 K. The sample

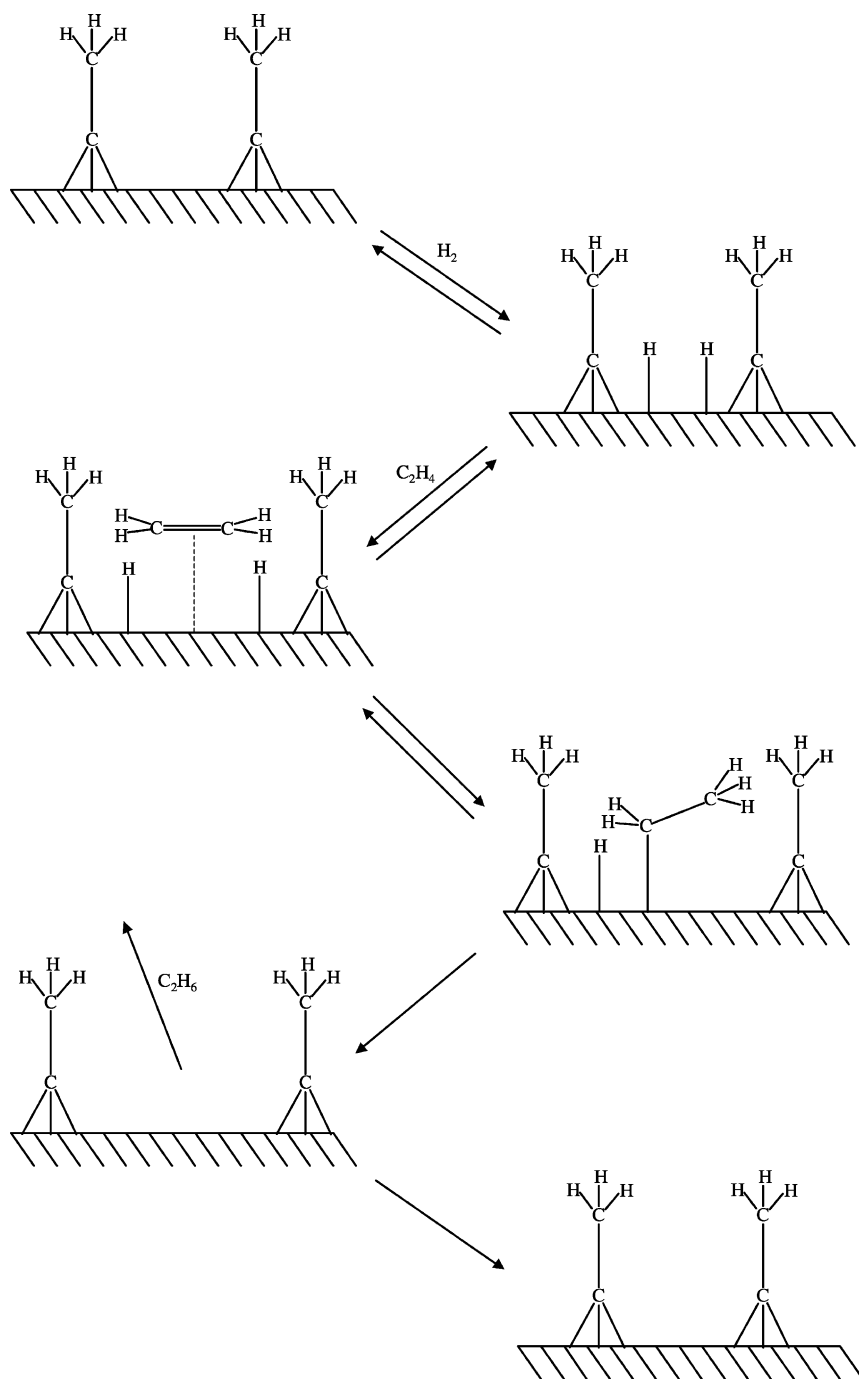


Fig. 3. Proposed mechanism for ethylene hydrogenation on Pt(111) and Rh(111).

temperature was monitored with a chromel–alumel thermocouple mounted in the sample holder in contact with the edge of the crystal, and sample cleanliness was checked with Auger electron spectroscopy. The clean, room-temperature sample was then transferred to the STM chamber. Large scale images of the sample showed steps with no preferred orientation, with a spacing that corresponds to a crystal miscut angle less than 1° .

2.3. Platinum nanoparticles on alumina: fabrication, characterization, and reaction studies

The details of the fabrication of Pt nanoparticle array model catalysts by electron beam lithography have been reported elsewhere [17,18]. Briefly, a highly collimated electron beam is used to expose a thin layer of polymethylmethacrylate (PMMA) spin-coated on a Si(100) wafer coated with 15 nm of alumina (Al_2O_3). The electron irradiation breaks the polymer backbone and increases the solubility of irradiated polymer in a developing solution. After development, a 15 nm thick Pt film was deposited on the surface via electron beam evaporation. The remaining PMMA was removed with acetone. An Al_2O_3 -supported Pt nanoparticle array model catalyst with 28 ± 2 nm diameters and 100 ± 2 nm interparticle spacing was used in this study. A field emission scanning electron microscope (FESEM) image of one such array is shown in Fig. 4. The sample was characterized by FESEM, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The catalysis study was carried out in an ultra-high vacuum chamber coupled

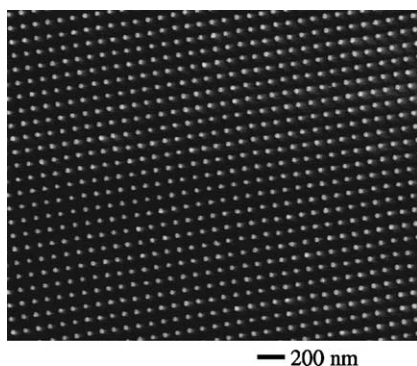


Fig. 4. FESEM image of the platinum nanoparticle array showing a diameter of 28 ± 2 nm and a periodicity of 100 ± 2 nm.

with a high-pressure cell. The details of the experimental apparatus and procedure are published elsewhere [19]. To study the poisoning effects of CO on ethylene hydrogenation, CO was pre-mixed with the reaction gases in the gas tubing before being introduced into the high-pressure reaction cell. The products were then analyzed with a gas chromatograph (Hewlett-Packard 5890 series II).

3. Results and discussion

3.1. Reaction rate studies on Pt(111)

The effect of CO on hydrogenation of ethylene to ethane was investigated over Pt(111) at temperatures between 400 and 523 K. Fig. 5 shows the Arrhenius plot of $\ln(\text{initial turnover frequency (TOF)})$ versus $1/T$ for ethylene hydrogenation with (●) and without (■) CO over Pt(111), where TOF is defined as the number of ethane molecules generated per surface atom per second. Activation energies obtained from the slopes are 20.2 ± 0.1 and 9.6 ± 0.4 kcal/mol, respectively. The result in the absence of CO is consistent with previous studies (10.8 kcal/mol for Pt(111) [12] and 9.9 kcal/mol for a Pt supported catalyst [20]).

The measured activation energy in the presence of CO, 20.2 ± 0.1 kcal/mol, is close to the desorption energy of CO on Pt(111). In the mTorr and above pressure range, CO is known to form a structure on the surface with a coverage of 0.60 ML [21]. At this coverage, the heat of adsorption of CO is 22 ± 4 kcal/mol [22]. The similarity between the ethylene hydrogenation activation energy and the CO adsorption energy will be shown to be due to CO blocking sites on the surface necessary for ethylene hydrogenation.

3.2. Scanning tunneling microscopy studies under reaction and CO poisoning conditions on Rh(111)

Adsorbate mobility was investigated on Rh(111) at room temperature. A pressure of 20 mTorr of H_2 was first introduced, then 20 mTorr of ethylene, and finally 5 mTorr of CO. Ethylene is known to form ethylidyne on the surface of Rh(111) [7]. At room temperature and above, ethylidyne is known to be mobile on the surface of metal single crystals, and is unobservable

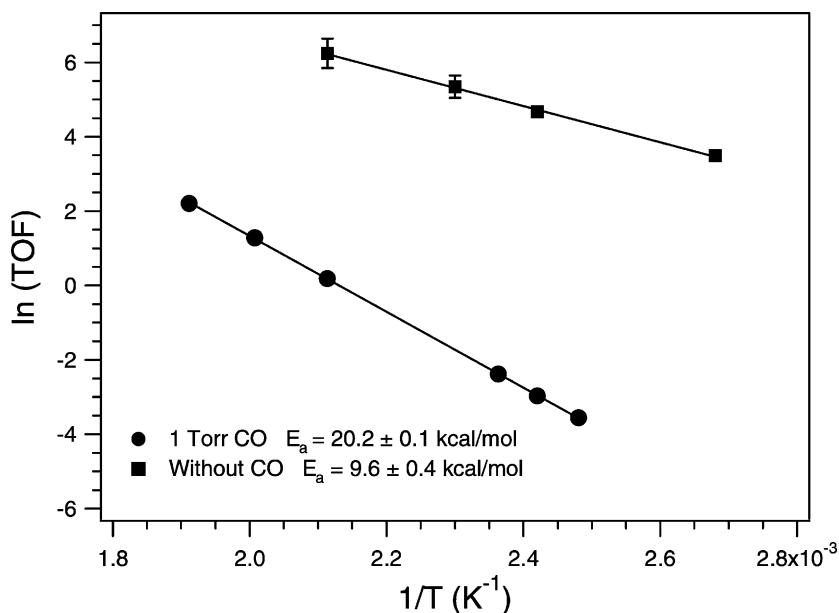


Fig. 5. Logarithmic plot of initial turnover frequency (TOF) vs. $1/T$ for ethylene hydrogenation with (●) and without (■) CO over Pt(1 1 1); activation energies obtained from the slopes are 20.2 ± 0.1 and 9.6 ± 0.4 kcal/mol, respectively.

by STM [8]. CO is known to also poison ethylene hydrogenation on Rh(1 1 1) [23].

When 20 mTorr of hydrogen was introduced to a clean surface of Rh(1 1 1), no ordered structure was observed by STM. This was expected as hydrogen adsorbs dissociatively at room temperature and the hydrogen atoms diffuse too quickly to be observed. After addition of 20 mTorr of ethylene to the hydrogen covered surface, no ordering could be observed in the images, though SFG experiments have shown that ethylidyne is present on the surface under high-pressures of hydrogen and ethylene [3].

Addition of 5 mTorr CO to this mixture of hydrogen and ethylene however, produced an ordered structure, as shown in Fig. 6. Ethylidyne and CO are known to form a mixed $c(4 \times 2)$ structure at low-pressure on Rh(1 1 1) [24]. The ordered structure observed is likely this mixed $c(4 \times 2)$, indicating that the ethylidyne on the surface has stopped diffusing on the surface. At this point we are unable to rule out that there are also areas of (2×2) structure, which CO is known to form at these pressures [25]. If this were the case, the remaining ethylidyne would be compressed, possibly also forming a (2×2) structure, which is known to form at low-temperatures and pressures [26]. The time

scale of an STM image is on the order of seconds, so an ordered image means that molecules are stationary on the surface for that amount of time. This lack of mobility would mean that vacant sites are not available for ethylene to adsorb, which would preclude ethylene hydrogenation. Thus, hydrogenation can only occur if some of the CO molecules desorb. This is why the activation energy for ethylene hydrogenation becomes that of the heat of desorption of carbon monoxide.

3.3. Reaction rate studies on platinum nanoparticles deposited on alumina

The activation energies of ethylene hydrogenation reactions with and without CO on a Pt nanoparticle model catalyst were investigated from 313 to 523 K. The reaction gas, which was recirculated, was 10 Torr C_2H_4 , 100 Torr H_2 , 800 Torr Ne, and varying amounts of CO. Generally speaking, the activity of Pt with 0.3 Torr of CO was less than 5% of the activity without CO at the same temperature. The temperature range investigated for ethylene hydrogenation without CO was from 313 to 423 K. Above 423 K, the reaction proceeds too fast to permit an accurate measurement of reaction rate. Since the catalytic activity of Pt was

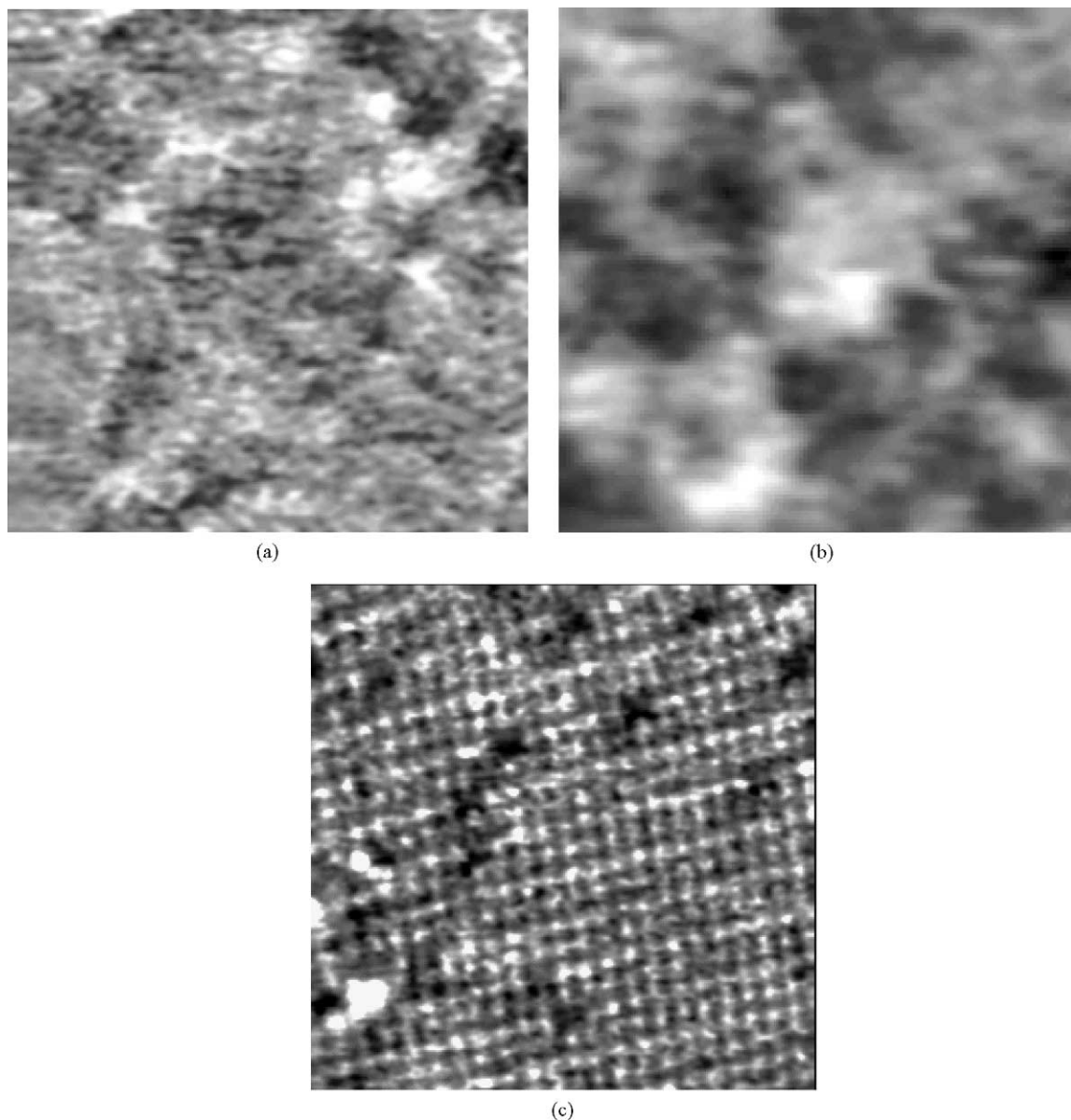


Fig. 6. $(100 \text{ \AA})^2$ STM image of Rh(111) taken under: (a) 20 mTorr H_2 ; (b) 20 mTorr H_2 and 20 mTorr ethylene; (c) 20 mTorr H_2 , 20 mTorr ethylene, and 5 mTorr CO ($I = 200 \text{ pA}$, $V = 103 \text{ mV}$). (a) and (b) are disordered and show no discernible surface features. (c) shows the rectangular $c(4 \times 2)$ structure. The images have been filtered to remove noise.

severely depressed in the presence of CO, the temperature range investigated for the hydrogenation reaction with CO was from 373 to 523 K. Below 373 K, the reaction was too slow and the catalytic reactivity was difficult to distinguish from the background reaction.

Above 523 K side reactions become significant and compete with the ethylene hydrogenation pathway.

The Arrhenius plot for the ethylene hydrogenation with and without CO on the Pt nanoparticle model catalyst is shown in Fig. 7. Assuming the geometrical

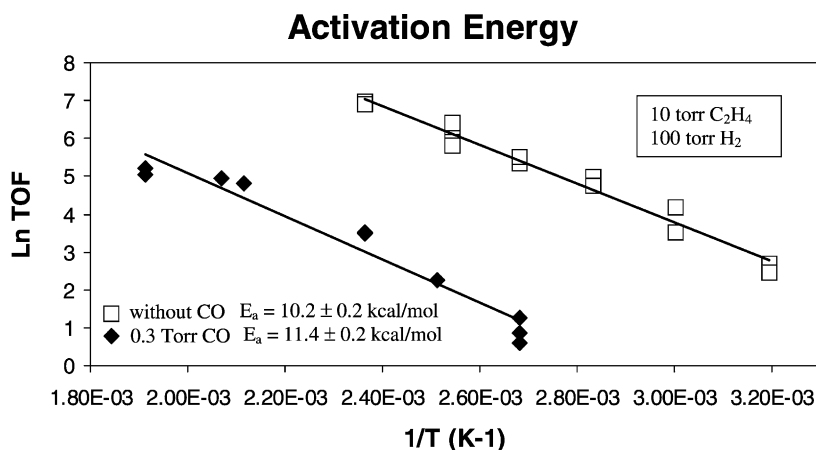


Fig. 7. Arrhenius plot of the rate of ethylene hydrogenation on platinum nanoparticle arrays, with 0.3 Torr CO in the gas phase and without CO. The activation energy is 10.2 ± 0.2 kcal/mol without CO and 11.4 ± 0.2 kcal/mol with 0.3 Torr of CO.

shape of the nanoparticles and that all Pt sites are active, the metal surface area would be 7.0 mm^2 . Previous work using the structure-insensitive ethylene hydrogenation reaction on the Pt nanoparticle array led to a calculated active metal surface area of $4.9 \pm 2.5 \text{ mm}^2$ [19]. It is clear from the graph that the activation energy for ethylene hydrogenation without CO, 10.2 ± 0.2 kcal/mol, is practically the same as with 0.3 Torr CO, 11.4 ± 0.2 kcal/mol. Ethylene hydrogenation catalyzed by Pt nanoparticles in the presence of 0.6 Torr CO also yielded the same activation energy.

The difference between activation energies of ethylene hydrogenation on single crystals and nanoparticles in the presence of CO is interesting. It suggests that there are platinum sites in small concentration that are still available for ethylene hydrogenation on the nanoparticle arrays. Since CO hydrogenation is known to be enhanced at oxide–metal interfaces [27], these interface sites may remain free of CO and can continue hydrogenating ethylene.

4. Conclusions

We have studied CO poisoning of ethylene hydrogenation on platinum and rhodium single crystals as well as on platinum nanoparticles in the mTorr and Torr pressure regimes. GC studies on Pt(111) have shown that CO poisons the reaction, and the activation energy increases from 10.8 to 20.2 kcal/mol. This

CO-poisoned activation energy is near the desorption energy of CO. Only when CO molecules desorb can ethylene hydrogenation take place and thus the activation energy for the reaction becomes similar to the heat of desorption for CO.

STM studies of the ethylene hydrogenation system on Rh(111) show that when CO is introduced to a surface covered with hydrogen and ethylidyne, an ordered structure appears on the surface. Based on these results, we have proposed a model for CO poisoning on single crystals in which CO adsorbs on vacant hollow sites, preventing the diffusion of ethylidyne. With the immobile adsorbates filling the surface, there is no room for ethylene to adsorb, and hence ethylene hydrogenation cannot occur.

Studies of CO poisoning on platinum nanoparticles showed a decrease in activity when CO was present, but not a significant increase in activation energy. This suggests that the oxide–metal interface sites that are present in small concentration remain active for ethylene hydrogenation because they remain free of adsorbed CO.

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