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Evidence for Precursor-Assisted Activation of Cyclobutane on Ru(001): Enhanced Rate of Reaction in the Presence of a Multilayer

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Over the years, much emphasis has been placed on understanding both gas-phase and liquid-phase heterogeneously catalyzed reactions. While considerable experimental data exist for both gas−solid and liquid−solid catalytic reactions, little is known regarding the mechanistic link that connects these two areas of catalysis. Our goal is to provide experimental insight into this mechanistic link. In particular, the work reported here is concerned with both monolayer and multilayer adsorption of cyclobutane on the Ru(001) single-crystalline surface at 90 K under ultrahigh vacuum (UHV) conditions. The results that have been obtained are unique with respect to dissociative chemisorption that is induced by the presence of a condensed adsorbate phase. These multilayer adsorbates can be thought of as extrinsic precursors[1] that are trapped in a weak potential above the monolayer. Since we have observed a much higher dissociation rate for monolayer adsorbates in the presence of a multilayer at a temperature at which the monolayer would not dissociate in the absence of the multilayer, we believe that these extrinsic precursors lower the barrier to dissociative chemisorption of cyclobutane through their interaction with those molecules adsorbed directly on the Ru(001) surface. The results reported here have relevance to UHV studies involving multilayer adsorbates.

The experiments were carried out in a stainless steel ultrahigh vacuum chamber (base pressure of 7×10^{-11} Torr) described elsewhere.[2−4] Surface cleanliness was checked periodically and maintained by using standard techniques.[2,5] The sample temperature was always kept below 800 K except in the presence of adsorbed oxygen to prevent the formation of graphite on the surface. Cyclobutane (C_4H_8) was synthesized in our laboratory via a Wurtz coupling reaction in which 1,4-dibromobutane was used as the starting material.[6] After completion of the synthesis, the cyclobutane product was purified to greater than 99% purity (as verified by mass spectrometry) by performing several freeze−pump−thaw cycles on our gas-handling manifold. The purified cyclobutane was background dosed onto the clean Ru(001) sample at a surface temperature of 90 K. Cyclobutane exposures between 0.35 and 100 L (1 Langmuir (L) = 1×10^{-6} Torr•s) were obtained by continuously flowing cyclobutane into the chamber at pressures between 1×10^{-8} and 1×10^{-7} Torr (uncorrected for ion gauge sensitivity) for times ranging between 35 and 1000 s.

The TDMS of cyclobutane (*m*/*e* 56), collected for various initial exposures of cyclobutane at a temperature ramp rate of 5 K/s, are displayed in Figure 1. At low exposures a single desorption peak is observed at 170 K, which is labeled as α_1; this peak is assigned to desorption of molecular cyclobutane from the first adsorption layer. The population of the α_1 peak increases with increasing exposure until it saturates at an exposure of approximately 2 L. Once the α_1 peak saturates, a second desorption peak labeled as α_2 is observed. The α_2 desorption peak, which is assigned to zeroth-order multilayer desorption of molecular cyclobutane, continues to grow at a constant rate for all exposures investigated. The temperature of the leading edge of this zeroth-order desorption peak is approximately 120 K.

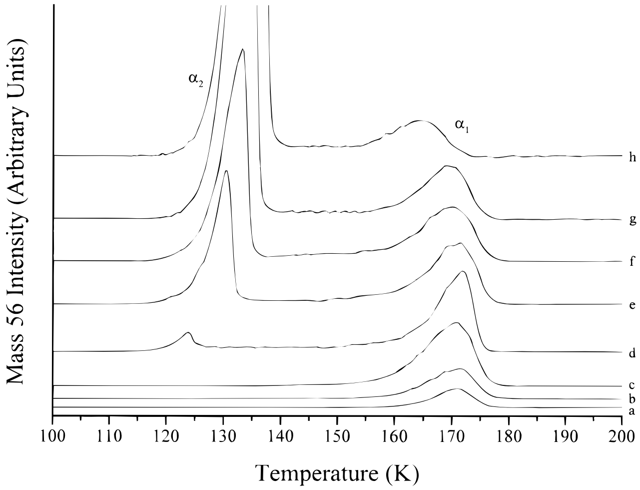

Figure 1. TDMS spectra of *m*/*e* 56 (C_4H_8) collected after exposure of the clean Ru(001) surface to cyclobutane exposures of (in Langmuir (L)) (a) 0.35, (b) 0.70, (c) 1.50, (d) 2.00, (e) 3.50, (f) 5.00, (g) 10.00, and (h) 20.00. The heating rate for all spectra is 5 K/s.

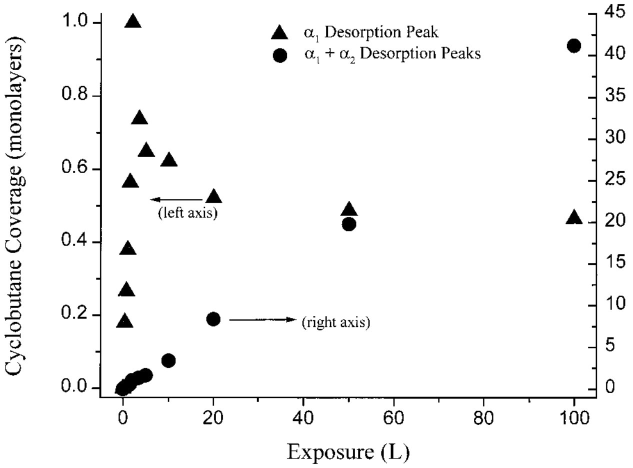

Figure 2. Cyclobutane coverage (in monolayers (ML)) as a function of initial cyclobutane exposure for the α_1 desorption peak and total cyclobutane desorption ($\alpha_1 + \alpha_2$ peaks). All coverages are normalized to a monolayer saturation coverage of unity at 2 L initial exposure. The left axis corresponds to the monolayer coverage and the right axis to the total desorption coverage. Error bars are approximately given by the size of the symbol.

Close examination of the α_1 peak for exposures greater than 2 L shows that the intensity of this peak decreases with increasing exposure and simultaneously downshifts in temperature. Figure 2 displays the time-integrated area of the α_1 peak and the total cyclobutane desorption (sum of the α_1 and α_2 peaks) as a function of initial cyclobutane exposure. While the total cyclobutane desorption increases linearly for all exposures, the monolayer peak area goes through a maximum at an exposure of 2 L. The decrease in the population of the α_1 peak is attributed to

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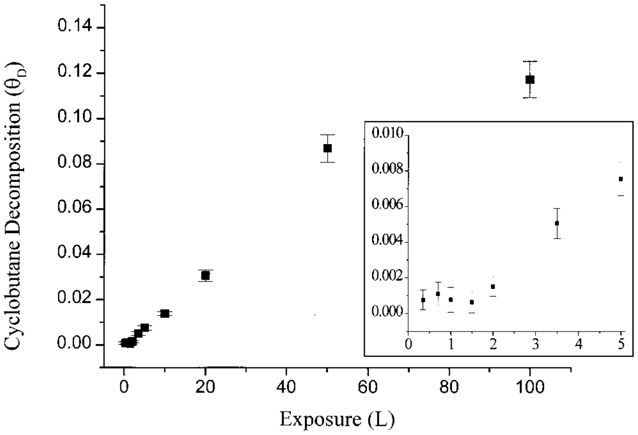

Figure 3. Cyclobutane decomposition to carbon adatoms, θ_D (number of decomposed cyclobutane molecules per surface ruthenium atom), displayed as a function of initial cyclobutane exposure, which occurs during the TDMS experiments shown in Figure 1. The inset shows an expanded view of the data for exposures between 0.35 and 5 L.

multilayer-induced decomposition of cyclobutane in the monolayer. This observation of multilayer-assisted reaction of the monolayer at a temperature well below that at which the monolayer would otherwise react is of great significance and heretofore unprecedented to our knowledge. A quantification of the amount of multilayer-induced cyclobutane decomposition is discussed next.

Immediately following each TDMS experiment, the sample was cooled to 90 K, the ruthenium surface was exposed to 10 L of molecular oxygen (Matheson, 99.9999%), and another TDMS experiment was performed. This resulted in the desorption of reaction-limited CO (*m/e* 28), which was formed by the reaction of oxygen adatoms with carbon adatoms. The carbon was left on the surface as a result of cyclobutane decomposition that occurs during the initial TDMS experiment.[7,8] With this method, the ratio of CO to CO_2 production was ~100, and background adsorption of CO was found to be negligible. The surface coverage of carbon adatoms, θ_C (number of carbon atoms per surface ruthenium atom), deposited by the decomposition of cyclobutane, was calculated by comparing the time-integrated area of the reaction-limited CO desorption in each experiment to the desorption of a saturation coverage of CO on Ru(001), $\theta_{CO,sat} = 0.67$.[9,10] The surface coverage of cyclobutane, which decomposes to carbon adatoms on the surface, θ_D, during the initial TDMS experiment, can be calculated from the relation $\theta_D = \theta_C/4$. These results, quantifying the amount of cyclobutane decomposition to carbon adatoms as a function of initial exposure, are shown in Figure 3. It should be mentioned that for cyclobutane exposures above 20 L, butene desorption is observed around 200 K. This is the only hydrocarbon observed in the TDMS experiments other than cyclobutane and affects only those values of θ_D obtained for exposures above 20 L.[11] If the amount of butene desorption were combined with the data of Figure 3 to yield the surface coverage of cyclobutane which decomposes to *either* carbon adatoms *or* butene, the plot would be approximately linear for all exposures (i.e., the value at 100 L would increase sufficiently to bring it into a linear relationship with the rest of the data).

Examination of the data in the inset of Figure 3 shows that the decomposition of cyclobutane maintains the relatively constant value of $\theta_D \approx 0.001$ for all submonolayer cyclobutane coverages (exposures below 2 L). The reactivity is most likely limited to decomposition at surface defect sites. It is well-known that the activation barrier for dissociative chemisorption of light hydrocarbons at defect sites on transition metal surfaces is lower than the activation barrier at terrace sites on these surfaces.[12,13] As the surface is annealed in each TDMS experiment, the cyclobutane is mobile and thus able to sample many surface sites, including the small concentration of defect sites at which this decomposition occurs.

For cyclobutane exposures greater than 2 L, θ_D increases above this value of $\theta_D \approx 0.001$ observed for submonolayer coverages. This increase in θ_D is approximately linear as a function of exposure for exposures between 2 and 20 L. We attribute the increase in θ_D with the multilayer thickness to the increased contact time between the multilayer and monolayer. The linearity (in Figure 3) is a consequence of activation barriers for multilayer desorption and multilayer-induced decomposition, which are nearly equal. For exposures above 20 L the calculated values for θ_D, corresponding to complete dehydrogenation, begin to saturate. However, the total amount of cyclobutane decomposition attributed to *both* surface carbon deposition and isomerization of cyclobutane to form butene increases approximately linearly over the entire range of exposures studied here. Qualitative examination of the data in Figures 2 and 3 leads to the conclusion that the presence of the multilayer induces the decomposition of cyclobutane in the monolayer.[14] The observation of this multilayer-induced surface reactivity is significant to all studies concerned with producing saturated monolayer adsorbate coverages. Care should be exercised when producing saturated monolayers by "overexposing" the surface to an adsorbate and then annealing the multilayer to leave what is assumed to be a saturated monolayer; clearly, we have shown that the multilayer can induce decomposition of the monolayer in this work.

In conclusion, we have observed the multilayer-induced decomposition of molecularly adsorbed cyclobutane in the monolayer on Ru(001) at surface temperatures at or below 140 K. The rearrangement of the molecular cyclobutane in the monolayer results in a geometry that is more favorable for dissociation compared to the adsorption geometry of monolayer cyclobutane at the vacuum interface. These results provide a mechanistic link between gas-phase and liquid-phase heterogeneous catalysis. The enhanced reaction rate of monolayer cyclobutane with the Ru(001) surface in the presence of a condensed phase strongly suggests that the activation barrier to dissociative chemisorption of cyclobutane is lowered in the presence of the multilayer. This implies that the adsorbate−adsorbate interactions at the liquid−solid interface are sufficiently large to dramatically increase the reaction rate over that observed at the gas−solid interface.

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(14) While the increase in carbon adatom coverage is relatively linear for all exposures, the area of the α_1 peak decreases rapidly as a function of exposure between 2 and 10 L and then asymptotes to an essentially constant value at higher exposures. This is caused by adsorbate−adsorbate interactions between cyclobutane molecules and partially decomposed hydrocarbon moieties in the 2 to 10 L exposure range and by adsorption of cyclobutane above carbon adatoms at higher exposures. The latter is evidenced by the shift in desorption temperature of the α_1 peak.