

LETTERS

Millisecond FT-IR Spectroscopy of Surface Intermediates of C₂H₄ Hydrogenation over Pt/Al₂O₃ Catalyst under Reaction Conditions

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Time-resolved rapid-scan FT-IR spectra of ethylene hydrogenation over alumina-supported Pt catalyst at 473 K were recorded under continuous H₂/N₂ flow (1 atm) and pulsed release of C₂H₄ (30 millisecond duration). Two surface species were observed, namely ethylidyne (CH₃CPT₃) with peaks at 2880 and 1339 cm⁻¹ (lifetime 300 ± 50 ms), and a substantially shorter-lived intermediate with an intense band at 1200 cm⁻¹ and weak absorptions in the 2875–2860 cm⁻¹ region (lifetime around 100 ms). Comparison of the C₂H₄ + H₂ results with those of experiments using D₂ or C₂D₄ suggests that the 1200 cm⁻¹ species is a surface ethyl intermediate (CH₃CH₂Pt). This is the first observation on the lifetime of surface ethyl species under reaction conditions. The rise of the final ethane product, monitored by the ν(CH) absorption at 2893 cm⁻¹ was found to reach a maximum already in the first recorded time slice. This suggests that the observed CH₃CH₂Pt species is a surface-trapped form of the kinetically relevant, only weakly interacting C₂H₅ radical intermediate.

Vibrational spectroscopic studies of ethylene hydrogenation catalyzed by Pt under steady-state conditions over the past two decades has led to the detection and structural characterization of several surface intermediates.^{1,2} Early HREELS work on single-crystal Pt surfaces revealed a C₂H₃ species that was identified as ethylidyne (CH₃CPT₃).^{3,4} Reflection–absorption infrared and HREELS studies of ethylene adsorbed on Pt(111) over a large temperature range from cryogenic to room temperature led to the detection of π-bonded and di-σ-bonded C₂H₄,^{5–8} with the latter identified as the precursor of ethylidyne.^{9–10} The same species were observed by transmission FT-IR spectroscopy of pressed wafers of finely dispersed Pt particles on silica or alumina.^{10–12} While the strongly held ethylidyne species passivate the Pt surface, thus preventing dehydrogenation of newly adsorbed ethylene molecules, they are not kinetically significant intermediates of ethylene hydrogenation.^{10,13,14} Hy-

drogenation is believed to be initiated by the reaction of weakly π-bonded C₂H₄ with surface hydrogen.^{15–20} Using the surface-sensitive sum frequency generation (SFG) spectroscopy for recording the CH stretching region coupled with GC monitoring of the gas-phase composition, Somorjai and co-workers have studied C₂H₄ hydrogenation over Pt(111) under high-pressure conditions at RT.^{2,19} Aside from demonstrating that weakly bound π-C₂H₄ is the key species being hydrogenated, the spectra revealed ethylidyne bands as well as peaks assigned to surface ethyl species. Formation of ethyl intermediates from π-C₂H₄ followed by hydrogenation to ethane was proposed as the main reaction path. Ethyl, π-C₂H₄ and various spectator species were also detected by FT-IR in steady-state hydrogenation experiments over alumina-supported small Ir clusters.²¹

Direct evidence for the kinetic relevancy of reaction intermediates requires time-resolved monitoring under reaction conditions. Time-resolved FT-IR spectroscopy at millisecond resolution by the rapid-scan technique, or in the micro and nanosecond regime with the step-scan method,²² offers an

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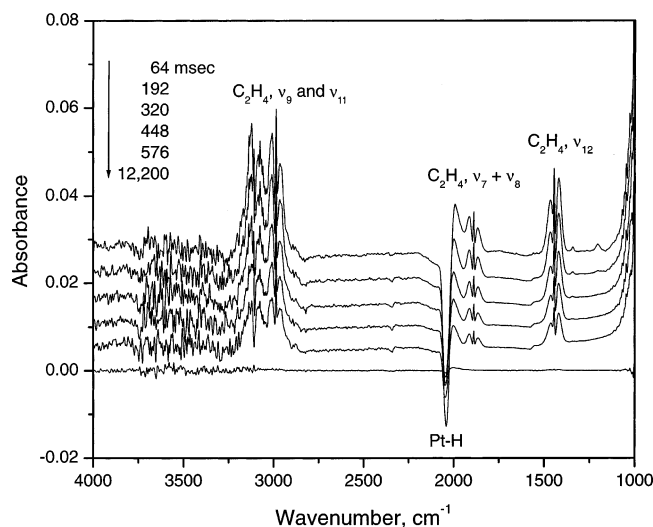


Figure 1. Rapid Scan spectra of $\text{C}_2\text{H}_4 + \text{H}_2$ reaction induced by 30 ms ethylene pulses over $\text{Pt}/\text{Al}_2\text{O}_3$ at 473 K. The six traces were recorded at 64, 192, 320, 448, 576, and 12,200 ms after opening of the ethylene valve. Times indicate midpoints of the corresponding interferogram recordings. Fresh ethylene pulses were released every 12.8 s.

opportunity for recording vibrational spectra over a large continuous time span. By contrast to photoinitiated reactions, triggering of the reaction with short pulses synchronized with the spectral monitoring is the principal technical challenge of time-resolved experiments in the case of thermal catalytic systems. We report here millisecond resolution FT-IR experiments of C_2H_4 hydrogenation over a supported Pt catalyst under flow conditions at 473 K using pulsed ethylene release from a fast valve for catalysis triggering. The approach takes advantage of the fact that, for small molecules with sparse infrared spectra, wide spectral regions exist that are free of interfering gas-phase absorptions of the reactants.

Millisecond time resolution was achieved by continuous flow of an H_2/N_2 mixture (9 L min^{-1} , ratio 0.006–0.013, total pressure 1 atm, flow regulated by MFC valves (MKS Instruments)) over an Al_2O_3 -supported, finely divided Pt catalyst (Exxon HFR-100, 5% Pt, calcined at 823 K, BET surface area 180 m^2g^{-1}) while injecting 30 ms pulses of C_2H_4 through a fast valve (Parker-Hannifin Corp., General Valve Division model Iota One). The reactant pulses were synchronized with the recording of rapid-scan FT-IR spectra (Bruker model IFS88). The catalyst was prepared in the form of a pressed wafer with an embedded W grid. The latter is made of a 0.49 in. diameter tungsten foil (thickness 0.002 in.) featuring laser-drilled 0.012 in. holes. Electrical heating of the grid, which was held by a Ni jaw similar to a design described in the literature,²³ afforded temperatures up to 873 K. The catalyst was situated in the center of a home-built 100 cm^3 stainless steel reactor cell equipped with two flange-mounted CaF_2 windows for transmission infrared spectroscopy. The reactant mixture entered the cell through a 1/4 in. tube on one side and exited through an exhaust line on the other. Ethylene pulses (85 psi back pressure) were injected into the continuous H_2/N_2 flow 7 cm upstream from the center of the reactor cell, resulting in a time delay of 30 ms for the olefin pulse to reach the catalyst. Opening of the pulsed valve was synchronized with the forward motion of the interferometer mirror. Details of the rapid-scan method were described in a previous paper.²⁴

Figure 1 shows transient overview spectra of the $\text{C}_2\text{H}_4 + \text{H}_2$ reaction at 473 \pm 20 K recorded 64, 192, 320, 448, 576, and 12,200 ms after opening of the ethylene valve (times indicate

midpoints of the corresponding interferogram recordings). The $t = 64$ ms trace shows that the gas-phase spectrum of C_2H_4 with absorptions at 3000 cm^{-1} (ν_9 and ν_{11}), 1890 cm^{-1} ($\nu_7 + \nu_8$), and 1440 cm^{-1} (ν_{12})²⁵ is fully developed within the first 100 ms after release of the ethylene pulse. This is consistent with the fact that the C_2H_4 pulse arrives at the catalyst location within 30 ms after opening of the valve (9 L min^{-1} flow through a 1/4 in. tube over a distance of 7 cm). The subsequent decrease of C_2H_4 gas phase infrared bands reflects mostly the removal by gas flow as shown by comparison with rapid-scan experiments in which no H_2 reactant was added to the N_2 . The derivative-shaped signal around 2000 cm^{-1} is due to the surface Pt–H groups²⁶ (since the band is not observed in the $\text{C}_2\text{H}_4 + \text{D}_2$ runs, it is inconsistent with CO impurity known to absorb in the same spectral region).²⁷ The shape of the signal is attributed to two coinciding phenomena: a transient shift of the band to lower frequency due to hydrocarbon adsorption on the metal surface, and depletion at 2050 cm^{-1} as a result of ethylene hydrogenation. The protocol for obtaining the transient spectra shown in Figure 1 consisted of the recording of 99 interferograms (double-sided/forward–backward at 160 kHz and 4 cm^{-1} resolution) following a C_2H_4 pulse, corresponding to 396 single-sided interferograms. Four consecutive interferograms were automatically averaged for S/N improvement, furnishing interferogram time slices at 128 ms resolution. A total of 50 such sets of single-beam spectra generated by 50 ethylene pulses were stored as the result of one experiment. Final time-resolved spectra for a given time delay were obtained by calculating the ratio of each of the 50 corresponding stored single beam spectra against the single beam spectrum taken just before the pulse. The 50 ratioed spectra were then averaged to yield the absorbance time slice for a given delay (midpoint of the interferogram scan). The results of 10 such experiments were averaged for further S/N improvement.

A more detailed look at the rapid-scan spectra of Figure 1 reveals bands originating from transient surface intermediates and final products, shown on an expanded scale in Figure 2. The top trace (a) of Figure 2 recorded at $t = 64$ ms indicates transient absorptions at 2893, 2880, 2875, 1339, and 1200 cm^{-1} . The 2880 ($\nu_s(\text{CH}_3)$) and 1339 cm^{-1} ($\delta_s(\text{CH}_3)$) bands are due to the well-established ethylidyne surface intermediate (CH_3CPT_3) of C_2H_4 hydrogenation.¹¹ Ethylidyne is a spectator species that is known to slowly hydrogenate to ethane.¹³ A first-order fit indicates that CH_3CPT_3 decays with $\tau_{1/e} = 300 \pm 50$ ms at 473 K under the given H_2/N_2 flow conditions ($\text{H}_2/\text{N}_2 = 0.013$). A second, shorter-lived intermediate absorbing at 1200 cm^{-1} that is kinetically unrelated to ethylidyne is readily discerned from the $\text{C}_2\text{H}_4 + \text{H}_2$ spectra. The transient is not observed in the absence of H_2 (Figure 2A, trace e and Figure 2B, trace f), or in experiments in which H_2 is replaced by D_2 (Figure 2A, trace d and Figure 2B, trace e). This rules out the possible assignment to surface adsorbed $\pi\text{-C}_2\text{H}_4$ which also has an infrared band around 1200 cm^{-1} .^{5–12} Moreover, the accompanying $\pi\text{-C}_2\text{H}_4$ at 1500 cm^{-1} is absent, and no $\pi\text{-C}_2\text{D}_4$ absorption at 1320 cm^{-1} ^{10,11} was detected in $\text{C}_2\text{D}_4 + \text{H}_2$ experiments. As in the case of the ethylidyne, the decay rate of the 1200 cm^{-1} species was found to increase with increasing H_2 concentration in the H_2/N_2 flow mixture. These observations indicate that the 1200 cm^{-1} band with a 1/e time around 100 ms (corresponding to a TOF of 10 for $\text{H}_2/\text{N}_2 = 0.013$) is due to a second $\text{C}_2\text{H}_4 + \text{H}_2$ surface intermediate that is more reactive than ethylidyne, as can be seen from traces (a) through (d) of Figure 2B.

The most probable candidate is a surface ethyl species. In fact, $\text{CH}_3\text{CH}_2\text{Pt}$ is expected to have a CH_2 wagging mode around

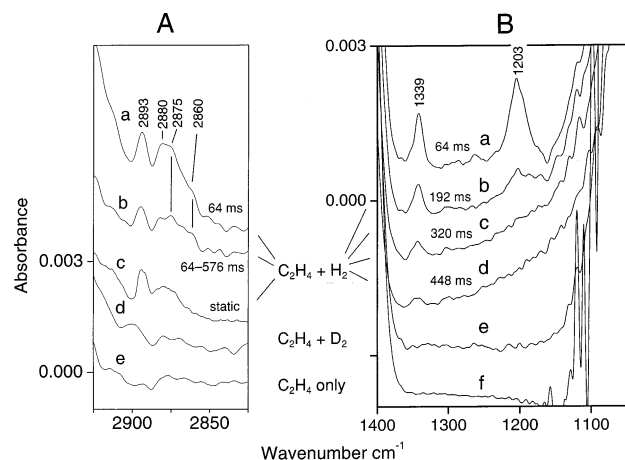


Figure 2. Rapid-scan FT-IR spectra of surface intermediates of C_2H_4 hydrogenation at 473 K. The first four traces (a through d) of the fingerprint region (B) show the time evolution of the $\text{C}_2\text{H}_4 + \text{H}_2$ reaction following an ethylene pulse. The three top traces of the CH stretching region (A) depict (a) the 64 ms time slice; (b) the spectral changes between 64 and 576 ms; (c) the static spectrum recorded after 5 min $\text{C}_2\text{H}_4 + \text{H}_2$ reaction under static conditions. The bottom traces show the 64 ms spectra when using C_2H_4 and D_2 , or C_2H_4 alone (no H_2 added to N_2 flow). The large noise below 1200 cm^{-1} of trace (f) is due to the use of an 8 micron band gap MCT detector in this experiment. All other spectra were recorded using a 12 micron band gap MCT. Fresh ethylene pulses were released every 12.8 s. Sample sources: N_2 , 99.999%; C_2H_4 , Matheson, Research Grade; C_2D_4 , Cambridge Isotope Laboratories, 98% D ; H_2 , Matheson, 99.99%; D_2 , Isotech, 99.8% D .

1200 cm^{-1} according to ethyl-Pt coordination model compounds.^{11,28,29} A band at 1175 cm^{-1} observed by HREELS has been attributed to an ethyl surface species generated by $\text{CH}_3\text{-CH}_2\text{Cl}$ photodissociation on a single-crystal $\text{Pt}(111)$ surface at 100 K,³⁰ and reflection absorption infrared spectra recorded upon dissociation of $\text{CH}_3\text{CH}_2\text{I}$ on $\text{Pt}(111)$ at 150 K showed a band at 1185 cm^{-1} .³¹ The latter is in agreement with the HREELS result considering the spectral resolution of the electron energy loss method. Dissociative adsorption of ethane deposited through a supersonic beam onto $\text{Pt}(111)$ at 150 K gave an intense band at 1145 cm^{-1} , also assigned to the CH_2 wagging mode.³² This indicates that the frequency of this mode can vary by tens of cm^{-1} depending on the nature of species coadsorbed on the Pt surface, and may explain the higher value of 1200 cm^{-1} for ethyl surrounded by coadsorbed reactant and spectator species upon C_2H_4 hydrogenation. The corresponding band of ethyl species on $\text{Cu}(110)$ was reported at 1129 cm^{-1} (190 K). It is known that CH_2 deformation modes are red-shifted on Cu relative to Pt surfaces.³³ The essential information obtained from the literature spectra is that the CH_2 wagging mode of surface ethyl species is the single most intense infrared absorption in the fingerprint region, and the only one that does not overlap with gas-phase C_2H_4 absorptions. Furthermore, an absorption was detected at 2850 cm^{-1} by SFG spectroscopy of C_2H_4 hydrogenation over $\text{Pt}(111)$ and assigned to surface ethyl intermediate.² The same assignment was made for an infrared band of a surface intermediate produced by ethyl chloride dissociation on oxide-supported Pt catalyst,³⁴ and $\nu(\text{CD})$ bands of perdeuterated ethyl-Pt moieties were reported upon ethyl iodide decomposition on single-crystal Pt surfaces.³⁵ As can be seen from a comparison of the 64 ms time slice (trace a) and the difference of the 64 and 576 ms spectra (trace b) of Figure 2A, we observe rapidly decreasing shoulders at 2875 and 2860 cm^{-1} , in agreement with the literature spectra of $\text{C}_2\text{H}_5\text{Pt}$. These bands are overlapped by the CH_3CPT_3 mode at 2880 cm^{-1} and

gas-phase C_2H_6 (see below). Despite the limited spectral information of the transient available in our experiment (reported bands at 2957, 2916, 1440, 1420, and 1010 cm^{-1} are overlapped by gas-phase C_2H_4 or Al_2O_3 absorptions),^{31,32} ethyl is the only known H_2 concentration-dependent species with the observed infrared characteristics. Hence, we conclude that millisecond FT-IR spectroscopy allows the detection and monitoring of the temporal behavior of surface intermediates in a flow reactor at 473 K and propose assignment of the fast decaying species to surface-trapped ethyl. This is the first observation on the lifetime of surface ethyl species under reaction conditions.

There is one additional transient infrared peak that is observed exclusively when both C_2H_4 and H_2 are present, namely at 2893 cm^{-1} , and it is attributed to final gas phase ethane product. This was readily confirmed by recording an FT-IR spectrum following exposure of a static mixture of C_2H_4 and H_2 (in N_2) in the same reactor cell to the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst at 473 K (Figure 2A, trace c). Under these conditions, no ethylidyne or surface-trapped ethyl species are detected, consistent with the millisecond lifetime of the surface intermediates. While the shoulder in the $2870\text{--}2880\text{ cm}^{-1}$ region overlaps with the CH stretch absorptions of CH_3CPT_3 and $\text{CH}_3\text{CH}_2\text{Pt}$, the 2893 cm^{-1} band of gas phase ethane is not obstructed by any other species. We find that the final ethane product is already fully developed in the initial, 64 ms spectrum, and subsequently decays at the same rate within error bars as gas-phase C_2H_4 .

While ethyl species are believed to be intermediates of Pt-catalyzed hydrogenation,^{1,2} the key question is whether the $\text{CH}_3\text{-CH}_2\text{Pt}$ species monitored here is a kinetically relevant precursor of the final ethane product. This would be signaled by a kinetic relationship between the C_2H_6 rise and the decay of the 1200 cm^{-1} band. However, we find that the ethane growth is already at its maximum in the first recorded spectral time slice (64 ms). Therefore, the observed surface ethyl species seems not to be the main contributor to ethane growth under reaction conditions at 473 K; the intermediate responsible for the bulk of ethane production must be short-lived on the time scale of 100 ms. In fact, turnover rate estimates of C_2H_4 hydrogenation over Pt surfaces at 473 K suggest a lifetime of less than a millisecond.³⁶ We propose to explain this by a large variation (spread) in the strength of the C_2H_5 interaction with the Pt surface, with the weakest interacting radicals having the highest hydrogenation rate (millisecond or faster), and those with a full C-Pt bond detected here being the most stable. A possible origin of this variation in the strength of ethyl-surface interaction is a heterogeneity in the surface coverage.³⁷

An alternative explanation for the observed surface ethyl intermediate could, in principle, involve trapping by the Al_2O_3 support. Alumina typically features both Brønsted (Al-OH) and Lewis acid sites (trivalent Al)³⁸ at which radicals could conceivably be trapped. Reaction of Al-OH groups with C_2H_5 would be expected to yield $\text{Al-O-C}_2\text{H}_5$ moieties. However, the infrared spectrum of this group³⁴ does not feature a strong absorption around 1200 cm^{-1} , and we did not detect the expected bleach in the $3500\text{--}3800\text{ cm}^{-1}$ region of the $\text{C}_2\text{H}_4 + \text{H}_2$ rapid-scan spectra that would signal reaction of Al-OH of the alumina support. Trapping of ethyl radicals at Lewis acid sites, if it occurred, would most probably result in the formation of $\text{Al-C}_2\text{H}_5$ groups. However, literature infrared spectra of such species show three about equally intense bands in the $1180\text{--}1300\text{ cm}^{-1}$ region,³⁹ inconsistent with the transient spectra observed in our experiments. It is therefore highly unlikely that the observed transient is due to ethyl radicals trapped by the alumina support.

In conclusion, this work shows that FT-IR monitoring of ethylene hydrogenation over Pt/Al₂O₃ catalyst in a transmission FT-IR cell under practical flow rates affords orders of magnitude higher time resolution than reported thus far for this reaction. The approach furnishes time-resolved spectra at high sensitivity in spectral regions free of gas phase reactant absorptions, and is especially suitable for small molecule systems with sparse infrared spectra. In next steps, we will increase the spectral range for detection of transient intermediates by further shortening of the optical path between the infrared windows, thereby reducing the gas phase ethylene absorption. Further improvement of the sensitivity will allow us to determine quantitatively the kinetic behavior of the ethyl surface intermediate and isotopic modifications as functions of flow and temperature conditions, making full use of the 10 ms time resolution of which the rapid-scan technique is capable. While millisecond time resolution using this technique coupled with pulsed release of reactants through a mechanical valve proves sufficient for the monitoring of trapped surface intermediates, the microsecond and nanosecond resolution of the step-scan FT-IR technique will be required for detection of the highly reactive, weakly interacting radicals. Recent detection in our laboratory of very small radicals in a zeolite by step-scan FT-IR spectroscopy revealed that ambient temperature lifetimes in 3-D supports are on the time scale of tens to hundreds of microseconds.^{22,40–42}

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References and Notes

- (1) Zaera, F. *Prog. Surf. Sci.* **2001**, 69, 1.
- (2) Somorjai, G. A.; McCrea, K. R. *Adv. Catal.* **2000**, 45, 385.
- (3) Salmeron, M.; Somorjai, G. A. *J. Phys. Chem.* **1982**, 86, 341.
- (4) Kesmodel, L. L.; Dubois, L. H.; Somorjai, G. A. *Chem. Phys. Lett.* **1978**, 56, 267.
- (5) Cassuto, A.; Mane, M.; Jupille, J. *Surf. Sci.* **1991**, 249, 8.
- (6) Demuth, J. E. *Surf. Sci.* **1979**, 84, 315.
- (7) Steiniger, H.; Ibach, H.; Lehwald, S. *Surf. Sci.* **1982**, 117, 685.
- (8) Zaera, F. *Langmuir* **1996**, 12, 88.
- (9) Cremer, P. S.; Stanners, C.; Nremantsverdriet, J.; Shen, Y. R.; Somorjai, G. A. *Surf. Sci.* **1993**, 328, 111.
- (10) Mohsin, S. B.; Trenary, M.; Robota, H. J. *J. Phys. Chem.* **1988**, 92, 5229.
- (11) Sheppard, N.; De la Cruz, C. *Adv. Catal.* **1996**, 41, 1.
- (12) Mohsin, S. B.; Trenary, M.; Robota, H. J. *J. Phys. Chem.* **1991**, 95, 6657.
- (13) Davis, S. M.; Zaera, F.; Gordon, B. E.; Somorjai, G. A. *J. Catal.* **1985**, 92, 240.
- (14) Beebe, T. P.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1986**, 108, 663.
- (15) Zaera, F.; Chrysostomou, D. *Surf. Sci.* **2000**, 457, 71.
- (16) Kubota, J.; Ichihara, S.; Kondo, J. N.; Domen, K.; Hirose, C. *Langmuir* **1996**, 12, 1926.
- (17) Ohtani, T.; Kubota, J.; Kondo, J. N.; Hirose, C.; Domen, K. *J. Phys. Chem. B* **1999**, 103, 4562.
- (18) Cremer, P. S.; Su, X.; Somorjai, G. A.; Shen, Y. R. *J. Mol. Catal. A* **1998**, 131, 225.
- (19) Cremer, P. S.; Su, X.; Shen, Y. R.; Somorjai, G. A. *J. Am. Chem. Soc.* **1996**, 118, 2942.
- (20) Ofner, H.; Zaera, F. *J. Phys. Chem. B* **1997**, 101, 396.
- (21) Argo, A. M.; Odzak, J. F.; Lai, F. S.; Gates, B. C. *Nature* **2002**, 415, 623.
- (22) Yeom, Y. H.; Frei, H. In *In-Situ Spectroscopy of Catalysts*; Weckhuysen, B. M., Ed.; American Scientific Publisher: New York, 2004.
- (23) Basu, P.; Ballinger, T. H.; Yates, J. T., Jr. *Rev. Sci. Instrum.* **1988**, 59, 1321.
- (24) Yeom, Y. H.; Frei, H. *J. Phys. Chem. A* **2002**, 106, 3350.
- (25) Herzberg, G. *Infrared and Raman Spectra*; Van Nostrand: New York, 1945; p 326.
- (26) Soma, Y. *J. Catal.* **1979**, 59, 239.
- (27) Hensley, D. A.; Kesmodel, L. L. *J. Chem. Phys.* **1991**, 95, 1368.
- (28) Kettle, S. F. A. *J. Chem. Soc.* **1965**, 5737.
- (29) Morrow, B. A. *Can. J. Chem.* **1970**, 48, 2192.
- (30) Lloyd, K. G.; Roop, B.; Campion, A.; White, J. M. *Surf. Sci.* **1989**, 214, 227.
- (31) Zaera, F.; Hoffmann, H.; Griffiths, P. R. *Vacuum* **1990**, 41, 735.
- (32) Newell, H. E.; McCoustra, M. R. S.; Chesters, M. A.; De La Cruz, C. *J. Chem. Soc., Faraday Trans.* **1998**, 94, 3695.
- (33) Jenks, C. J.; Bent, B. E.; Bernstein, N.; Zaera, F. *J. Phys. Chem. B* **2000**, 104, 3008.
- (34) McGee, K. C.; Driessen, M. D.; Grassian, V. H. *J. Catal.* **1995**, 157, 730.
- (35) Hoffmann, H.; Griffiths, P. R.; Zaera, F. *Surf. Sci.* **1992**, 262, 141.
- (36) Zaera, F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1984**, 106, 2288.
- (37) Neurock, M.; van Santen, R. A. *J. Phys. Chem. B* **2000**, 104, 11127.
- (38) Pines, H. *The Chemistry of Catalytic Hydrocarbon Conversions*; Academic Press: New York, 1981; p 13.
- (39) Takeda, S.; Tarao, R. *Bull. Chem. Soc. Jpn.* **1965**, 38, 1567.
- (40) Yeom, Y. H.; Frei, H. *J. Phys. Chem. B* **2003**, 107, 6286.
- (41) Vasenkov, S.; Frei, H. *J. Am. Chem. Soc.* **1998**, 120, 4031.
- (42) Vasenkov, S.; Frei, H. *J. Phys. Chem. A* **2000**, 104, 4327.