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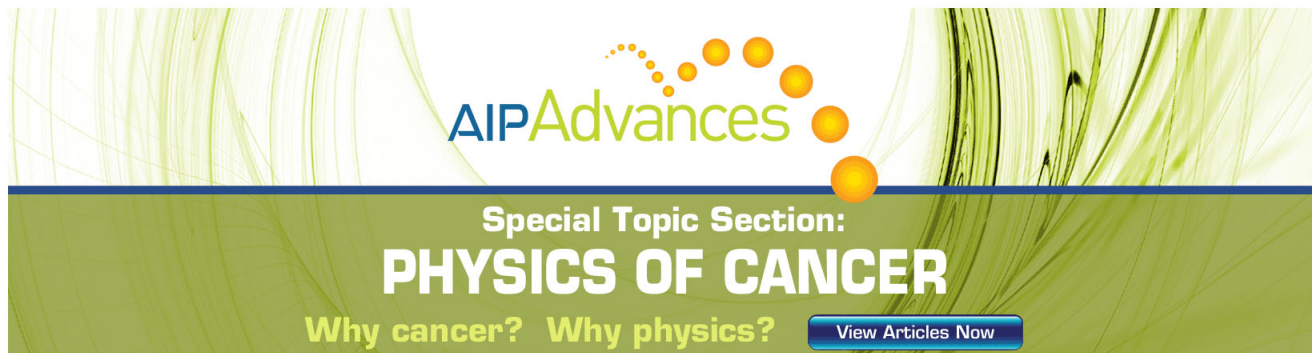
Evidence of stable high-temperature D$_x$-CO intermediates on the Ru(0001) surface

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We demonstrate the formation of complexes involving attractive interactions between D and CO on Ru(0001) that are stable at significantly higher temperatures than have previously been reported for such intermediate species on this surface. These complexes are evident by the appearance of new desorption features upon heating of the sample. They decompose in stages as the sample temperature is increased, with the most stable component desorbing at >500 K. The D:CO ratio remaining on the surface during the final stages of desorption tends towards 1:1. The new features are populated during normally incident molecular beam dosing of D$_2$ on to CO pre-covered Ru(0001) surfaces (180 K) when the CO coverage exceeds 50% of the saturation value. The amount of complex formed decreases somewhat with increasing CO pre-coverage. It is almost absent in the case of dosing on to the fully saturated surface. The results are interpreted in terms of both local and long-range rearrangements of the overlayer that give rise to the observed CO coverage dependence and limit the amount of complex that can be formed. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.3689553]

INTRODUCTION

The dissociation mechanisms of CO are of interest because they represent the first step in the production of synthetic liquid fuels from syngas (CO + H$_2$) via the Fischer-Tropsch process.[1,2] Two basic mechanisms have been proposed for the dissociation of CO on metal surfaces: direct dissociation of CO (carbide formation) and dissociation via a hydrogenated intermediate. In the latter case, there is increasing interest in the possible role of formyl as an intermediate species.[3] Theoretical and experimental works to date suggest that a hydrogen-assisted pathway should be more favorable on close-packed surfaces, whereas the carbide mechanism is preferred on stepped and corrugated surfaces.[1,4–8] Theoretical studies have provided support for dissociation via H$_x$CO intermediates on Ru(0001) (Ref. 5) and Co(0001).[6] Evidence for a hydrogen-assisted pathway has been reported for Ni (Ref. 4) and Ru (Ref. 7) surfaces. Andersson *et al.* reported dissociation at under-coordinated sites, such as steps, as being most favorable on Ni surfaces, with direct dissociation occurring under ultrahigh vacuum (UHV) conditions in the absence of hydrogen, whereas dissociation via a COH species was most favorable under methanation conditions.[4] Mitchell *et al.* reported the formation of formyls and formaldehydes

upon exposure of a saturated CO layer on Ru(0001) (sample temperature T_s < 130 K) to atomic hydrogen produced using a hot tungsten filament source.[7] These products decomposed progressively upon annealing, with the release of molecular hydrogen. All hydrogen was desorbed and the original CO overlayer reconstituted at T_s < 300 K. In contrast, Morgan *et al.* did not observe the formation of H-CO species after similar irradiation of CO overlayers on a stepped Ru surface.[9] They also performed density functional theory (DFT) calculations to search for stable formyl structures on the (0001) surface. It was found that highly coordinated metastable formyl could be formed on the flat surface, but that such species would be unstable at temperatures above 170 K.

Riedmuller *et al.* studied the interaction of CO with hydrogen pre-covered Ru(0001).[10,11] CO was found to displace and ultimately drive the H-atoms off the surface. In the process, stable CO-islands were formed in a "sea" of hydrogen.[10] It was also shown by Ciobica *et al.* in DFT calculations that hydrogen and CO tend to phase separate on the Ru-surface.[12] In the reverse case, for atomic hydrogen exposures of CO overlayers on Ru, Morgan *et al.* reported overlayer compression, attributed to the formation of immiscible H and CO islands, with eventual desorption of CO.[9] In molecular beam experiments, Ueta *et al.* demonstrated that CO molecules act as geometrical site blockers for deuterium adsorption and that an effective blocking radius can be assigned to the adsorbed CO molecules.[13] At low normal incident energy and high

coverages of CO, deuterium adsorption was effectively blocked. At higher energies, some dissociative chemisorption was still possible and presumably the D atoms are guided to special sites on the surface by the adsorbed CO.

Groot and co-workers modeled the adsorption of hydrogen on CO pre-covered Ru(0001) using DFT calculations and quantum and classical molecular dynamics calculations.[14,15] In the calculations it became apparent that dissociative chemisorption of hydrogen on CO/Ru(0001) becomes an activated process, in contrast to experimental observations.[14] In addition, Groot *et al.* found that the influence of CO on H_2 dissociation was not simply a site-blocking effect; Ru was actually slightly more reactive with CO pre-adsorbed.[15] The formyl species seen in DFT calculations of Morgan *et al.*[9] were not seen in those calculations. This is not necessarily a contradiction since the phase space sampled by the calculations of Morgan *et al.*, which involved H-atoms, was not explored by Groot *et al.*, who started from H_2 molecules. Both the calculations of Morgan *et al.* and Inderwildi *et al.*[6] indicate that hydrogenation of CO results in the formation of a species with the C-O bond orientated parallel to the surface.

The formyl species identified in the studies of both Inderwildi *et al.*[6] and Morgan *et al.*[9] were unstable and decompose at low temperature making experimental observation difficult. However, in this paper we present the evidence of D_x-CO complex species that are stable on Ru(0001) above room temperature. Formation of these species was critically dependent on the CO pre-coverage and on the incident kinetic energy of the D_2 molecules. They are populated when CO overlayers with fractional coverages >0.5 of the saturation coverage are dosed with energetic D_2 via a normal incidence molecular beam. They decompose in stages during heating for sample temperatures in the range of 375–550 K, releasing D_2. The new features in the temperature programmed desorption (TPD) D_2 traces are strongly correlated with the associated CO desorption traces.

EXPERIMENTAL

The experimental setup[16] consists of a triply differentially pumped molecular beam line connected to an UHV chamber with an ion sputter gun and a residual gas analyzer. A differentially pumped quadrupole mass spectrometer (QMS) is mounted on a linear drive in line-of-sight with the molecular beam. This QMS is used to measure the velocity distribution of incident D_2 by time-of-flight techniques, and to measure TPD spectra. The sample is mounted in the center of the UHV chamber on a rotatable liquid nitrogen cooled manipulator. The Ru(0001) crystal used for these studies is oriented to within 0.1° of the (0001) face. The surface was cleaned by repeated cycles of Ar^+ sputtering followed by annealing to 1500 K for several minutes and then annealing for several minutes at 1200 K in an oxygen atmosphere (1×10^{-8} mbar O_2). The final cleaning step was Ar^+ sputtering followed by annealing to 1500 K for several minutes. The surface cleanliness was checked by reference to the TPD spectra of CO (Ref. 17) and NO.[18] CO-covered surfaces were prepared by background dosing of CO, which was performed at sample temperatures <200 K. Absolute CO coverage (θ_{CO}) values

were determined by comparison with the CO saturation coverage on the basis of the total integrated areas of the TPD traces. The saturation coverage was assumed to be 0.65 ML (relative to Ru surface atoms).[19]

D_2 was dosed on the clean and CO-covered surfaces using a well-collimated molecular beam at normal incidence. During exposure to D_2 the surface temperature was held constant at 180 K. The saturation coverage of D atoms on the clean surface was assumed to be 1 ML (relative to Ru surface atoms).[20] The kinetic energy of the incident D_2 was controlled by nozzle-heating (room temperature to 1700 K). Assuming no relaxation during beam expansion, the population of the Boltzmann vibrational distribution in the ground state (v = 0) would be ~93% at the highest nozzle temperature of 1700 K. Hence, vibrational excitation can be considered as having little or no influence on D_2 dissociation in our experiments. However, due to poor rotational cooling of D_2 during supersonic expansion at high-nozzle temperatures, our high-energy beams have broad translational and rotational energy distributions, in particular at the highest temperatures. The molecular beam exposures were used to determine the D_2 dissociation probability on clean and CO pre-covered surfaces[13,21] by means of the adsorption reflection technique of King and Wells.[22] The TPD traces presented in this paper were acquired during subsequent heating of the sample at a rate of ~6 K/s.

RESULTS AND DISCUSSION

Figures 1(a)–1(e) show normalized CO and D_2 TPD traces that were acquired following King and Wells measurements of D_2 sticking on CO-covered Ru(0001) for various CO pre-coverages.[13] In all cases the energy of the D_2 in the molecular beam was 37.3 kJ/mol. The CO TPD traces develop in a characteristic fashion with increasing coverage, consistent with previous reports of CO desorption from Ru(0001).[17,23,24] The doublet structure at ~475 K is fully saturated at θ_{CO} ~ 1/3 ML. When θ_{CO} exceeds this value a second lower temperature desorption peak begins to develop. This feature is fully saturated at θ_{CO} ~ 2/3 ML. The structure of the CO overlayer is dependent on the coverage and the surface temperature.[25] On the basis of those phase diagrams, the conditions utilized in the current work ($T_s = 180$ K) should give rise to a ($\sqrt{3} \times \sqrt{3}$)R30° structure at $\theta_{CO} = 1/3$ ML, while a ($2\sqrt{3} \times 2\sqrt{3}$)R30° structure should emerge near the saturation coverage. A ($5\sqrt{3} \times 5\sqrt{3}$)R30° structure has been reported at saturation coverage.[19,26]

The shape of the CO desorption traces is not significantly affected by the dosing of D_2 on to the surface, which is consistent with previous results.[23] In contrast, the shape of the D_2 desorption trace does vary depending on the CO pre-coverage. At the lowest θ_{CO}, D_2 desorbs in a single broad peak spanning the temperature range of ~275–450 K. The desorption trace is very similar to that of a saturation coverage of D_2 desorbing from the bare Ru(0001) surface. With increasing θ_{CO}, this desorption peak becomes progressively sharper and is confined to a narrower temperature range (~275–350 K for $\theta_{CO} > 1/3$ ML) with a common leading edge, consistent with a repulsive interaction between D and CO.[10,27,28] For θ_{CO}
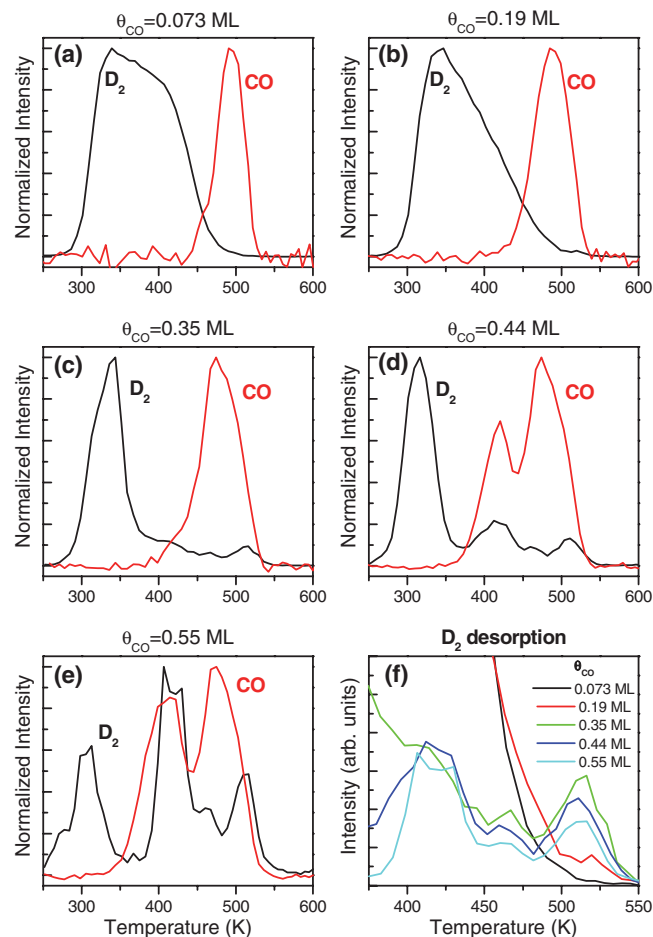
FIG. 1. Normalized D_2 (black) and CO (red) TPD traces measured after molecular beam dosing of D_2 (translational energy 37.3 kJ/mol) on to Ru(0001) covered with (a) 0.073 ML, (b) 0.19 ML, (c) 0.35 ML, (d) 0.44 ML, and (e) 0.55 ML CO. Panel (f) shows portions of the D_2 desorption traces from panels (a)–(e), plotted on a common intensity scale.

≤ 0.19 ML, all D_2 desorbs in a single peak and there is only a small region of overlap between the D_2 and CO desorption ranges. The shape of the D_2 traces for $\theta_{CO} < 1/3$ ML is consistent with those reported by Peebles *et al.*[28] and by Diemant *et al.*[23] for co-adsorbed layers produced by backfilling.

For $\theta_{CO} \geq 0.35$ ML, the low-temperature D_2 peak is fully desorbed prior to the onset of CO desorption. However, additional high-temperature features are evident in the desorption traces. The shape of these features becomes progressively clearer with increasing θ_{CO}. At least three peaks are apparent at $T_s \sim 425$ K, ~ 460 K, and ~ 510 K. The positions of these peaks approximately coincide with the trailing edge of the low-temperature CO desorption peak, the leading edge of the high-temperature CO desorption peak, and the trailing edge of the high-temperature CO desorption peak, respectively. This suggests that this portion of adsorbed D is being stabilized by the CO molecules. Figure 1(f) shows a close-up of the 375–550 K region of the D_2 desorption traces for the five different CO pre-coverages, plotted on a common intensity scale. There are indications that some stabilization of D may already be occurring for $\theta_{CO} = 0.19$ ML in the form of a longer trailing edge and the possible presence of a new high-temperature

component. However, the stabilization is most effective and its multi-component nature is only evident for the D_2 exposures to overlayers with $\theta_{CO} \geq 0.35$ ML. Within the accuracy of the measurements, the amount of D_2 incorporated in the two highest temperature features (both associated with the ~ 475 K CO desorption peak) decreases with increasing θ_{CO}. In contrast, the intensity of the D_2 feature associated with the lower temperature CO desorption peak appears roughly constant with θ_{CO}.

Figure 2 illustrates the effect of varying the translational energy of D_2 in the molecular beam on the resultant D_2 desorption traces for CO pre-coverages of 0.44 ML, 0.55 ML, and 0.65 ML. Panels (a)–(d) show the desorption traces that arise after D_2 dosing at beam energies of 8, 20.5, 29.3, and 37.3 kJ/mol, respectively. For $\theta_{CO} = 0.44$ ML, all three high-temperature D_2 peaks are already fully developed after the exposure with a kinetic energy of 8 kJ/mol. However, the low-temperature desorption peak is barely present in this trace. This peak becomes progressively more evident with increasing D_2 kinetic energy. In the case of $\theta_{CO} = 0.55$ ML there is no significant D_2 desorption after the 8 kJ/mol exposure. The two highest temperature desorption features are present after the 20.5 kJ/mol exposure. All three high-temperature desorption peaks emerge after the 29.3 kJ/mol exposure, while the low-temperature peak develops only after the exposure at 37.3 kJ/mol. Hence the D_2 features are populated in order of stability (decreasing temperature). In the case of molecular beam dosing of D_2 on to the fully saturated CO overlayer ($\theta_{CO} = 0.65$ ML), D_2 desorption was only observed after the exposure at 37.3 kJ/mol. In this case only a very minor amount desorbs at $T_s > 500$ K. Note that, since the D_2 exposures were made as part of King and Wells dissociation probability determinations,[13] Figures 1 and 2 represent a comparison of comparable exposure times. The D_2 TPD traces shown do not necessarily represent overlayers that have been fully saturated with D_2.

Analysis of the integrated areas of the two highest temperature desorption features (~ 460 K and ~ 510 K) for the traces shown in Figure 2 yield relative peak areas of $\sim 1:2$ for the TPD traces in which both features are deemed to be fully saturated. There is a greater variability in the relative size of the D_2 feature at ~ 425 K since it does not appear to exhibit the same trend with increasing CO coverage as the two higher temperature features. As an indicative value, the ratio of the integrated areas of the ~ 425 K and ~ 460 K peaks is $\sim 3.5:1$ for the 37.3 kJ/mol exposure of the 0.55 ML CO overlayer.

Figure 2 illustrates that with increasing θ_{CO} it becomes increasingly difficult to populate the stabilized states. The sequential nature in which the features are populated with increasing beam energy (in particular the traces for $\theta_{CO} = 0.55$ ML) indicates that they are related to each other (associated on the surface) rather than the result of separate desorption from independent regions. Such a sequential population would only occur for independent regions if those regions have substantially different sticking probabilities. We regard this as an unlikely proposition.

The measured CO and D_2 TPD traces can be converted to traces of the corresponding residual ML coverages. This is
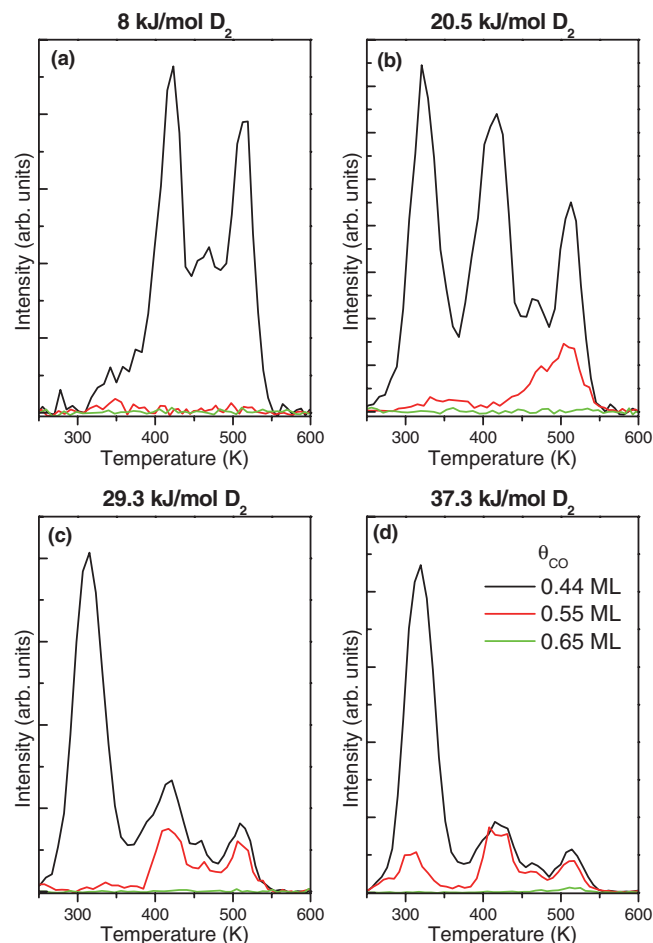
FIG. 2. D_2 TPD traces obtained after molecular beam dosing of D_2 with translational energies of (a) 8 kJ/mol, (b) 20.5 kJ/mol, (c) 29.3 kJ/mol, and (d) 37.3 kJ/mol on to Ru(0001) with $\theta_{CO} = 0.44$ ML (black), $= 0.55$ ML (red), and $= 0.65$ ML (green). Note that the intensity scales on the individual panels differ from each other.

FIG. 3. Residual coverages of D (in ML) as a function of increasing sample temperatures (see text for details). The D_2 beam energy was 37.3 kJ/mol; the heating rate during desorption was $\sim$6 K/sec. Inset: Residual D coverages at $T_s = 375$ K and $T_s = 450$ K plotted against the fraction of the Ru surface that is nominally available to accommodate D atoms at the onset of the D_2 exposure. The linear fits that are applied to the non-zero data points are intended to guide the eye.

done on the basis of the nominal CO exposures, the total integrated areas of the D_2 and CO TPD traces, and the assumed saturation coverages of CO and D relative to Ru surface atoms (0.65 ML and 1 ML respectively). Figure 3 shows the result of such a conversion for the D_2 desorption traces collected after molecular beam dosing of 37.3 kJ/mol D_2 onto 0.35, 0.44, 0.55, and 0.65 ML CO. The estimated residual D coverage is plotted as a function of sample temperature. The horizontal lines attached to the left-hand side axis indicate the maximum D_2 coverages that would be anticipated if only the fraction of the Ru surface that is nominally bare at the onset of D_2 dosing [$F_{bare} = (0.65 - \theta_{CO})/0.65$] were to be fully saturated by D atoms.

The inset of Figure 3 illustrates how the residual D coverage at $T_s = 375$ K (corresponding to D incorporated in all three high-temperature D_2 features) and at $T_s = 450$ K (D incorporated in the two highest temperature desorption features) varies as a function of F_{bare}. The absolute amount of D incorporated in these features is relatively small in all cases. The decrease in intensity of the stabilized features with increasing θ_{CO} suggests that the amount of stabilized D_x-CO complex that can be formed is correlated with uncovered fraction of the Ru surface. However, for the sub-saturation coverages the
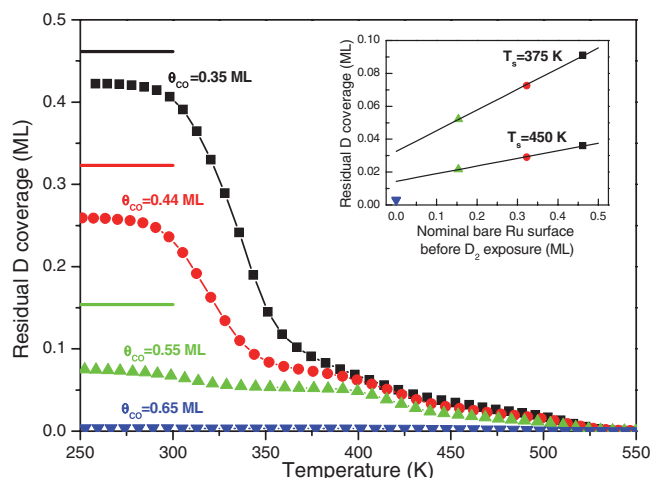
decrease in D as a function of increasing CO pre-coverage is less than would be anticipated solely on the basis of the available F_{bare}. The fully saturated surface breaks the trend, with almost no stabilized D being formed on the "ideal" overlayer.

During desorption of the final D_2 peak at $\sim$510 K the fractional CO coverage remaining on the surface is quite low ($\leq$0.16 ML). Hence, this feature (once formed) remains stable at low residual coverages of CO even though it was not populated directly by molecular beam dosing of D_2 on to a surface with a comparably low pre-coverage of CO (see Figure 1(b)). This is the confirmation that presence of the high-temperature desorption features must involve an attractive interaction. Explanations based on solely repulsive interactions (for instance, trapping of individual D atoms by CO encirclement, thereby hindering recombination) would cease to be effective at low fractional CO coverages.

Figure 4 shows a close-up of the residual D coverages as a function of temperature during desorption of the high-temperature D_2 peaks. The corresponding residual CO coverages are also plotted on the same axes. The highest temperature D_2 feature (peak at $\sim$510 K) represents a D coverage of $\sim$0.015 ML to $\sim$0.025 ML depending on the CO precoverage. The inset of Figure 4 shows the D:CO ratio that remains on the surface during the desorption of this feature. The ratio tends towards $\sim$1:1 during desorption of the trailing edge ($\sim$525 K), which is suggestive of the composition of a formyl radical. Assuming that all three high-temperature D_2 desorption features arise from D rearrangement within a single pre-formed D_x-CO complex (i.e., that the CO content within the complex remains constant), then the corresponding D:CO ratios prior to the desorption of $\sim$460 K and $\sim$425 K D_2 features would be $\sim$1.5:1 and $\sim$3:1, respectively. The basic chemical composition of such a complex would thus change from $D_6(CO)_2$ (peak at $\sim$425 K) through $D_3(CO)_2$ (peak at $\sim$460 K) to $D_2(CO)_2/2DCO$ (peak at $\sim$510 K). These D:CO
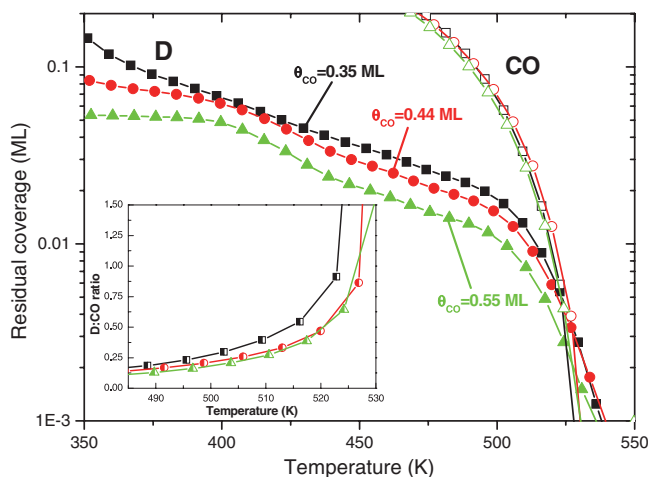
FIG. 4. Residual ML coverages of D (filled symbols) and CO (open symbols) as a function of increasing sample temperatures (see text for details). The D_2 beam energy was 37.3 kJ/mol; the heating rate during desorption was ~6 K/sec. Inset: Corresponding D:CO ratios plotted as a function of sample temperature.

ratios and formulae should be treated as merely indicative, particularly with regard to the feature at ~425 K. As noted above, the intensity trends of this feature as a function of CO coverage and D_2 beam energy are not necessarily correlated with those of the two higher temperature features. Furthermore, the assumption that the CO content of the stabilized species remains constant while various fractions of the D content are sequentially desorbed is one of convenience rather than supported by any specific evidence.

It is important to emphasize that the current results, while clearly indicating the presence of CO-stabilized D on the Ru(0001) surface, offer no insight into the configuration of the species that are formed. Indeed, although we characterize the new TPD features in terms of D_x-CO species throughout this text, it is conceivable that the true nature of the complexes formed would be more correctly characterized by a formalism such as D_x-CO_y-Ru. The D_x-CO formulation was selected because the TPD data show a correlation between the desorption of D_2 and CO, whereas no explicit indication of a substrate influence is available. Of course for metallic samples, the substrate atoms can be considered as being implicitly involved in interactions between adsorbed species. For example, DFT calculations in which H atoms were forced to occupy sites close to CO on Ru(0001) produced modified H-Ru bond lengths.[12] In the current case it is possible that Ru atoms play a central role in the stabilized complex. This would be the case if, for instance, the stabilization is the result of D atoms being forced subsurface under the influence of CO, such as has been reported for the Ni(110) surface.[29] The possibility of subsurface hydrogen is interesting given the potential role on bulk hydrogen in catalytic hydrogenation.[30] However, it should be noted that DFT calculations indicate that hydrogen occupation of subsurface sites is generally unfavorable relative to the surface sites of bare Ru(0001), although it has been seen in the case of high coverage exposures ($\theta_H > 1$).[12,31] Also, in the case of Ni(110) the CO-induced segregation of H to the subsurface was repulsive for the CO.[29]

Even though the precise configuration can only be speculated upon, the TPD data do clearly demonstrate that D can remain associated with CO on the Ru(0001) surface at unprecedented high temperatures. Similar desorption features have not been reported either for diffuse dosing of D_2[23,28] or for dosing with thermal atomic hydrogen.[9] Mitchell *et al.* claim the observation of formyl in HREELS, but did not report desorption above 300 K.[7] The possibility that the features observed in the current work might be solely due to the presence of defects on the Ru surface can be discounted on the basis of the clear correlation of their appearance with a specific CO coverage range. As illustrated in Figures 1 and 3, the new desorption features develop as a result of D_2 dosing of overlayers where $0.35 \leq \theta_{CO} < 0.65$. Hence, they require the existence of CO overlayers with a certain pre-existing molecular density and/or order, but not a fully saturated layer. Population of these states also requires the use of hyperthermal molecular beam dosing of D_2. This indicates a high barrier to formation necessitating that the atoms be "forced" into the structure.

Thus, the picture emerges of stable D_x-CO complexes with a high (and CO-coverage dependent) barrier to formation. Translationally excited D_2 is required to populate these states, coupled with a relatively high CO pre-coverage. The latter may be required in order to hinder the ability of CO molecules to migrate away during the formation process. Formation of the most stable form of the complex may involve some local rearrangement of CO molecules, such as is suggested by the metastable species identified by Morgan *et al.*[9] With increasing θ_{CO} it becomes increasingly difficult for the individual molecules involved to undergo the necessary re-orientation. Consequently, the D_2 translational energy required to efficiently populate the state increases, while the amount that can be formed decreases. In this case, the absence of complex formation during exposure of the saturation CO coverage would be due to the inability of the molecules to re-arrange.

Only a limited amount of the most stable form of the complex can be formed irrespective of θ_{CO} (see Figure 3). Assuming again a 1:1 D-to-CO ratio in the most stable form, then for the 0.35 ML pre-coverage only ~7% of the available CO molecules is incorporated in this form. The corresponding values for the 0.44 ML and 0.55 ML pre-coverages are ~4.5% and ~2.6%, respectively. These values suggest that after the initial stages of complex formation it is easier to grow existing sites via the incorporation of D in more weakly bound forms than to create new instances of the most stable configuration. The initial formation and subsequent growth of D-containing regions may promote a wider rearrangement (compression) of the CO overlayer, thereby making it increasingly resistant to additional direct insertion of deuterium.

The fact that the D:CO ratio tends toward 1:1 in the final stages of desorption is suggestive in the context of the proposed role for formyl species in the hydrogenation of CO. However, the assumption in relation to CO that was used to derive this ratio is unconfirmed. It is not given that all of the CO molecules remaining on the surface during the final stages of desorption form an integral part of the most stabilized form of the complex. Indeed, the attempt to

reduce the composition of the system to its simplest forms may be misleading in this case. The fact that the stabilized D_2 desorbs in stages argues against the stabilized components being "simple" species, formyl or otherwise. Collective attractive interactions of varying strength between multiples adsorbates (conceivably also involving Ru atoms) is necessary in order to account for the multiple desorption features. For instance, the relative intensity of the two highest temperature desorption features implies a collective interaction involving a minimum of at least three D atoms. These core species may consist of dense CO islands in which the deuterium binding energy is higher than on the bare surface, permitting the islands to remain intact during progressive thermal decomposition. Ultimately the most stable form of the complexes only decomposes upon simultaneous desorption of all its constituents. Confirmation of such novel D_x-CO configurations will require direct experimental evidence, for instance from high-resolution electron energy loss spectroscopy or reflection absorption infra-red spectroscopy, in conjunction with appropriate DFT calculations.

CONCLUSION

We have demonstrated that it is possible to stabilize D on CO pre-covered Ru(0001) at significantly higher temperatures than previously reported. The population of these stabilized species is dependent upon the CO pre-coverage (>0.19 ML) and upon dosing D_2 with relatively high translational energy. The D_2 energy required to efficiently populate the species increases with increased θ_{CO}. They thermally decompose in stages to their original constituents. The results are interpreted in terms of attractive complexes that have a high barrier to formation, necessitating that D be "forced" into the structure. The observed CO coverage dependence is attributed to the twin requirements that the overlayer be sufficiently compressed to prevent CO migration during the formation process but still capable of accommodating a local molecular rearrangement. Wider rearrangement of the overlayer as a result of the formation results in the amount of the complex that can be formed being self-limiting. Although energetic D_2 and a high CO pre-coverage are required for the population of the complex species, once present the most stable form is stable up to $\sim$500 K when the fractional coverage of CO is relatively low. Hence the complexes must involve an attractive interaction between the components. These results are supportive of a possible role for hydrogenated intermediates in the dissociation of CO on flat Ru surfaces.

ACKNOWLEDGMENTS

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