

The Chemistry of Trimethylamine on Ru(001) and O/Ru(001)

B. F. Hallac and M. Asscher*

Department of Physical Chemistry and the Farkas Center for Light Induced Processes, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Received March 27, 2007. In Final Form: May 20, 2007

The interaction and reactivity of trimethylamine (TMA) has been studied over clean and oxygen-covered Ru(001) under UHV conditions, as a model for the chemistry of high-density hydrocarbons on a catalytic surface. The molecule adsorbs intact at surface temperature below 100 K with the nitrogen end directed toward the surface, as indicated from work function change measurements. At coverage less than 0.05 ML (relative to the Ru substrate atoms), TMA fully dissociates upon surface heating, with hydrogen as the only evolving molecule following temperature-programmed reaction/desorption (TPR/TPD). At higher coverage, the parent molecule desorbs, and its desorption peak shifts down from 270 K to 115 K upon completion of the first monolayer, indicating a strong repulsion among neighbor molecules. The dipole moment of an adsorbed TMA molecule has been estimated from work function study to be 1.4 D. Oxygen precoverage on the ruthenium surface has shown efficient reactivity with TMA. It shifts the surface chemistry toward the production of various oxygen-containing stable molecules such as H₂CO, CO₂, and CO that desorb between 200 and 600 K, respectively. TMA at a coverage of 0.5 ML practically cleans off the surface from its oxygen atoms as a result of TPR up to 1650 K, in contrast to CO oxidation on the O/Ru(001) surface. The overall reactivity of TMA on the oxidized ruthenium surface has been described as a multistep reaction mechanism.

1. Introduction

The initial stages of hydrocarbon chemistry on catalytic metal surfaces often involves C–X (X = C, H, O, or halides) bond scission, resulting in methyl radical or longer-chain fragments residing on the surface. Upon substrate heating, these subsequently react among neighboring fragments to form new molecules or further decompose. In an attempt to better understand the elementary steps of this chemistry, various methyl halides were studied where the methyl radical became the initial adsorbate as a result of parent molecule thermal or photochemical fragmentation.^{1–8}

The chemistry of trimethylamine (TMA–(CH₃)₃N) on Mo-(100) was studied by means of LEED, XPS, AES, and TPD under UHV conditions.^{9–11} The advantage in using TMA as the source of the methyl fragments is the particularly high density of initial methyl adsorbates on the surface, following parent molecule dissociation.

In these studies of TMA, its chemical reactivity was discussed in terms of Lewis acids and Lewis bases on different metal surfaces.^{9–11} Dissociative adsorption of TMA molecules resulting in its respective fragments was recorded on a clean Mo surface by careful examination of the carbon Auger peak shapes. When the surface became partially passivated by the dissociation products, parent molecule desorption could be detected. A

significant change in reactivity of molybdenum surfaces was noted when the surface was pretreated with oxygen. The surface became less reactive so that TMA is adsorbed in a molecular form and does not decompose anymore upon surface heating during the TPD experiment.

In summary, the Mo surface could be significantly passivated by the decomposition products or following incorporation of 0.8 ML or more of oxygen atoms into the surface region.

Upon heating the TMA-covered Mo sample, different products were obtained, divided into two classes: (1) diatomic molecules H₂, N₂, and CO; and (2) the polyatomic molecules CH₄ and HCN. The combination of surface spectroscopy techniques with isotopic labeling has led these authors to suggest a sequential dehydrogenation mechanism to describe the reactivity of TMA on the Mo surface.⁹ The rate-limiting step in the decomposition of TMA was the C–N bond scission. Intact methyl groups adsorbed on the surface were suggested to accumulate as a result of the TMA dissociation. The combination of previous work^{12,13} and C–Auger line-shape analysis has demonstrated that despite the presence of all the constituent atoms on the surface neither methane nor hydrogen cyanide were observed in TPD. Similar results were obtained from studies of the chemistry of methylamine on Ni(111) using HREELS and TPD.¹⁴

The chemistry of methyl bromide on Ru(001) and Cu/Ru(001) has been studied earlier^{15,16} utilizing Δp -TPD and $\Delta\Phi$ -TPD techniques, attempting to study the chemistry of methyl on clean and modified Ru(001). Methyl bromide species underwent decomposition, similar to TMA, producing coadsorbed bromine atoms and methyl at coverage below 0.6 ML. The methyl fragments further dissociated at higher crystal temperature. The reactivity at the submonolayer coverage has been monitored by work function change measurements at temperature prior to any desorption. Similar behavior was reported previously in the chemistry of methyl iodide on Ru(001).^{15,40}

(1) Chinta, S.; Choudhary, T. V.; Daemen, L. L.; Eckert, J.; Goodman, D. W. *Angew. Chem., Int. Ed.* **2002**, *41* (1), 144–146.

(2) Dickens, K. A.; Stair, P. C. *Langmuir* **1998**, *14* (6), 1444–1450.

(3) Harris, J. J. W.; Fiorin, V.; Campbell, C. T.; King, D. A. *J. Phys. Chem. B* **2005**, *109* (9), 4069–4075.

(4) Kim, S. H.; Stair, P. C. *J. Phys. Chem. B* **2000**, *104* (14), 3035–3043.

(5) Kis, A.; Kiss, J.; Olsz, D.; Solymosi, F. *J. Phys. Chem. B* **2002**, *106* (20), 5221–5229.

(6) Parker, B. R.; Jenkins, J. F.; Stair, P. C. *Surf. Sci.* **1997**, *372* (1–3), 185–192.

(7) Peng, X. D.; Viswanathan, R.; Smudde, G. H.; Stair, P. C. *Rev. Sci. Instrum.* **1992**, *63* (8), 3930–3935.

(8) Smudde, G. H.; Yu, M.; Stair, P. C. *J. Am. Chem. Soc.* **1993**, *115* (5), 1988–1993.

(9) Henry, R. M.; Walker, B. W.; Stair, P. C. *Surf. Sci.* **1985**, *155* (2–3), 732–750.

(10) Walker, B. W.; Stair, P. C. *Surf. Sci.* **1980**, *91* (2–3), L40–L44.

(11) Walker, B. W.; Stair, P. C. *Surf. Sci.* **1981**, *103* (2–3), 315–337.

(12) Han, H. R.; Schmidt, L. D. *J. Phys. Chem.* **1971**, *75* (2), 227–&.

(13) Ignatiev, A.; Jona, F.; Jepsen, D. W.; Marcus, P. M. *Surf. Sci.* **1975**, *49* (1), 189–200.

(14) Gardin, D. E.; Somorjai, G. A. *J. Phys. Chem.* **1992**, *96* (23), 9424–9431.

(15) Livneh, T.; Asscher, M. *J. Phys. Chem. B* **1997**, *101* (38), 7505–7519.

(16) Livneh, T.; Asscher, M. *J. Phys. Chem. B* **1999**, *103* (27), 5665–5674.

The original motivation for this study has been the dynamics of energetic colliders with multilayers of TMA-covered Ru(001).¹⁷ Initially, however, exploration of the chemistry of the first layers on the ruthenium substrate is necessary. In this paper, therefore, we present the chemistry of the first layers of TMA on the Ru(001) single-crystal surface, studied by a combination of Δp -TPD and $\Delta\Phi$ -TPD techniques. TMA was found to adsorb intact on clean Ru(001) at low temperatures of <100 K. Upon heating above 100 K, a multistep dissociation process evolves of TMA to its constituent atoms with molecular hydrogen as the only desorbing molecules due to recombinative desorption. A 0.4 ML oxygen pre-covered ruthenium surface significantly reduced the dissociation rate while stabilizing the TMA molecules on the surface. On the other hand, the oxidized surface was not inert, and O-containing products were observed during TPD. Work function change measurements suggest the formation of a stable surface intermediate, assumed to be ethylidyne (CCH_3).

2. Experimental Section

The experiments described here were performed in an ultrahigh-vacuum (UHV) chamber at a base pressure of $2 \cdot 10^{-10}$ Torr obtained by two turbo-molecular pumps (510 s^{-1} and 180 s^{-1}). A sputter gun (Ar^+ ions at 600 V and sample current of $6 \mu\text{A}$) to clean the Ru(001) surface and a quadrupole mass spectrometer (QMS - VG SX-200) for Δp -TPD spectra were used. The QMS was surrounded by a Pyrex shroud with a 5-mm-diameter aperture to minimize detection of desorbing molecules from surfaces other than the sample. A Kelvin probe (Besocke type S) was employed for work function change measurements ($\Delta\phi$). Both Δp -TPD and $\Delta\phi$ -TPD measurements were performed as a function of crystal temperature using the same AC-resistive heating routine.

The Ru(001) sample was oriented, cut, and polished to within 0.5° of its crystallographic plane (Surface Prep. Services LTD). A standard sample cleaning procedure was described elsewhere.¹⁵ The sample was spot-welded between two 0.5-mm-diameter tantalum wires attached to tantalum rods and copper blocks in contact with a liquid nitrogen reservoir via a sapphire disk. W5%Re-W26%Re thermocouple wires spot-welded to the backside of the ruthenium sample were used for temperature determination and control.

Trimethylamine anhydrous (99% pure, Aldrich) was introduced into the vacuum chamber by back-filling the UHV chamber through a leak valve to the desired pressure following several freeze-pump-thaw cycles. The uncorrected ion gauge signal was transmitted to a computer and converted to Langmuir units ($1 \text{ L} = 10^{-6} \text{ Torr}\cdot\text{s}$). The pressure reading was subsequently corrected by a sensitivity factor for TMA, taken as 1:4.7 relative to N_2 .

3. Results and Discussion

3.1. TMA on Clean Ru. Adsorption of TMA on Ru(001) at 90 K shows a negative change in the contact potential difference (CPD) $\equiv \Delta\phi$ as detected by a Kelvin probe. The results shown in Figure 1 suggest that the decrease of the work function during adsorption originates from adsorption geometry of TMA via its nitrogen atom (as is the case of NH_3).^{18,19} A decrease to a maximum change of 2.2 V is obtained at an exposure of 3.8 L of TMA, which is equivalent to 0.67 ML (where $1 \text{ ML} = 1.5 \times 10^{15} \text{ Ru atoms per cm}^2$). Further exposure to 8.1 L (1.43 ML) leads to a work function increase of 0.1 V relative to the minimum value. A gradual decrease and saturation is noticed above 12.8 L (2.25 ML). TMA molecules undergo an apparent restructure during its multilayer formation, causing the oscillatory behavior

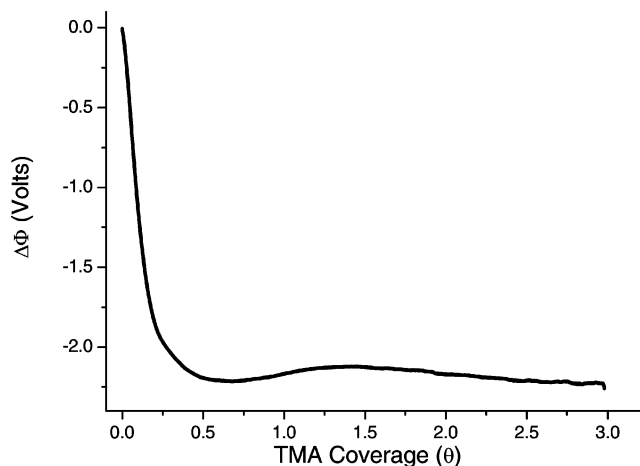


Figure 1. Work function change measured continuously while adsorbing TMA on clean Ru (001) surface at 90 K.

in the $\Delta\phi$ spectrum. A similar behavior was previously reported for the case of CD_3Cl adsorption on Ru(001).²⁰

The decrease in $\Delta\phi$ indicates a significant dipole moment of the adsorbed TMA. A simple calculation based on Helmholtz equation, $\Delta\phi = -4\pi N_0\theta\mu_0$,¹⁶ where N_0 is the density number of Ru(001) surface atoms (per unit area), θ is the TMA relative coverage on the metal surface, and μ_0 is the isolated molecular dipole moment, provides an estimate for $\mu_0 = 1.41 \text{ D}$ ($1 \text{ D} = 3.34 \times 10^{-30} \text{ C}\cdot\text{m}$). The justification to use this simplified model stems from the low coverage, and therefore, insignificant dipole-dipole interaction between the TMA adsorbates. This dipole moment is larger than the calculated gas-phase value for TMA in the literature (0.59 D).²¹ It is obvious that the new electron distribution, due to surface bonding and possibly partial electron donation via the nitrogen end of the molecule to the surface, enlarges the polarity of the adsorbed molecules.

3.1.1. Δp -TPD. On a clean surface, Δp -TPD of TMA from ruthenium follows mainly the desorption of the parent molecule and molecular hydrogen, which is the main product obtained as a result of parent molecule dissociation at low coverage. Hydrogen atoms accumulate on the surface as a result of methyl decomposition. Hydrogen molecules subsequently desorb at 350 K. Monitoring H_2 is central for a quantitative study of the dissociation probability of TMA on the ruthenium substrate. Figure 2 presents a series of TPD spectra taken at different TMA exposures on a clean Ru(001) surface recording the parent molecule desorption at mass 58 and that of H_2 (Figure 2, inset) at mass 2 at a heating rate of 2 K/s.

TMA desorbs intact from the surface at a threshold exposure of 0.3 L. At lower dosage, only molecular dissociation takes place, as indicated by the hydrogen uptake (Figure 2 inset). At larger TMA exposures, four new peaks gradually emerge. These peaks are assigned as α (270 K), β (240 K), λ (115 K), and δ (100 K). The separate, not fully resolved peaks are indicative of repulsive lateral interactions among the neighboring TMA molecules at higher coverage. We refer to each peak as representing the completion of a single layer of TMA on the surface except for α, β that belong to the first layer. The first layer of TMA is produced when exposing 0.5 L of TMA vapor on the clean surface. The coverage of TMA in the complete first layer is estimated to be 0.09 ML ($1 \text{ ML} = 1.5 \times 10^{15} \text{ molecules}$

(17) Hallac, B.; Asscher, M. Manuscript in preparation.

(18) Stolbov, S.; Rahman, T. S. *J. Chem. Phys.* **2005**, *123* (20).

(19) Sun, Y. K.; Wang, Y. Q.; Mullins, C. B.; Weinberg, W. H. *Langmuir* **1991**, *7* (8), 1689–1694.

(20) Lilach, Y.; Asscher, M. *J. Chem. Phys.* **2002**, *117* (14), 6730

(21) Chattaraj, P. K.; Sarkar, U.; Parthasarathi, R.; Subramanian, V. *Int. J. Quantum Chem.* **2005**, *101* (6), 690–702.

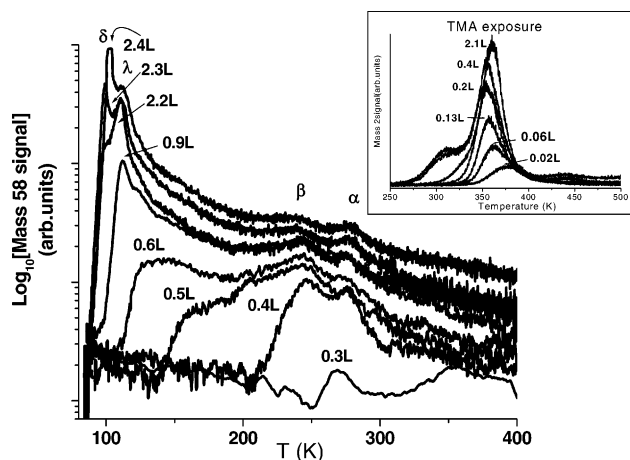


Figure 2. Δp -TPD spectra of the parent molecule (mass 58) and hydrogen (mass 2, inset) at a heating rate of 2 K/s.

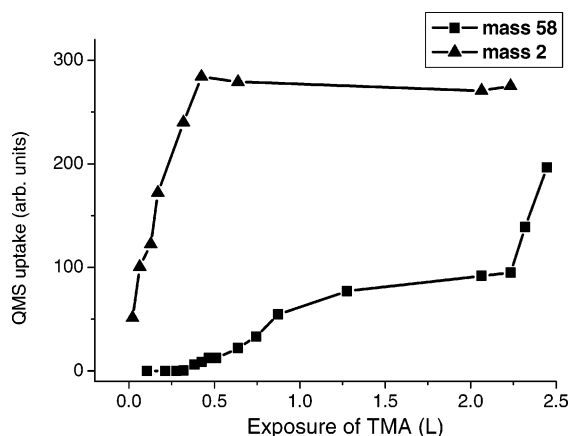


Figure 3. TPD uptake of hydrogen (mass 2, \blacktriangle) and TMA (mass 58, \blacksquare) as a function of TMA exposure (corrected for ion gauge sensitivity to TMA).

per cm^2). We assume the sticking probability for TMA to be unity, regardless of coverage as was suggested for ammonia.²²

At low coverage on a clean Ru surface ($\theta < 0.05$ ML), TMA thermally dissociates to produce hydrogen, nitrogen, and carbon atoms. Therefore, the parent molecule is not detectable in TPD below this coverage, whereas a sharp rise in the hydrogen uptake is apparent. Neither carbon- nor nitrogen-containing molecules could be detected. Above 0.4 L of TMA, the uptake of hydrogen approaches saturation. This reflects the onset of TMA desorption from the surface. Figure 3 summarizes the uptake of H_2 and TMA from the ruthenium surface. At high coverage, TMA desorbs intact, leaving behind the fraction of monolayer of TMA (0.05 ML) that fully dissociates.

3.1.2. $\Delta\phi$ -TPD. A set of $\Delta\phi$ -TPD (Figure 4a) spectra at various initial coverage mark the desorption and dissociation events of TMA upon surface heating. Differentiation of the $\Delta\phi$ -TPD spectra emphasizes the small changes in the slope of the work function change data. Two curves were chosen from Figure 4a to demonstrate the effect of differentiation ($d(\Delta\phi)/dT$) as shown in Figure 4b. The most pronounced peaks at 278 K and 375 K are assigned to the formation of ethylidyne ($\text{CCH}_3(\text{ad})$) and fragments such as (CH_x , CCH), respectively. Ethylidyne is known to be formed following a disproportionation mechanism between two $\text{CH}_2(\text{ad})$ fragments on the surface, as suggested

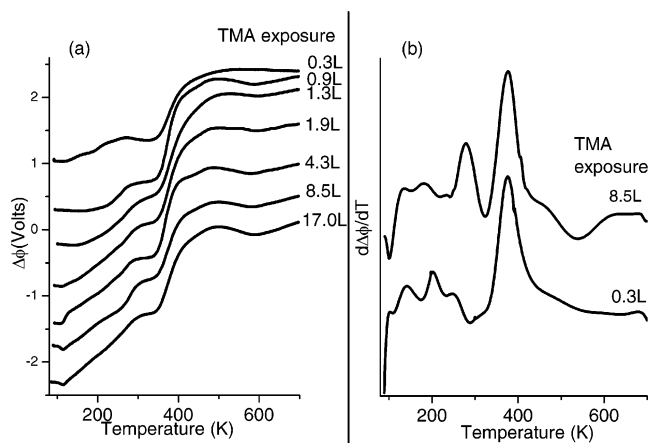


Figure 4. (a) $\Delta\phi$ -TPD following exposure of TMA on the clean Ru(001) surface at the indicated Langmuirs (1 L = 10^{-6} Torr \times s). The spectra were shifted (-2.3 , -1.7 , -1.4 , -0.8 , -0.2 , 0.3 , and 1.0 from high to low exposure, respectively) on the y-axis for clarity. (b) The differentiated curve of the $\Delta\phi$ -TPD spectra from (a).

previously for methyl radicals on ruthenium.¹⁵ At very low parent molecule coverage, ethylidyne formation is limited due to the low probability of two adjacent $\text{CH}_2(\text{ad})$ fragments to react. On the other hand, it is enhanced by the absence of coadsorbed species (e.g., halide or oxygen). In the temperature range 100–200 K, small peaks are resolved and assigned to desorption of TMA from δ and λ layers. These peaks are not intense due to the small effect of the upper TMA molecules (in the multilayer) on the overall work function change.

3.2. Oxygen on Ru (001). Oxygen is often used in order to modify the chemical and physical properties of metal surfaces.^{23–27} The interaction of oxygen with Ru(001) has been extensively studied. Similar to the case of the clean Ru(001), TPD and work function measurements were performed to study the behavior of TMA following various doses of oxygen precoverage on the Ru(001) surface. The work function change increases upon exposure of Ru(001) to oxygen at surface temperature of 600 K (not shown). A kink is observed in the increasing work function graph at 1.6 L, indicating the completion of a (2×2) ordered oxygen layer (0.25 ML) on the surface.^{28–36} This unique feature strongly depends on surface temperature.³⁰

3.3. TMA on O/Ru. **3.3.1. Δp -TPD.** Repulsive dipole–dipole interactions among neighboring parent TMA molecules as coverage increases reduce their reactivity toward dissociation

(23) Barros, R. B.; Garcia, A. R.; Ilharco, L. M. *J. Phys. Chem. B* **2004**, *108* (15), 4831–4839.

(24) Bottcher, A.; Niehus, H. *Phys. Rev. B* **1999**, *60* (20), 14396–14404.

(25) Huang, H. H.; Seet, C. S.; Zou, Z.; Xu, G. Q. *Surf. Sci.* **1996**, *356* (1–3), 181–188.

(26) Queeney, K. T.; Friend, C. M. *J. Phys. Chem. B* **1998**, *102* (46), 9251–9257.

(27) Thiam, M. M.; Kondo, T.; Horimoto, N.; Kato, H. S.; Kawai, M. *J. Phys. Chem. B* **2005**, *109* (33), 16024–16029.

(28) Asscher, M.; Romm, L.; Zeiri, Y. *Colloids Surf., A* **2002**, *208* (1–3), 187–198.

(29) Bottcher, A.; Niehus, H. *J. Chem. Phys.* **1999**, *110* (6), 3186–3195.

(30) Kim, J. H.; Lee, J. H.; Kato, H.; Horimoto, N.; Kawai, M.; Lee, Y. S. *J. Korean Phys. Soc.* **2003**, *42* (3), 408–412.

(31) Lilach, Y.; Asscher, M. *J. Phys. Chem. B* **2004**, *108* (14), 4358–4361.

(32) Madey, T. E.; Engelhardt, H. A.; Menzel, D. *Surf. Sci.* **1975**, *48* (2), 304–328.

(33) Romm, L.; Asscher, M.; Zeiri, Y. *J. Chem. Phys.* **1999**, *110* (6), 3153–3167.

(34) Romm, L.; Asscher, M.; Zeiri, Y. *J. Chem. Phys.* **1999**, *110* (22), 11023–11028.

(35) Romm, L.; Zeiri, Y.; Asscher, M. *J. Chem. Phys.* **1998**, *108* (20), 8605–8614.

(36) Wolter, H.; Meinel, K.; Ammer, C.; Wandelt, K.; Neddermeyer, H. *Phys. Rev. B* **1997**, *56* (23), 15459–15470.

(22) Takaoka, T.; Kusunoki, I. *Surf. Sci.* **1998**, *413*, 30–41.

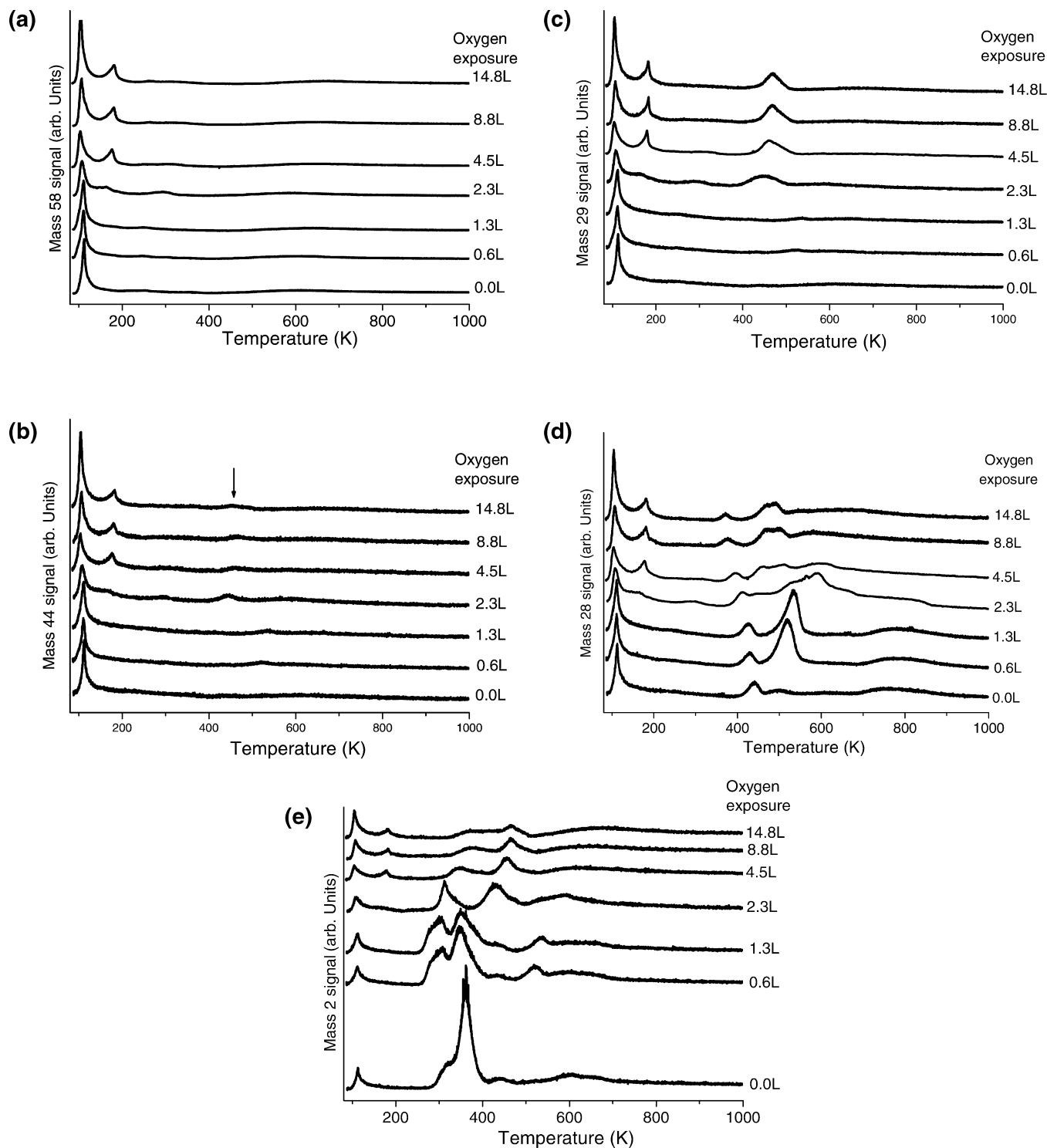


Figure 5. (a–e) $-\Delta p$ -TPD spectra of TMA on O-covered surface. A constant amount of TMA (2.7 ± 0.1) L—equivalent to 0.48 ML—is exposed while varying the oxygen coverage, as indicated.

and accelerate desorption. The influence of oxygen on the behavior of TMA has been studied as a function of oxygen coverage (Figure 5a–e). A fixed exposure of TMA (2.7 L, equivalent to 0.48 ML) was maintained. It is noticed that the hydrogen uptake detected following the TMA decomposition on the O-covered surface significantly decreased compared to the case of clean ruthenium surface. The shapes of the TPD spectra are different in each case as well. This is related to the species from which hydrogen evolves at different O-covered surfaces and temperatures. Hydrogen is produced primarily from the dissociation of ethylidyne (CCH_3). The formation of CCH_3 , however, is less

favorable in the presence of oxygen, hence decreasing the amount of hydrogen uptake (see Figure 5e). At high O coverage, CCH_3 dissociation shifts to a higher temperature, which results in a respective shift of the hydrogen desorption. Concurrent with diminishing hydrogen yield, the parent molecule uptake increases.

In Figure 6, Δp -TPD spectra recorded the formation of products at masses 26, 27, 28, 29, and 30, that are specific to the O/Ru surface between 400 and 500 K. These masses are assigned to CN, HCN, CO, HCO, and H_2CO , respectively. CN is obtained as a fragment at the mass spectrometer ionizer. NO could have been a possible choice as a reaction product at mass

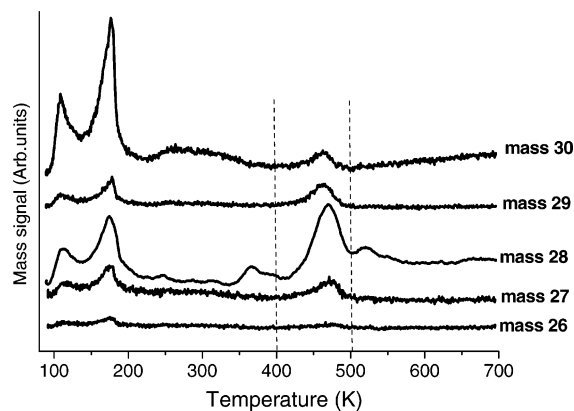


Figure 6. Δp -TPD following TMA exposure (1.9 L) on O-covered surface (0.7 ML of oxygen) tracking different masses.

30. However, analysis of fragmentation pattern within the quadrupole mass spectrometer (QMS) suggests that the peak at 470 K appears at both masses 30 and 29. This observation favors formaldehyde (H_2CO) accompanied by its HCO fragment at mass 29 as the source for mass 30 rather than NO that does not have any fragment at mass 29.

Oxygen, as a buffer layer, strengthens the bonding of TMA to the substrate. The λ peak appeared at 107 K on clean Ru, while on O/Ru, the same population of molecules (or a new site) has shifted up to 175 K. The binding energy of TMA, in the second layer, on the clean ruthenium is 6.4 kcal/mol (deduced from peak shape analysis, with a pre-exponential factor of 10^{13} s^{-1}), while on the O/Ru surface, the molecular binding energy significantly increased to 10.8 kcal/mol. Similarly, the activation energy for desorption of the δ layer is 5.1 kcal/mol and 6.1 kcal/mol on Ru(001) and on O/Ru(001), respectively. As expected, the upper (δ) layer is less affected by the presence of oxygen than the layer underneath (λ layer). The different nature of bonding of the molecules on the O-precovered surface shows also in the TPD peak shapes, namely, the λ and δ peaks are typically narrower on the clean surface than on the O/Ru surface. CO_2 is produced at small yield via a surface reaction between hydrocarbon fragments and the coadsorbed O atoms at high oxygen coverage, desorbing at 444 K (Figure 5b). At low O coverage, an incomplete oxidation reaction (460–570 K) dominates to form CO as shown in Figure 5d.

The carbon oxidation reaction kinetics has two pathways that depend on the amount of oxygen pre-adsorbed on the surface. One channel involves CO_2 formation at 400–500 K, as mentioned above. In Figure 5c, a peak at mass 2 emerges near 480 K at oxygen exposure of 2.3 L—equivalent to a coverage of 0.56 ML. This peak has been assigned to HCO produced in the QMS ionizer from formaldehyde that has desorbed from the surface. Other possible hydrocarbons at mass 29 such as CH_2CH_3 that may result from hydrogen loss (in the mass spectrometer ionizer) from C_2H_6 , which usually desorbs at low surface temperature, therefore are less favored. In Figure 5d, we reveal the formation of N_2 (mass 28) at 800 K from a clean Ru(001) surface and at low oxygen coverage. The broad peak between 600 and 800 K is identical to what was reported earlier in the literature for N_2 recombinative desorption from Ru(001).^{28,33–35,37,38} Apparently, at high oxygen coverage, the TMA dissociation is less probable;

hence, N_2 production is also deactivated. This additional evidence, along with hydrogen formation, supports the apparent stabilization of TMA due to oxygen preadsorption on Ru(001). At oxygen exposure above 2.3 L, nitrogen is not detectable anymore. A small peak at 430 K on the clean surface, as well as on the oxygen precovered surfaces, originates from background CO contribution. The growing peak between 520 and 530 K is attributed to CO formed preferentially at low oxygen coverage (0.6–2.3 L) as a result of surface oxidation of the coadsorbed carbon atoms. At low oxygen coverage, incomplete oxidation results in CO formation. As the amount of oxygen increased, full oxidation is gradually favored to produce carbon dioxide while the CO uptake diminishes.

A set of Δp -TPD spectra has been performed following the mass signals at 58, 44, 29, 28, and 2 as a function of TMA coverage. The oxygen coverage was kept constant at 0.7 ML. A complete monolayer is reached at TMA coverage of 0.05 ML, compared with 0.09 ML on clean ruthenium, suggesting a 40% lower TMA density on O-modified ruthenium surface. The second layer (λ) is detected at 174 K, and the multilayer (δ) appears at 100 K (see Figure 7a).

The production of CO and CO_2 is independent of the coverage of TMA as shown in Figure 7b,d. The formation of a product at mass 29 reflects formaldehyde (H_2CO) formation that increases linearly as a function of TMA coverage. This is indicated by the growing peak at 464 K (Figure 7c). Hydrogen is produced at low coverage of TMA and has reached saturation already at 0.04 ML (see Figure 7e).

The reaction between TMA and O_{ad} is manifested by following the depletion of oxygen as monitored by Δp -TPD between 1000 and 1650 K (Figure 8). Oxygen is consumed completely as a result of its reaction with TMA.

3.3.2. $\Delta\phi$ -TPD. Work function change measurements during sample heating, the $\Delta\phi$ -TPD mode, reveal the effect of oxygen at fixed TMA exposure of 2.7 L, as demonstrated in Figure 9a. A small hump observed at 142 K has been attributed to two channels: (1) desorption of the parent molecules from multilayer TMA coverage; (2) thermally activated restructuring of TMA into crystalline-like geometry.³⁹ If indeed a fraction of the adsorbed molecules flip over to the “methyl down” configuration, it may explain the observed work function increase. This is in contrast to the behavior of methyl bromide on Ru(001)¹⁵ where a rise in $\Delta\phi$ -TPD was reported at $T < 120$ K. In the case of methyl bromide, the change in work function has been attributed to the production and direct desorption of methane (no TPD signal at mass 16) from the surface. In our TMA/Ru and TMA/O/Ru systems, we have not detected any methane production prior to the parent molecular desorption at low temperatures of < 120 K. The next descending slope in the $\Delta\phi$ -TPD spectra up to 220 K is assigned to partial dissociation of the parent molecules at the first monolayer and production of CH_3 that further dissociates to CH_2 . This negative slope is not detected on the oxygen free surface (see Figure 4a). The shift of the minimum to higher temperature is consistent with and correlated to the gradual increase in oxygen coverage, which was shown to result in stronger binding of parent molecules, reflected by higher desorption temperature. The sharp rise between 220 and 400 K (Figure 9a) is attributed to desorption of the remaining TMA molecules that have not reacted with oxygen. A better view of

(37) Diekhoner, L.; Mortensen, H.; Baurichter, A.; Luntz, A. C. *J. Vac. Sci. Technol. A* **2000**, *18* (4), 1509–1513.

(38) Lilach, Y.; Romm, L.; Livneh, T.; Asscher, M. *J. Phys. Chem. B* **2001**, *105* (14), 2736–2742.

(39) Kawaguchi, T.; Hijikiga, M.; Hayafuji, Y.; Ikeda, M.; Fukushima, R.; Tomiie, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46* (1), 53–56.

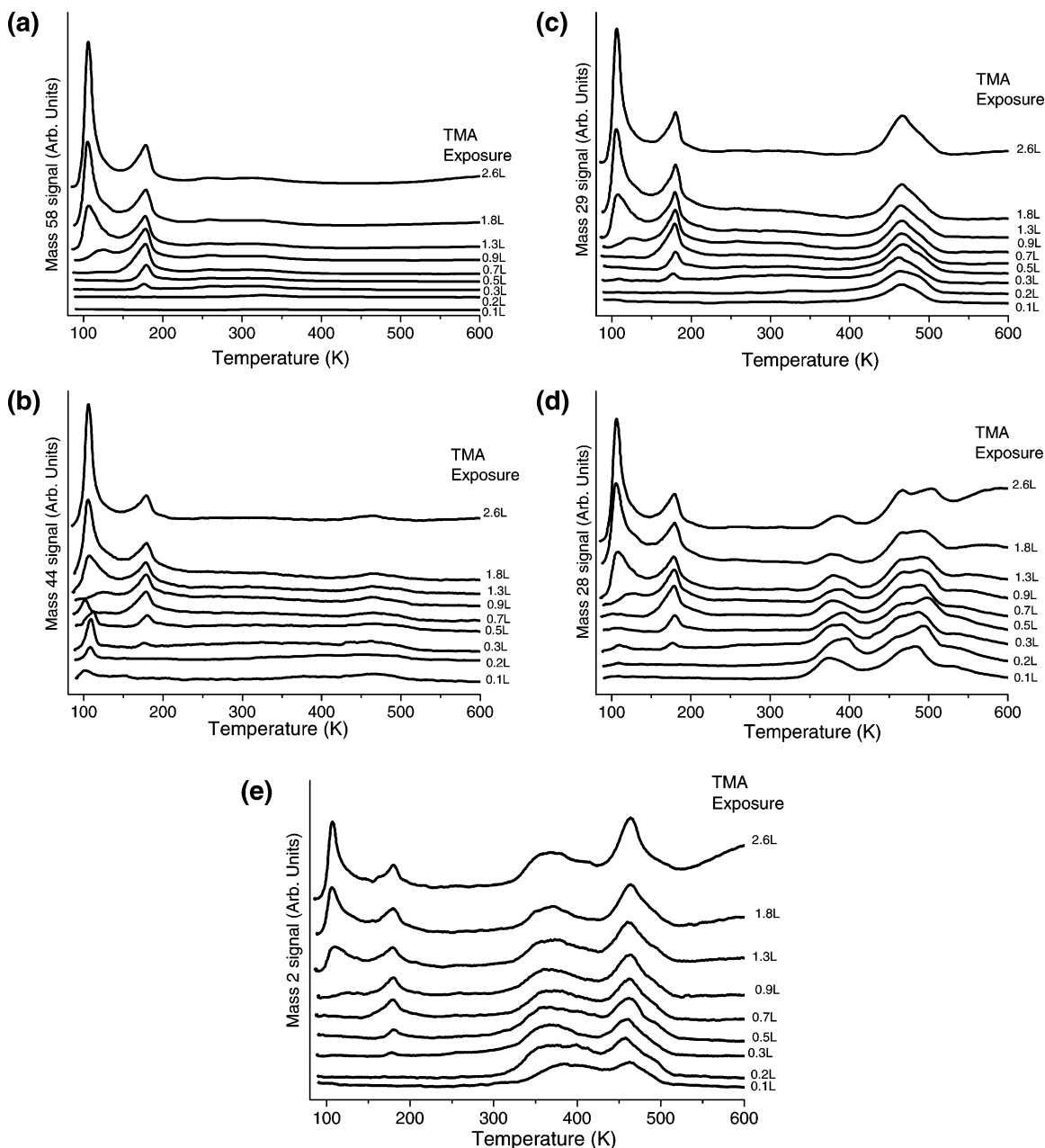


Figure 7. (a–e) $-\Delta p$ -TPD spectra of TMA on O-covered surface demonstrating fixed oxygen coverage of 0.7 ML at the indicated increasing postexposures of TMA.

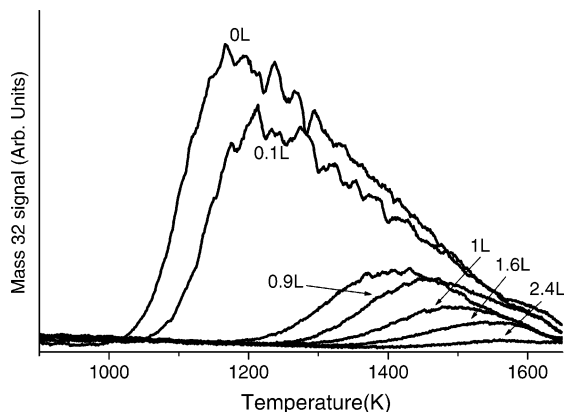


Figure 8. Δp -TPD monitoring oxygen consumption after reacting with TMA. The set is a function of increasing TMA exposure (as indicated on the graph) in a TMA/O/Ru structure.

the chemistry that occurs during sample heating can be obtained from the differentiated graphs presented in Figure 9b. At high TMA density (0.48 ML), a peak appears at 278 K. Disproportionation of two $\text{CH}_2(\text{ad})$ fragments to ethylidyne ($\text{CCH}_3(\text{ad})$) and adsorbed hydrogen have been proposed⁴⁰ to take place at this temperature (see Figure 4b). The reactivity of ethylidyne on oxygen-modified surfaces has been discussed in detail elsewhere.⁵ Reactions of ethyl groups investigated on O-modified Ru(001) reveal a decrease in the formation of CCH_3 in the presence of oxygen. The dissociation of CCH_3 on the O-presaturated sample produces carbidic deposits (C , CH_x), which react with oxygen to produce CO and formaldehyde. The presence of oxygen and other coadsorbed species (halides)⁵ hinders the dissociation of CCH_3 , causing a shift of the decomposition peak to higher values.

(40) Zhou, Y.; Henderson, M. A.; Feng, W. M.; White, J. M. *Surf. Sci.* **1989**, *224* (1–3), 386–406.

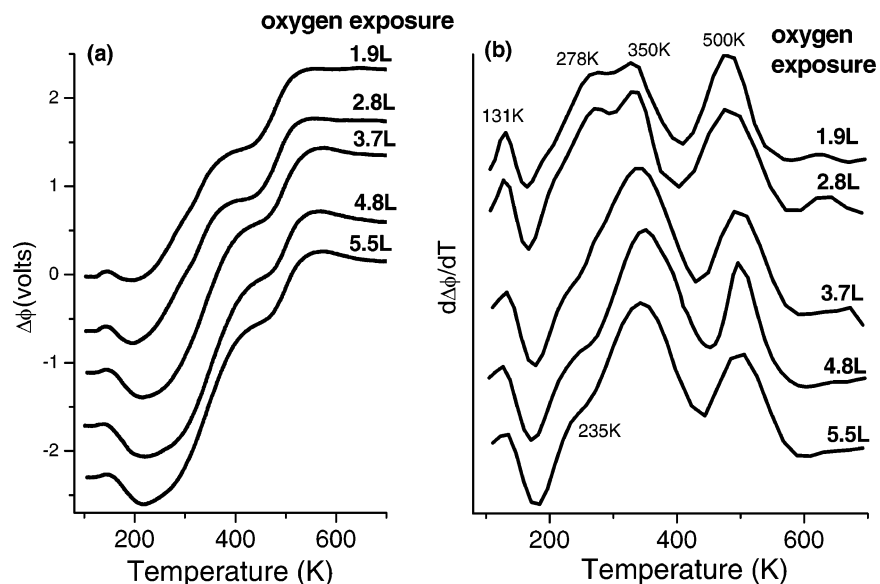


Figure 9. (a) $\Delta\phi$ -TPD spectra of TMA on O/Ru at different oxygen exposures as indicated on the graph. (b) The differentiated curves ($d(\Delta\phi)/dT$) of (a).

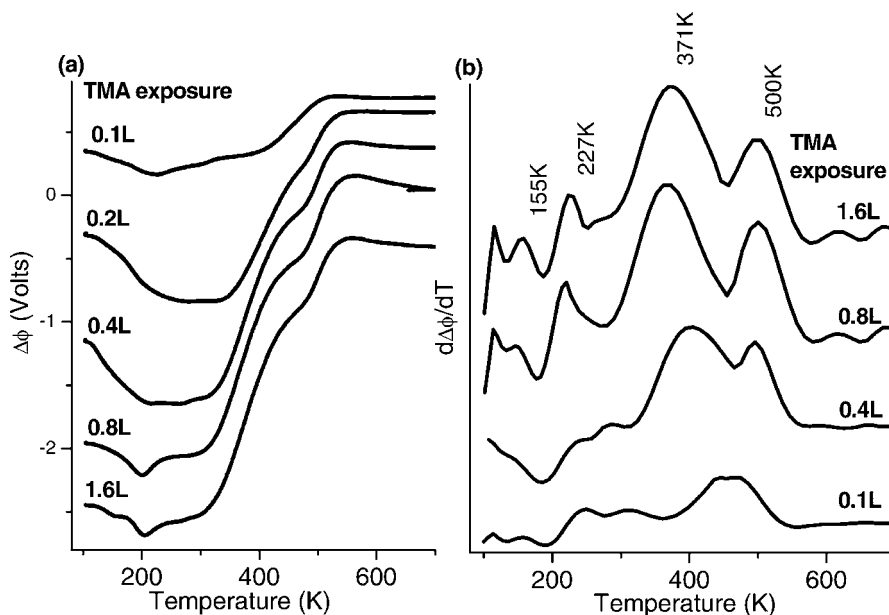
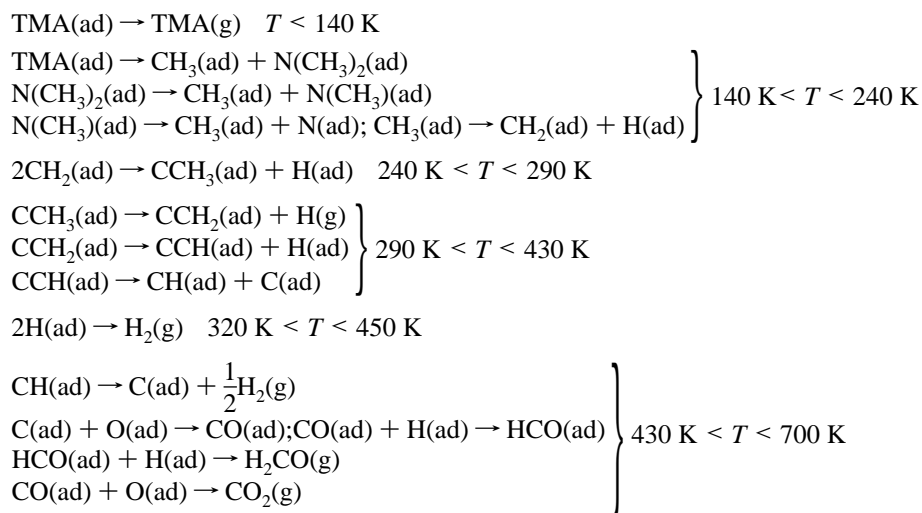


Figure 10. (a) $\Delta\phi$ -TPD of TMA on O/Ru at different TMA exposures as indicated on the graph. The surface pre-exposed to 5.7 L of oxygen (0.7 ML). (b) shows the differentiated curves of (a).

To conclude the above discussion, the following reaction pathways are proposed:



Coverage-dependent $\Delta\phi$ -TPD spectra of TMA on 0.7 ML O/Ru are depicted in Figure 10. The 371 K peak is attributed to the H_2 evolution as a result of rate-limited dissociation of the CH_x fragments (see mechanism described above). The diminishing hydrogen production as the coverage of oxygen increases suggests that a significant fraction of adsorbed hydrogen reacts to form HCO(ad). The $d(\Delta\phi)/dT$ peak at 227 K (Figure 10b) reflects ethylidyne formation, while the peak at 500 K arises predominantly from the reaction $HCO(ad) + H(ad) \rightarrow H_2CO(g)$, where oxygen is removed from the surface. This is supported by TPD shown in Figure 5e.

Conclusions

Trimethylamine molecules adsorb intact via its N end on Ru(001) surface at $T_s < 100$ K, a conclusion derived from work function change measurements. Heating the surface leads to desorption of the multilayer (100 K) and to dissociation when the coverage is less than 0.05 ML. Hydrogen, produced from the molecular multistep dissociation, thermally evolves from the surface at 360 K. The chemistry of TMA fragments on Ru(001) is different than that of methyl iodide on the same substrate. In contrast to previous studies of the CH_3 -Ru system,⁴⁰ methane is not formed in the case of TMA-Ru. This is attributed primarily

to the high methyl radical density and absence of the halide fragment that could interfere with the surface chemical processes. Other competitive reactions (e.g., further CH_x dissociation pathways) are preferred over the production of methane from CH_3 and the H atom. Neighboring methylene (CH_2) adsorbates react to produce ethylidyne (CCH_3) near 280 K. This mechanism, suggested for methyl halide dissociation,⁴⁰ is in agreement with our assignments of the $\Delta\phi$ -TPD results of TMA on Ru(001).

In the case of oxygen pre-coverage, rich chemistry of the methylene fragments with the surface oxygen atoms has been identified, forming formaldehyde and CO as main products. At high oxygen coverage, the C-N bond does not dissociate, in contrast to the behavior on the clean ruthenium, and hydrogen evolution diminishes as well. Overall increased stability of the parent TMA molecule results from oxygen pre-coverage.

Acknowledgment. This research was partially supported by a grant from the US-Israel Binational Science Foundation and by the Israel Science Foundation. The Farkas center is supported by the Bundesministerium für Forschung und Technologie and the Minerva Gesellschaft für die Forschung mbh.

LA700895R