

Near-Unity Reaction Probability in Olefin Hydrogenation Promoted by Heterogeneous Metal Catalysts

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Supplementary Information

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1. Experimental Details

The kinetic measurements were carried out in a modified version of an effusive molecular beam apparatus. An ultrahigh vacuum (UHV) chamber turbopumped to a base pressure of about 1×10^{-9} Torr is equipped with an ion gun for sample cleaning, a nude ion gauge for total pressure measurements, and a UTI 100C quadrupole mass spectrometer interfaced to a personal computer for partial-pressure data collection. The time evolution of up to 15 masses can be followed as a function of time with this setup. The effusive molecular beam is generated by using a 150 μm -diameter, 1.2 cm-long capillary tube. A polycrystalline and polished 1-cm-in-diameter Pt disk, approximately 1 mm in thickness, was mounted on an on-axis vertical manipulator capable of X–Y–Z– θ motion, and positioned directly in front of the doser for the kinetic measurements, approximately 1 cm away. The highly collimated nature of the gas beam was determined by experiments where the spot produced by condensation of thick layers of heavy hydrocarbons on the Pt surface at low temperatures were inspected visually as a function of distance; similar-sized spots were observed over a distance range of several cm between the doser and the sample. The reaction mixtures, made out of predetermined partial pressures of C_2H_4 and H_2 , were prepared in a fixed volume (0.617 L) within the gas manifold (left side in Figure 1), and dosed using a finely adjustable leak valve placed just before the capillary doser, which was used to set the absolute beam flux. Beam fluxes were followed by recording the pressure drop in the gas reservoir versus time using a MKS Baratron capacitance manometer, and also by following the pressure in the main chamber (using a nude ion gauge), as described below. The gas mixture was analyzed in

the UHV volume continuously during the kinetic runs by mass spectrometry, and the composition determined via a deconvolution process.

The reflection-absorption infrared absorption spectroscopy (RAIRS) and catalytic kinetic data were acquired in a second two-tier stainless-steel UHV chamber equipped with a sputtering gun for sample cleaning and with a UTI 100C quadrupole mass spectrometer interfaced to a personal computer, in a similar fashion as in the first apparatus. The second level, accessible by using a horizontal long-travel manipulator, is used for the RAIRS and atmospheric-pressure catalytic experiments. For RAIRS, the IR beam from a Bruker Equinox 55 Fourier-transform infrared (FT-IR) spectrometer is directed through a polarizer and a NaCl window, focused at grazing incidence onto the sample, and collected (after reflection and traveling through a second NaCl window) onto a narrow-band mercury-cadmium-telluride (MCT) detector. All spectra were acquired by averaging the data from 2000 scans taken at a resolution of 4 cm^{-1} , a process that takes about 5 min per experiment, and ratioed against spectra from the clean sample obtained in the same way but before gas dosing. Spectra were taken with both s- and p-polarized light to discriminate between the gas-phase molecules and the adsorbed species. A retractable small high-pressure cell equipped with NaCl windows was added to carry out the catalytic experiments while simultaneously performing the RAIRS characterization. The progress of the reactions was followed continuously via mass spectrometry analysis of the gas that leaks into the main UHV volume through the cell seal. An approximately 1 cm-in-diameter, 1-mm-thick Pt single crystal exposing a polished (111) surface was used for the RAIRS and atmospheric-pressure catalytic experiments.

In both systems, the platinum samples (the polycrystalline Pt disk in the molecular beam apparatus and the Pt(111) single crystal in the MS-RAIRS chamber) were spotwelded to a pair of tantalum wires attached to the copper electrical feedthroughs of the sample manipulators, which were set for cooling and resistive heating to any surface temperature between ~100 and 1100 K. The temperature of the samples was measured using a chromel-alumel thermocouple spotwelded to their side, and controlled by using homemade feedback electronics. The surfaces were cleaned by a combination of argon ion bombardment, annealing, and thermal treatments with O₂ to burn any remaining surface carbon contaminants, until known temperature programmed desorption (TPD) spectra for CO and H₂ were reproduced. The gases were purchased from commercial sources, H₂ from Liquid Carbonic (>99.995% purity) and C₂H₄ from Matheson (99.5%), and used as supplied.

For the turnover frequency calculations (TOF), the geometrical areas of the disks were used, and the Pt atomic density of Pt(111) surfaces, 1.5×10^{15} atoms/cm², was assumed in both cases. In the case of the polycrystalline Pt disk, this approximation may underestimate the total catalytic area because of the possible presence of microfacets, but our absolute TOF numbers are in any case affected by the accuracy of the estimation of the actual flux on the surface (as opposed to at the exit of the doser), and are only meant to provide a semi-quantitative indication of the catalytic activity. It also should be mentioned that, because of experimental limitations, we used a polycrystalline Pt disk instead of a Pt(111) single crystal in the molecular beam studies. However, annealed polycrystalline Pt surfaces are known to be dominated by (111) facets, and to be able to form ethylidyne surface species and catalytically promote ethylene hydrogenation.

We believe that the chemistry seen here with the polycrystalline Pt disk is representative of the catalysis seen with both single crystals and supported catalysts.

2. Beam Characterization

Absolute gas fluxes were estimated by following the drops in pressure in the fixed volume of the gas container within the gas manifold placed behind the beam assembly as a function of time. Typical data from those measurements are shown in Figure S1. The slopes of the pressure-versus-time raw data were used to calculate the overall conductance of the beam assembly, which were converted into fluxes at the exit of the capillary doser, in units of monolayer/s (ML/s, also in Figure S1), by assuming a monolayer density of 1.5×10^{15} molecules/cm². Alternative beam flux calculations using the total pressure of the UHV chamber and a pumping speed of 250 L/s yielded values consistent, within a <2% error range, with those estimated from the back pressure drops. The latter approach provided an easier way to follow beam fluxes in all experiments, and also true beam compositions (by measuring the H₂ and C₂H₄ partial pressures using the mass spectrometer), since the nominal compositions determined by the partial pressures used in making the gas mixtures in the gas manifold are altered upon diffusion through the leak valve (because of its lighter mass, H₂ displays much higher diffusion rates through small holes than ethylene); the final beams were significantly enriched in H₂.

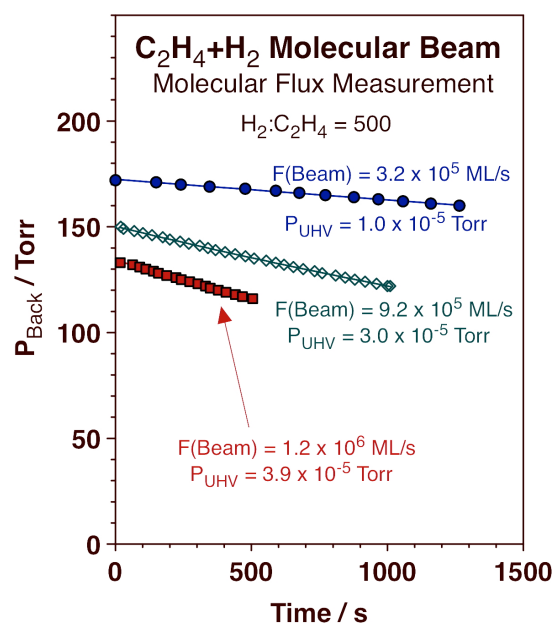


Figure S1. Plot of the molecular beam backing pressure versus time for three different H₂ + C₂H₄ gas mixtures. The time evolution of that pressure was used to estimate the beam flux at the exit aperture of the doser. The measured steady-state pressures in the main ultrahigh vacuum (UHV) chamber were also monitored, and used as an alternative way to follow the beam flux.

3. Dependence of Ethane Yield on Temperature

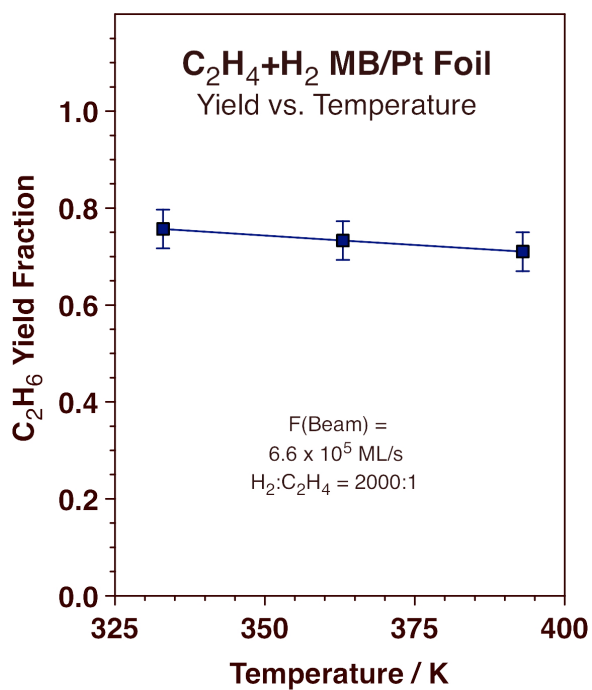


Figure S2. Reaction probability versus temperature for ethylene hydrogenation on Pt using a beam with a $F = 6.6 \times 10^5$ ML/s total flux and a $H_2:C_2H_4 = 2000$ composition. High probabilities, between 70 and 80 %, were measured in all cases, nearly independent of temperature (in the 325 - 400 K range).