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Ethylene hydrogenation catalysis on Pt(111) single-crystal surfaces studied by using mass spectrometry and *in situ* infrared absorption spectroscopy

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ABSTRACT

The catalytic hydrogenation of ethylene promoted by a Pt(111) single crystal was studied by using a ultrahigh-vacuum surface-science instrument equipped with a so-called high-pressure cell. Kinetic data were acquired continuously during the catalytic conversion of atmospheric-pressure mixtures of ethylene and hydrogen by using mass spectrometry while simultaneously characterizing the surface species in *operando* mode by reflection–absorption infrared spectroscopy (RAIRS). Many observations reported in previous studies of this system were corroborated, including the presence of adsorbed alkylidyne intermediates during the reaction and the zero-order dependence of the rate of hydrogenation on the pressure of ethylene. In addition, the high quality of the kinetic data, which could be recorded continuously versus time and processed to calculate time-dependent turnover frequencies (TOFs), afforded a more detailed analysis of the mechanism. Specifically, deuterium labeling could be used to estimate the extent of isotope scrambling reached with mixed-isotope-substituted reactants ($C_2H_4 + D_2$ and $C_2D_4 + H_2$). Perhaps the most important new observation from this work is that, although extensive H-D exchange takes place on ethylene before being fully converted to ethane, the average stoichiometry of the final product retains the expected stoichiometry of the gas mixture, that is, four regular hydrogen atoms and two deuteriums per ethane molecule in the case of the experiments with $C_2H_4 + D_2$. This means that no hydrogen atoms are removed from the surface via their inter-recombination to produce X_2 ($X = H$ or D). It is concluded that, under catalytic conditions, hydrogen surface recombination is much slower than ethylene hydrogenation and H-D exchange.

1. Introduction

The hydrogenation of olefins is one of the oldest catalytic processes ever reported, going back as far as 1897 [1,2], yet it is still quite prominent in many industrial applications, in oil refining and in the food industry to name a few. The basic reaction mechanism for this reaction was proposed many years ago by Horiuti and Polanyi, who suggested that the surface of the metal used as catalyst facilitates the dissociation of molecular H_2 into atomic hydrogen so that the adsorbed olefin then can incorporate such H species in a series of stepwise and reversible steps, to first form an alkyl surface intermediate and ultimately the final alkane [3]. This idea still offers the basic framework to explain olefin hydrogenations as well as olefin isomerizations (double-bond migration, *cis*–*trans* interconversion [4]), yet it overlooks some subtleties that make the full understanding of the performance of this catalysis elusive [5–9].

Issues still unresolved in the mechanistic description of the hydrogenation of olefins by transition metals include the sensitivity of the conversion to the structure of the surface and the role of the carbonaceous deposits that form on the surface [6,8,10–12]. Studies with model systems and modern surface-sensitive techniques from many research groups have been directed to answer these questions [7,9,13–20]. Our laboratory in particular has been dedicated to this problem for a number of years, focusing, like many others, on the study of the prototypical case of the hydrogenation of ethylene on Pt(111) single-crystal surfaces [10,21–41]. Much progress has been made, but key questions remain unanswered. At present, we are focusing on elucidating the participation of the hydrocarbon species strongly adsorbed on the surface, which in the case of ethylene conversion consist of ethylidyne moieties, in the catalytic conversion [8,10], and on determining the effect that those may have on the kinetics of molecular hydrogen adsorption and activation.

Toward that end, we have developed an instrument for the *operando* study of catalytic reactions based on the idea of the so-called high-pressure cell, which is incorporated into the ultrahigh-vacuum (UHV) equipment used for surface preparation and characterization in order to afford great control of the state of that surface before, during, and after catalysis via the ability to directly transfer it between the vacuum and catalytic environments without exposure to the outside atmosphere

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[42–46]. We rely on the use of infrared absorption spectroscopy in a single reflection mode (reflection–absorption infrared spectroscopy, or RAIRS [47–49]) for the *in situ* characterization of the adsorbed species during reaction, and on the continuous analysis of the gas phase using mass spectrometry to obtain kinetic data [41]. Below we provide some examples of the type of data obtained with this apparatus, discuss its advantages, and indicate the approach to be taken to address the questions mentioned above. We also include some new results from studies using isotope labeling that point to the relative slow nature of hydrogen recombination on the metal surface under catalytic conditions compared to the ethylene hydrogenation and ethylene H-D exchange steps. This is a surprising result, because hydrogen recombination is known to take place readily on clean surfaces [50–53] and to be key to the behavior of transition metals as catalysts in many hydrogenation processes [6, 54–56].

2. Experimental

The experiments were carried out in a two-tier stainless-steel apparatus described in more detail elsewhere [41,57]. The main chamber is kept under UHV by using a cryogenic pump, and is equipped with a UTI 100C quadrupole mass spectrometer interfaced to a computer to afford the continuous monitoring of the partial pressures of up to 15 masses in a single run. This mass spectrometer is typically used for temperature-programmed desorption (TPD) experiments, but in the work reported here, it was mainly employed to follow the kinetics of catalytic reactions, as discussed below. The UHV chamber is used for cleaning (with an ion-sputtering gun) and for characterization of the sample, a Pt(111) single crystal of about 1 cm in diameter. The crystal is mounted on a manipulator capable of cooling to liquid-nitrogen temperatures and of resistive heating to up to 1100 K and used to transfer it between the two tiers of the system, namely, between UHV and the catalytic reactor.

The reactor volume of our instrument is usually connected to the UHV side but contains a small retractable cell that can be sealed around the crystal to isolate it from the rest of the apparatus and pressurized to atmospheric pressures in order to carry out catalytic reactions. Two gas openings, the inlet directly facing the single-crystal surface and the outlet placed at the back of the cell, are used together with a closed loop and a bellows gas pump to circulate the reaction mixture around the catalyst, in an arrangement that makes our instrument behave as a continuously stirred tank reactor (CSTR). The cell is also equipped with two NaCl windows on opposite sides that, in the closed position, become aligned with two additional windows in the side chamber to allow for the focusing of an infrared beam in and out of the Pt surface. The light is directed at a grazing incidence angle to be able to perform reflection–absorption infrared spectroscopy (RAIRS) experiments. The gases from a controlled leak from the closed cell into the main UHV chamber are analyzed with the mass spectrometer continuously during reaction to acquire the kinetic data.

The RAIRS data were acquired by using a Bruker Equinox 55 FT-IR spectrometer [58]. In our setup, the IR beam is extracted from the inside of the FT-IR instrument, directed through a polarizer and the NaCl windows on one side of the high-pressure cell, and focused onto the sample at grazing incidence (~85°). The reflected beam is then collected, after traveling through a second set of NaCl windows, onto a narrow-band mercury–cadmium–telluride (MCT) detector. Most spectra for the species adsorbed on the platinum surface are averages from 2000 scans taken at a resolution of 4 cm^{-1}, a process that takes about 4 min per experiment, and ratioed against spectra from the clean sample obtained in the same way before gas dosing. However, in order to be able to perform kinetic measurements in a timely manner, the data for the analysis of the gas-phase species reported in Fig. 3 correspond to averages of only 64 scans; the lower number of scans afforded the collection of more spectra in less time (the strong signals from the gas-phase species do not require much signal averaging). The final RAIRS traces for the surface species were obtained by subtracting data obtained using s-polarized light from similar spectra recorded with p-polarized radiation in order to eliminate most of the contribution from the gas-phase species (a small residual signal is still seen in some spectra, as indicated below).

For the typical experiments reported here, the Pt surface was first cleaned by sputtering-annealing and oxygen treatments until the reported RAIRS spectra of a saturated layer of carbon monoxide on clean Pt(111) could be reproduced. Afterward, the sample was transferred to the side chamber, and background RAIRS data were acquired with both s- and p-polarized light. The Pt was exposed to the desired gases if a pretreatment was required (typically propylene, C_3H_6, >99% purity from Matheson; see below), a new set of RAIRS acquired, the high-pressure cell closed, and yet another pair of RAIRS traces recorded. The crystal was then heated to the desired temperature by using a homemade power supply with a feedback loop that uses the temperature reading from a chromel–alumel thermocouple spot-welded to the side of the metal, and the reaction mixture, premixed in a side gas manifold and typically consisting of 2 Torr of ethylene (C_2H_4, 99.5%, from Matheson, or C_2D_4, 99% D purity, from Cambridge Isotope Laboratories) and 50 Torr of hydrogen (H_2, >99.995% purity, from Liquid Carbonic, or D_2, >99.5% atom purity, from Matheson), was let into the reaction volume. The gas composition was monitored continuously with the mass spectrometer until the reaction reached completion, after which the volume of the reactor was pumped with a turbomolecular pump and the cell retracted to expose the crystal back to the UHV environment. RAIRS spectra were taken during the course of the catalytic conversion as well as immediately before and right after opening the cell.

3. Results

Our ability to follow the kinetics of the catalytic hydrogenation reaction by mass spectrometry (MS) was tested first. Complete mass spectra of the gas mixture present in the high-pressure cell used as the reactor were taken at different stages throughout the conversion to analyze its composition. An example of the data acquired this way is provided in Fig. 1. The mass spectrometry traces evolve over time, indicating the consumption of the reactant (ethylene) and the accumulation of the product (ethane): notice in particular the growth of the peaks at 29 and 30 amu typical of C_2H_6 with reaction time. Deconvolution of these

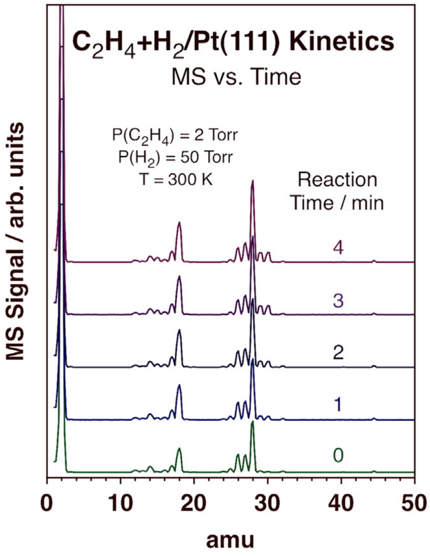

Fig. 1. Gas mixture mass spectra in the 0–50 amu range during the catalytic hydrogenation of ethylene promoted by a Pt(111) single-crystal surface, taken at different reaction times. In this case, the initial mixture is composed of 2 Torr of C_2H_4 and 50 Torr of H_2, and the catalyst is held at a constant temperature of 300 K. The conversion of ethylene to ethane is mainly manifested by the growth of the peaks at 29 and 30 amu.

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