Dependence on co-adsorbed water in the reforming reaction of ethanol on a Rh(111) surface†

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We have studied the reforming reaction of ethanol co-adsorbed with atomic oxygen (O*; * denotes adspecies) and deuterated water (D2O*) on a Rh(111) surface, with varied surface probe techniques under UHV conditions and with density-functional-theory calculations. Adsorbed ethanol molecules were found to penetrate readily through pre-adsorbed water, even up to eight overlayers, to react at the Rh surface; they decomposed at a probability promoted by the water overlayers. The production probabilities of H2, CO, CH2CH2 and CH4 continued to increase with co-adsorbed D2O*, up to two D2O overlayers, despite separate increasing rates; above two D2O overlayers, those of H2, CO and CH2CH2 were approximately saturated while that of CH4 decreased. The increased (or saturated) production probabilities are rationalized with an increased (saturated) concentration of surface hydroxyl (OH*), formed by O* abstracting D from D2O*, whose intermolecular hydrogen bonding with adsorbed ethanol facilitates proton transfer from ethanol to OD* and thus enhances the reaction probability. The decreasing behavior of CH4 could also involve the competition for H* with the formation of H2 and HDO.

1. Introduction

As an efficient approach to produce hydrogen for use in fuel-cells, the reforming reaction of ethanol has drawn considerable attention.1 Ethanol has advantages of low toxicity, high availability, high hydrogen density and ease of handling and storage; it can be readily extracted from fermentation of biomass like sugarcane and corn.2–4 Among various reforming reactions, oxidative steam reforming of ethanol (OSR, C2H5OH + (3 – x)H2O + xo2 → (6 – 2x)H2 + 2CO2) is promising, because its hydrogen yield and exothermicity can be balanced by controlling molar ratios of reagents (ethanol, steam and oxygen).5,6 The mechanism of OSR of ethanol has thus been widely investigated. Earlier mechanistic studies find that the reaction is initiated with scission of O–H bond of adsorbed ethanol, forming surface ethoxy (CH3CHO*, * denoting adspecies);6–9 either C–Hx or C–H8 bond is sequentially cleaved, producing surface acetaldehyde (CH2CHO*) and oxamettallacycle (CH3CH2O*), respectively. The surface acetaldehyde ultimately leads to the production of CH3CHO, CH4, CH3COOH, CO and CO2, while the surface oxamettallacycle to CH2CH2 and CO.6,7,10

The reagent oxygen (molecular) is dissociated into atomic oxygen (O*) on catalyst surfaces; the O* promotes the decomposition probability of ethanol and could also alter the reaction path toward acetaldehyde, as indicated on Rh(100) and Rh(111) surfaces.11–13 This alteration highly promotes the production of H2, along with side products CO, CH4 and H2O. With increased oxygen content, the reaction path shifts further to acetate (CH2COO*) intermediates; the production of H2 is suppressed but that of CO2 is highly promoted.13 The reagent water (steam) in OSR is typically regarded as another supplier of reagent oxygen or an assistance to the side process—water–gas-shift reaction—of the reforming reaction. Preceding studies on a Rh(111) surface showed comparable effects of hydroxyl (OH*; from dissociated H2O*) and O*; the OH* further enhanced the reaction probability of ethanol on the Rh surfaces pre-covered with O* but affected little the reaction path.13 Nevertheless, this effect evolves with the quantities of adsorbed water is not clarified. This issue becomes critical as the advantages of OSR depend largely on the molar ratios of its reagents. The present study aims to remedy this lack of knowledge and to shed light on detailed mechanisms.

We have studied the reactions of ethanol co-adsorbed with O* and deuterated water (D2O*) on a Rh(111) single crystal under ultrahigh vacuum (UHV) conditions. The Rh(111) substrate, as a model system, was chosen because Rh-based catalysts become the most promising catalyst in the reforming reaction6,7,10 and (111) facets typically make up a great fraction of the surface of the...
Rh catalysts. Temperature-programmed desorption (TPD) and synchrotron-based photoelectron spectroscopy (PES) were applied to probe the catalyzed reactions, and density-functional-theory (DFT) modelling to illuminate the picture how ethanol interacts with co-adsorbed water. The results show that the reactions of ethanol adsorbed on the Rh surface pre-covered with O\(^*\) and molecular water proceeded despite adsorbed water increased up to eight overlayers. The reactions persisted as the pre-adsorbed water did not obstruct completely the adsorption of ethanol; besides, the adsorbed ethanol diffused, through exchanging positions with the pre-adsorbed water, toward the Rh surface to react. Furthermore, the decomposition probability was evidently enhanced. The production probabilities of all species, including \( \text{H}_2, \text{CO}, \text{CH}_2\text{CH}_2 \) and \( \text{CH}_4 \), were increased with co-adsorbed water, up to two water overlayers; above two water overlayers, those of \( \text{H}_2, \text{CO} \) and \( \text{CH}_2\text{CH}_2 \) exhibited a trend of saturation while that of \( \text{CH}_4 \) decreased. The behavior is strongly correlated with the concentration of surface OD\(^*\). We discussed in detail the mechanisms with our DFT simulations.

2. Methods

2.1 Experimental section

Our experiments were conducted in UHV chambers at a base pressure \( 4 \times 10^{-10} \) torr. The Rh\((111)\) single crystal, polished to a roughness \( < 10 \) nm and an orientation accuracy \( < 0.1^\circ \), was purchased from MaTeck GmbH. Before each experiment, alternative cycles of sputtering and subsequent annealing (900 K) were conducted to clean the crystal surface. We confirmed the cleanliness of the crystal surface with surface probe techniques such as low-energy electron diffraction and Auger electron spectroscopy. The crystal was then quenched to desired temperatures for adsorption: molecular oxygen (O\(_2\)) at 300 K, deuterated water (D\(_2\)O) and ethanol at 120 K. The adsorption was performed with a doser pointing toward the crystal, at a background pressure \( 5 \times 10^{-8} \) to \( 5 \times 10^{-9} \) torr. Adsorbed O\(_2\) on Rh\((111)\) at 300 K was dissociated into atomic oxygen (O\(^*\)). The deuterated water (purchased from Merck, 99.8%) was further purified by several freeze–pump–thaw cycles before the adsorption experiments. Their exposures were reported in Langmuir units (1.0 L = \( 10^{-6} \) torr s). We collected TPD spectra with a quadruple mass spectrometer (Hiden) to monitor various masses and by ramping the sample at a rate of 3 K s\(^{-1}\); we shielded and placed the spectrometer near the crystal surface (about 2 mm). The PES experiments were conducted at the BL09A2 beamline (U5 spectroscopy) at National Synchrotron Radiation Research Center in Taiwan. The photon beam had a fixed energy 600 eV and was incident normal to the surface; emitted photoelectrons were detected at an angle 58° off from the surface normal. The energy resolution attained 0.1 eV. All PES spectra shown in the current work were normalized to their photon flux. The binding energy (BE) indicated in the spectra is referred to the bulk Rh 3d\(_{5/2}\) at 307.1 eV.

2.2 Computational section

Our computations were performed with Vienna \textit{Ab initio} Simulation Package (VASP),\(^{25-27}\) a DFT-based computational package with a 3D periodic boundary condition. The computational level was at GGA-PAW, the generalized gradient approximation\(^{29}\) with Perdew–Wang 1991 formulation\(^{29}\) utilized for the exchange-correlation function. The valence electrons were treated by plane waves with a maximal kinetic energy (cutoff energy) of 600 eV; the core electrons were treated by the cost-effective pseudopotentials implemented in VASP, the projector-augmented wave method (PAW). The integration in the Brillouin-Zone (BZ) was sampled by the Monkhorst–Pack scheme\(^{29}\) with the \( k \)-point at 0.05 \( \times 2 \) (1/\( \AA \)) interval in the reciprocal space. For the structural optimizations and energetic calculations of stable adsorptions, we applied quasi-Newton method with an energetic convergence of \( 1 \times 10^{-4} \) eV and a gradient convergence of \( 1 \times 10^{-2} \) eV \( \AA^{-1} \); those of transition states were utilized by Nudged Elastic Band method\(^{31}\) at the same convergence criterions. The chosen convergence condition has been widely applied in previous studies;\(^{32,33,34}\) a convergence test, with a more strict convergence condition (\( 1 \times 10^{-6} \) eV and \( 1 \times 10^{-3} \) eV \( \AA^{-1} \)), had also been performed to justify the present calculations.\(^{34}\) The vibrational analysis, with the finite displacement approach at the \( \Gamma \) point,\(^{35,36}\) was utilized to confirm the optimized local minimums (without imaginary frequency) and apply zero-point energy (ZPE) corrections on the DFT computed energies.

The Rh\((111)\) surface was constructed with a Rh slab consisting of five layers of \( 4 \times 4 \) surface units and equivalent five-layer distant vacuum space to avoid artificial interaction between separate Rh slabs; the bottom two Rh layers were fixed at the computed lattice constants to represent the semi-infinite bulk crystal beneath the surface and the top three layers were free to relax. The adspecies, such as water, ethanol and their fragments, were then placed on the Rh surface for optimization of their adsorption structures and related energies.

3. Results and discussion

3.1 TPD and PES experiments

The reactions of ethanol were monitored primarily with TPD. We compared the TPD spectra from ethanol on Rh\((111)\) pre-covered with O\(^*\) at 0.08 ML and water at varied coverages to investigate quantitatively the effect of water on the reactions. Adsorbed water molecules alter the OSR reaction of ethanol because they are dissociated into OH\(^*\). The dissociation on Rh\((111)\) is largely assisted by pre-adsorbed O\(^*\).\(^{37}\) Our previous work showed, in line with other studies,\(^{37}\) that water adsorbed on Rh\((111)\) pre-adsorbed with 0.08 monolayer (ML) O\(^*\) (denoted as Rh\((111)\)O\(^*_0\)(0.08 ML)) yielded a maximal production of OH\(^*\),\(^{31}\) so we examined the present effect on Rh\((111)\)O\(^*_0\)(0.08 ML). We used deuterated water (D\(_2\)O), instead of typical water (H\(_2\)O), for our TPD measurements. These isotopic variants behavior similarly, since their adsorption energies, activation energies for dissociation and their interaction with ethanol are determined by their electronic structures, rather than their isotopic properties. Adsorbed D\(_2\)O, unlike H\(_2\)O, contributed no TPD signals of \( \text{H}_2 \) and H\(_2\)O, two major products from decomposed ethanol on Rh\((111)\)O\(^*_0\)(0.08 ML), but gave clear, separate D\(_2\) (or DH) and D\(_2\)O (or DHO) signals. The use of D\(_2\)O avoids mixing signals from...
different processes and thus permits ready identification of the role of water in the ethanol reaction.

We noted in the series of TPD experiments that adsorbed ethanol penetrated readily through pre-adsorbed water overlayers to react at the Rh(111)O(0.08 ML) surface. Fig. 1a shows the D$_2$O ($m/z = 20$ u) TPD spectra from Rh(111)O(0.08 ML) exposed to D$_2$O of varied amounts (denoted as Rh(111)D$_2$O(0.08 ML)), 0.3 L D$_2$O adsorbed on Rh(111)O(0.08 ML) at 120 K gave a single desorption feature around 195 K (the bottom in Fig. 1a), assigned to desorbing sub-monolayer D$_2$O from the surface. The desorption temperature of the sub-monolayer or monolayer D$_2$O on Rh(111)O(0.08 ML) is higher than that on Rh(111)O(0.08 ML), because of the formation of a hydrogen-bonded network of D$_2$O* and OD* and also the interaction of D$_2$O* with O*. The desorbing D$_2$O came from two channels: D$_2$O* in the D$_2$O*-OD* hydrogen bonded network and that from disproportionation of OD* (2OD* → D$_2$O* + O*). As the exposure of D$_2$O increased, the monolayer feature was enhanced; above 1.0 L, the monolayer feature remained similar whereas an additional feature grew about 150 K (top and second in Fig. 1a), which is assigned to the desorption of multilayer D$_2$O. As the integrated intensity of the D$_2$O desorption feature increased almost linearly with the exposure and as the desorption feature of 1.0 L D$_2$O corresponds about to a full monolayer D$_2$O, the sticking coefficient of D$_2$O onto the sample at 120 K is nearly 1; 1.0 L D$_2$O yielded about a single water overlayer on either Rh(111)O(0.08 ML) or Rh(111)D$_2$O(0.08 ML). The D$_2$O TPD spectra altered significantly when ethanol was adsorbed atop Rh(111)D$_2$O(0.08 ML). For Rh(111)D$_2$O(0.3 ML)O(0.08 ML) and Rh(111)D$_2$O(0.5 ML)O(0.08 ML) exposed to ethanol (the third and bottom in Fig. 1b), the monolayer feature of D$_2$O about 195 K, attenuated, in comparison to those without ethanol (the third and bottom in Fig. 1a), while the multilayer one, about 150 K, emerged. At higher D$_2$O coverages (the first and second in Fig. 1b), the multilayer feature became obviously enhanced whereas the monolayer one remained smaller than its counterparts without ethanol (the first and second in Fig. 1a). Nevertheless, the integrated intensities of the D$_2$O lines with and without co-adsorbed ethanol were similar, as plotted in Fig. 1c. The comparison implies that the diminished monolayer D$_2$O was compensated by the increased multilayer D$_2$O – a fraction of the first overlayer D$_2$O on Rh(111) migrated to the multilayer region and desorbed. The migration was induced because the adsorbed ethanol diffused toward the Rh surface and exchanged position with the underneath D$_2$O. The involvement of D$_2$O in the ethanol reaction is reflected on systematically increased DHO desorption signals, which result from surface OD* (from D$_2$O* + O* → 2OD*, discussed below) abstracting H from ethanol and desorbing as DHO. On such ethanol on Rh(111)D$_2$O(0.08 ML), O* were entirely consumed and no trace of it was observed with increased temperature, contrasting ethanol and D$_2$O separately adsorbed on Rh(111)O(0.08 ML). Details are explained in ESI (Fig. S2†) and DFT calculations below.

The TPD spectra for the reaction products of ethanol reveal more the effect of D$_2$O. Fig. 2a–c show the TPD spectra from 3.0 L ethanol adsorbed on Rh(111)O(0.08 ML), Rh(111)D$_2$O(1.0 L)O(0.08 ML) and Rh(111)D$_2$O(2.0 L)O(0.08 ML). The ethanol (C$_2$H$_5$OH, $m/z = 45$ u) spectra (top lines in Fig. 2a–c) show desorption at 150 and 200 K, corresponding to multilayer and monolayer ethanol respectively. The CO ($m/z = 28$ u), ethylene (C$_2$H$_4$, $m/z = 27$ u), H$_2$O ($m/z = 18$ u), methane (CH$_4$, $m/z = 16$ u) and H$_2$ ($m/z = 2$ u) spectra also show their desorption at various temperatures, the second to the bottom lines in Fig. 2a–c, reflecting the reforming reaction of adsorbed ethanol. Preceding studies argued that adsorbed ethanol on Rh(111) produced ethoxy readily via O–H bond scission and the ethoxy decomposed predominantly via C–H$_2$ bond cleavage, which led to formation of oxometallacycle intermediate (CH$_2$CH$_2$O*) and further decomposition producing CO, H$_2$ and surface carbon ultimately. The decomposition probability was enhanced and the reaction pathway was largely altered to the one via C–H$_2$ bond cleavage, which formed acetaldelyde (CH$_2$CHO*) intermediates and promoted the production of H$_2$ along with the side products of CH$_4$ and H$_2$O. The evident CH$_4$ and H$_2$O signals in Fig. 2a confirm the altered reaction pathway; the CH$_3$CH$_2$ signals imply the existence of CH$_3$CH$_2$O*, whose C–O bond cleavage yields CH$_2$CH$_2$* and hence that the channel via CH$_3$CH$_2$O* remained active. The observed desorbing species from Rh(111)D$_2$O(0.08 ML) (Fig. 2b and c) were the same as those from Rh(111)O(0.08 ML) (Fig. 2a) whereas their intensities differed. Both desorbing multilayer (150

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**Fig. 1** D$_2$O TPD spectra from Rh(111)O(0.08 ML) exposed to (a) D$_2$O of varied amounts, as indicated, and to (b) D$_2$O of varied amounts and subsequently 3.0 L ethanol. (c) Plots the integrated intensities of the D$_2$O desorption features in (a) and (b) as a function of D$_2$O exposure; black squares and red spheres denote the data from the sample without and with ethanol, respectively.
adsorbed background H2O and the cracking pattern of desorbing spectra (Fig. 1b), as the signals were contributed primarily from ethanol interacting with D2O (Fig. 2b and c); the sticking coefficient for ethanol onto D2O overlayers was smaller than that for ethanol onto Rh(111)O (Fig. 3). The H2O (m/z = 18 u) spectra became highly enhanced (Fig. 2b and c) and resembled the corresponding D2O spectra (Fig. 3). They were estimated according to desorbing and remaining carbon-related species.

The ethanol(int) decreased when D2O overlayers increased; it decreased at 8.0 L D2O (corresponding to 0.08 ML D2O) to 50% of that on Rh(111)O (top of Fig. 2d). The decrease occurred largely because of a smaller sticking coefficient for ethanol onto D2O overlayers than that onto Rh(111)O. We note that the ethanol(int) decreased remarkably between 0.0–2.0 D2O overlayers but only a little between 2.0–8.0 D2O overlayers; increasing D2O above 2.0 overlayers blocked in effect the diffusion of adsorbed ethanol toward the Rh(111) surface. Additionally, total adsorbed ethanol (including both multilayer ethanol and ethanol(int)) decreased with D2O overlayers in a similar manner (Fig. S3†); the ethanol(int) made up a great proportion, about 70 ± 5%, of total adsorbed ethanol and the proportion varied insignificantly with increasing D2O overlayers. The result agrees with the above D2O TPD spectra (Fig. 1). The produced species responded with increased D2O in separate manners. The produced CH4, like ethanol(int), decreased monotonically with increased D2O; the H2 increased at D2O overlayers ≤2.0 L but decreased at higher ones; the CO varied little; the CH2CH2 increased with D2O whereas became saturated above 1.0 L. As ethanol(int) decreased with the D2O overlayers, the comparison implies that the probability of the ethanol(int) undergoing decomposition to produce CO and CH2CH2 was enhanced under the D2O overlayers.

Fig. 3 plots the ratios of the quantities of the produced species to ethanol(int) as a function of D2O exposure, to illuminate the altered probability; the red lines are drawn to guide the eyes. The ratios for all products have a similar trend below 2.0 L D2O exposure—they all increased with D2O exposure despite of varied increasing rates. Above 2.0 L D2O exposure, two separate trends are exhibited. For the first kind, the ratio was either saturated, such as H2 and CH2CH2 (first and bottom), or increased slowly, such as CO (second); the other kind, for CH4, showed a decreasing trend (third). Among these four products, CH2CH2 was exclusively contributed from the reaction route via CH2CH2O* intermediates and CH4 via CH4CHO* intermediates; the other two products, H2 and CO, were produced from both the reaction routes. The dissimilar production probabilities of these four products above 2.0 L D2O exposure are not simply concluded according to the separate reaction routes. Nevertheless, the similar increasing
trend below 2.0 L D2O exposure can be understood through the formation and increased concentration of surface hydroxyl (OD*).

Previous studies indicate that hydroxyl (OH* or OD*) can further enhance the reaction probability of ethanol on Rh surfaces pre-covered with O*, through the intermolecular hydrogen bonding between surface OH* (OD*) with ethanol or its fragments. The dependence on D2O coverages of the above production probabilities is strongly correlated with the quantities of OD*. To examine the correlation, we have monitored the production of OH* on Rh(111)H2O*/O* (0.08 ML) with PES spectra. No substantial difference is anticipated in the formation of OH* on Rh(111)H2O*/O* (0.08 ML) and OD* on Rh(111)D2O*/O* (0.08 ML). Fig. 4a exemplifies the O 1s PES spectra for the produced OH* as a function of H2O exposure. The bottom panel shows the O 1s line, centered about 529.6 eV, for 0.08 ML O*; upon adsorption of 0.3 L H2O at 120 K, the O 1s signals for OH* appeared about 530.5 eV (the second from the bottom), in addition to those for H2O* centered about 532.4 eV. The OH* was formed mainly by O* abstracting H from H2O* (H2O* + O* → 2OH*). With increased H2O coverage up to 1.0 L, both H2O* (light blue fitting curve) and OH* (blue) signals increased while...

Fig. 3  Ratios of the quantities of reaction products to ethanol$_\text{int}$ as a function of O* coverage. These quantities were measured with the integrated intensities of the corresponding desorption features. The ethanol$_\text{int}$ contains those desorbing from and reacting at Rh(111) surface. The red lines are drawn to guide the eyes.

Fig. 4  (a) O 1s spectra for Rh(111)O* (0.08 ML) (bottom) and subsequently exposed to 0.0–2.0 L H2O, as indicated, at 120 K. The black fitting curves in (a) consist of those for O* (red), OH* (blue) and H2O* (light blue). (b) Plots the quantities of OH*, measured with the integrated intensities of the fitting curve (blue) for OH*, as a function of H2O exposure.
O* (red) ones decreased – O* was protonated to OH*; above 1.0 L, the OH* signals became saturated despite the H2O* ones continued to grow (top). As the observed OH* signals measured the numbers of OH* on the Rh surface, the quantities of OH* increased monotonically with H2O exposure up to 1.0 L and became saturated above 1.0 L (Fig. 4b). The signal at 2.0 L was slightly attenuated by multilayer water; annealing to 160 K to remove multilayer water restored the OH* signals to about that at 1.0 L. The increased OH* corresponds well to the increased production probabilities of these four products (Fig. 3) below 2.0 L D2O exposure: the OD* (OH*) promoted the production probabilities. Above 2.0 L D2O exposure, the OD* was saturated, so the production probabilities of H2 and CH2CH2 were saturated and that of CO increased only slightly; either of them agreed with the saturation of OD* to a great extent. The saturated OD* however could not explain the declining production probability of CH4 above 2.0 L D2O exposure. Our analysis based on DFT calculations below gives a more comprehensive picture to understand the evolution of the production probabilities with co-adsorbed D2O.

3.2 DFT computation and discussion

The experimentally observed phenomena of water and ethanol co-adsorbed on Rh(111) and Rh(111)O* surfaces are mechanistically rationalized according to the schematic plot in Fig. 5. We used H2O molecule for the computation and compared the results to the above experimental ones with D2O, because we focused on the properties associated with the electronic structures of Rh(111) surface and adsorbed water (for which H2O and D2O are identical), such as desorption energies (E_{des}), reaction energy (\Delta E), activation energies (E_a) and electronic distributions. For water molecularly adsorbed on the surfaces, its E_{des} on Rh(111) surface (top panel, 0.37 eV) is slightly smaller than that on Rh(111)O* surface (middle panel, 0.48 eV), due mainly to a weak hydrogen bond between adsorbed H2O* and surface O*; the hydrogen bond is evident through the analysis of induced charge that some negative charge is induced on O* (green transparent sphere) and some positive charge on H2O* (yellow transparent sphere); the computed Bader charge for O* is \(-0.90|e|\) and those for O and H of H2O* are 1.00 and \(-1.92|e|\), respectively. The increased E_{des} on Rh(111)O* contributes partly to the increased desorption temperature of first water overlayer (from 170 K to 195 K on Rh(111) surface) in the TPD experiment (Fig. 1a).

The H2O* on Rh(111)O* surface can further cleave its O-H bond and yield OH*, with energies \Delta E/E_a = 0.17/0.93 eV. Upon adsorbing ethanol on the OH* covered surface, the hydrogen bond is readily formed [CH3CH2OH*...OH*, middle panel], revealed through the induced charges – positive one (yellow) on the H of CH3CH2OH* and negative one (green) on the O of OH*; the computed Bader charges for H and O of OH* are 1.00 and \(-1.52|e|\), respectively and that for O of CH3CH2OH* is \(-1.63|e|\). The hydrogen bond (0.5 eV) stabilizes the adsorption of ethanol and significantly lowers the energies for ethanol dissociation forming CH3CH2O* + H2O* (\Delta E/E_a = -0.66/0.23 eV), compared to the dissociation without the hydrogen bond (\(-0.19/0.58\)).

The yielded CH3CH2O*, with a much stronger adsorption energy (\(-2.47\) eV), further decomposes (lower panel), while the yielded H2O* desorbs easily from the surface. As a result, the intermolecular hydrogen bond between co-adsorbed

Fig. 5 Schemes of reactions of molecular water, atomic oxygen and ethanol co-adsorbed on a Rh(111) surface. The top panel shows that sole water on the Rh(111) surface has a smaller E_{des}. The middle one shows that water adsorbs on the Rh(111)O* surface with a greater E_{des} and dissociates into OH*; the OH* abstracts H from co-adsorbed ethanol with a small energetic barrier; the green and yellow transparent spheres denotes induced negative and positive charge respectively. The bottom panel shows that the decomposition of CH3CH2O* produces CH2CH2, H2, CH4 and CO.
CH$_3$CH$_2$OH* and OH* stabilizes the ethanol adsorption and induces a low-barrier and highly exothermic proton transfer process so assists the ethanol dissociation and squeezes water out from the surface. The result explains the TPD observation in Fig. 1b that later adsorbed ethanol exchanged positions with pre-adsorbed surface water so water desorbing from the water multilayer regime increased.

The surface ethoxy (CH$_3$CH$_2$O*) is further dissociated on the surface (bottom panel, Fig. 5) through sequences of C–H, C–O and C–C bond cleavages and ultimately produces the products CH$_3$CH$_2$, H$_2$, CH$_4$ and CO, as observed in the TPD spectra (Fig. 2). The detailed energetics and reaction routes are plotted in Fig. S5 in the ESI† the energetics showed trends similar to those from previous studies (Table S1†). The four products are formed through routes of two kinds, shown with the cyan and yellow arrows in the figure; the measured CH$_3$CH$_2$ and CO came from direct desorption of their surface adspecies (cyan arrows), while the measured H$_2$ and CH$_4$ from combinatorial desorption with proton (yellow ones) as their precursors were H$_2$* and CH$_4$*. Respectively, the quantities of CH$_3$CH$_2$ and CO correspond mostly to that of decomposing ethanol (schemes (a) and (b) in Fig. S5†); the increased ratios (production probabilities) of CH$_3$CH$_2$ and CO (Fig. 3) thus reflect a promoted decomposition probability of ethanol, by co-adsorbed water (or OD*). When OD* was saturated above 2.0 L D$_2$O exposure, the decomposition probability became (or nearly) saturated so the production probabilities of CH$_3$CH$_2$ and CO either remained constant or increased only little.

In contrast, the production of combinatorially desorbing CH$_4$ and H$_2$ depends to a great extent on the fragments from decomposed ethanol as well as surface H* (schemes (c) and (d) in Fig. S5†). Surface OH* (OD*) from adsorbed water not only enhances ethanol decomposition (by abstracting H of ethanol) but also consumes surface H* to yield H$_2$O* (HDO*), via a moderate energetic reaction ($\Delta E/E_a = -0.01/0.85$ eV). Accordingly, the production of CH$_4$ or H$_2$ is balanced between (saturated) production probability of CH$_4$ (H$_2$) at a greater water exposure (≥2.0 L) to not only a saturated probability of ethanol decomposition but also a high consumption rate of H* (a high ratio of OH* (OD*) to ethanol(int)). As the consumption of H* by OH* (OD*) is completely about/below 200 K (Fig. 3), the formation of H$_2$ and CH$_4$ competes for the rest H* . It is noted that the formation of H$_2$ was more competitive than that of CH$_4$ even at a smaller water exposure (<2.0 L); with increased water exposure, the H$_2$ production was increased at a rate much greater than that for the CH$_4$ production (Fig. 3). The formation of CH$_4$ was not favored because of an inhomogeneous distribution of CH$_3$*. The channel of producing CH$_3$*, via CH$_3$CHO* intermediates, yields less H*, so less H* is directly available to CH$_3$* in contrast, both channels produce H* so H* readily finds another H* nearby to form H$_2$. Additionally, a considerable fraction of the precursor CH$_3$* underwent dissociation, leading ultimately to formation of surface C*. Consequently, with limited H* at a greater water exposure, the production of H$_2$ was sustained while that of CH$_4$ decreased. Our DFT calculations show that an increased OH* (OD*) concentration decreases the adsorption energies of CH$_3$*, H* and OH* but in contrast, enhances the $E_a$ for formation of CH$_4$, H$_2$ and H$_2$O, which implies equally raised difficulty for their formation. The energetics varied with the OH* (OD*) concentration accounts little for the decreased production probability of CH$_4$.

4. Conclusion

We have used TPD, PES and DFT calculations to investigate the reactions of ethanol co-adsorbed with atomic oxygen (O*) and deuterated water (D$_2$O*) on a Rh(111) surface under UHV conditions. The results show that adsorbed ethanol penetrated readily through pre-adsorbed water overlayers to react with the Rh surface; for 2.0 L ethanol adsorbed on Rh(111)$_{D_2O^*}$, the ethanol(int) (which interacted with Rh surface) made up about 75% of total adsorbed ethanol (ethanol(int) + ethanol in multilayer regime), a fraction similar to that on Rh(111)$_{O^*}$, but amounted to 50% of the ethanol(int) on Rh(111)$_{O^*}$. The decreased ethanol(int) with water overlayers results primarily from a smaller sticking coefficient of ethanol onto the water overlayers. In the reaction aspect, the decomposition probability of ethanol(int) was remarkably enhanced, as the surface OD*, from D$_2$O* + O* → 2OD*, abstracted readily H from ethanol(int). The production probabilities of CO, H$_2$, CH$_3$CH$_2$ and CH$_4$ were increased in proportion to the concentration of OD*, despite their increasing rates differed. Above two water overlayers, corresponding to a saturated concentration of OD*, the production probabilities of CO, H$_2$, CH$_3$CH$_2$ were about saturated, whereas that of CH$_4$ was decreased. The atypical behavior of CH$_4$ could be additionally associated with the availability of H*. As the formation of CH$_4$ (CH$_3$* + H* → CH$_4$) competes for H* with that of H$_2$ (H* + H* → H$_2$) and HDO (OD* + H* → HDO), both a greater ratio OD*/ethanol(int) at a great water coverages and an inhomogeneous distribution of the precursor CH$_3$* could result in the decreased production probability of CH$_4$.

Conflicts of interest

There are no conflicts to declare.

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