The promotion of CO dissociation by molybdenum oxide overlayers on rhodium

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ABSTRACT

A considerable promotional effect of MoOx species observed at high pressures on the catalytic activity of rhodium initiated the present UHV model study. The MoOx overlayers formed on Rh films (0.15–20.0 ML) supported by TiO2(110) substrate were characterized by AES, TPD, work function (WF) measurements and CO adsorption. On the mixed oxide support produced by depositing 1.2 ML Mo onto TiO2(110), a new recombative CO desorption state was observed with Tp=700 K, assigned as β-CO and related to the promotional effect of MoOx species diffused onto Rh particles of 1.0 ML coverage. The development of β-CO needs 0.5–0.7 ML threshold Rh coverage, attributable to particle size effect and geometric factors governing the CO adsorption. The β-CO state with Tp=725–742 K could also be detected on Rh films covered by MoOx moieties formed by the oxidation of Mo overlayers in O2. Remarkably, recombative CO desorption with Tp=700 K could be observed on the Rh nanoparticles covered by MoOxCy produced from pure Mo deposits by CO adsorption, too. In harmony with the promotional effect of MoOx overlayer found at high pressures, it is established that the dissociation of CO is maximal at 0.2–0.3 ML Mo coverage, attributed to the presence of active sites at the oxide-metal interface. The low desorption peak temperature (700 K) of associative CO desorption observed in the presence of MoOx and MoOxCy overlayers indicates a low activation energy for the reactions of Oa and Ca atoms, allowing high reaction rates for these intermediates. The MoOx species exerted both promotion and inhibition effects on CO adsorption at sub-monolayer coverages, but above 1 ML it completely suppressed the reactivity of rhodium layers towards CO, suggesting that its surface concentration is a critical factor.

1. Introduction

The shortage of platinum metals capable of catalyzing several industrially important reactions induces great efforts in the scientific community to make their application more efficient and more economical. It was recognized long ago that the catalytic performance of important, but rather expensive rhodium metal can be influenced advantageously by different additives, including molybdenum and its oxides [1]. Metal oxides are mostly involved in heterogeneous catalysis inherently since they are widely used to support the finely dispersed, catalytically active metal particles. Moreover, it turned out that the so-called reducible oxide supports, like MoOx [1], TiOx [2,3], FeOx [4], etc., from which oxide particles can migrate onto the surface of metal nanoclusters, can act as promoters. Iron oxide in the form of encapsulation layer was found to exert promotional effect on the CO oxidation over a Pt catalyst [4]. It has been established by high pressure investigations that the rate of an industrially important reaction, the hydrogenation of CO is maximal at intermediate TiOx coverages [5]. In harmony with this, we verified in a UHV model study that the extent of CO dissociation is also maximal at the same coverage range [6]. Besides the promotion of CO hydrogenation on Rh catalysts by MoOx [1], molybdenum oxides were found to facilitate other reactions on different metals as well. The catalytic activity of Pt/Al2O3 catalyst in propane oxidation reaction significantly increased in the presence of molybdenum and tungsten oxide additives, accompanied by excellent thermal stability of the modified catalyst [7]. Remarkably, a considerable catalytic promotional effect of different reducible oxides, like MoOx, TiOx and CoOx has been reported for the rather inert Au(111) surface [8] in the water gas shift (WGS) reaction. MoO2 supported Au and Cu particles showed also outstanding activity in the WGS reaction and it was suggested that the oxide support was directly involved in the WGS process [9]. MoOx-promoted Au/SiO2 catalysts were found to be more active in reverse water-gas shift reaction (RWGS) by an order of magnitude than the un-promoted ones [10].

Some UHV model studies on the catalytic effect of molybdenum additives have also been performed. It was reported that on the Pt(111)
surface, oxidized Mo deposits blocked the Pt surface sites leaving essentially unchanged the adsorption behavior of CO on the uncovered part of platinum [11], but in a high-pressure study it was suggested that at the Rh-MoOₓ interface CO can be bonded through its C atom to the Rh and via its O atom to MoOₓ [12]. It seems obvious that the more reduced is the MoOₓ species, corresponding to lowering in x, the higher is its activity towards carbon monoxide and oxygen. As an extremity, a Mo-covered Pt(110) single crystal can be much more reactive than the bare or MoOₓ-covered one [13,14]. The effect of a pure Mo overlayer on the reactivity of the supporting metal can hardly be established, since molybdenum mostly interacts with the reaction mixture. The reaction of Mo with oxidative reactants can occur even if it is covered completely by monolayer thick platinum metals [15]. Hence, as a result of the high affinity of Mo towards oxygen and due to the low surface free energy of the forming MoOₓ species, under oxidation conditions the end product of a bimetallic platinum metal-molybdenum system can be a platinum metal covered by MoOₓ, irrespective of the deposition sequence of platinum metal and molybdenum. Depending on the oxidative or reductive nature of reaction mixture, the molybdenum can be present with variable oxidation states and may show complex redox properties. It has been reported that the oxidation state of Mo in an additive and the surface composition of Mo-Rh catalyst nanoparticles can be changed considerably in oxidative and reductive gases [16]. Consequently, it is desirable to carry out experiments with well-defined molybdenum oxides to elucidate the mechanism of their catalytic promotion. UHV model studies on MoOₓ modified Rh catalysts can eliminate several variables being present in real catalysis, making possible to identify the important factors influencing the catalyst activity and stability.

The hydrogenation of carbon monoxide on Rh was found to be greatly promoted in the presence of molybdenum oxide [12], and the experimental data suggested a mechanism including enhanced CO dissociation. It has been reported that the Mo:Rh content must be 0.6 for the sake of optimal hydrogenation activity of amides [17]. For the promotion of WGS reaction on Pt, the Mo:Pt ratio had to be less than 0.7 [18], and a complete deactivation of Pt sites for CO hydrogenation was found at higher Mo load [12]. In harmony with these findings, in our previous model study we found that the reactivity of MoO₂ and MoO₃ supported Rh particles (0.4 ML) towards CO was completely suppressed after an annealing to 600 K due to MoO₃ migration to the rhodium [19]. To adjust finely the surface concentration of MoOₓ species, two methods are applied in the present work. First, self-assembled MoOₓ overlayers are formed on Rh particles supported by mixed titanium molybdenum oxides by heat treatments. The redox reactions between molybdenum deposits and TiO₂(110) substrate, surveyed in details in the literature [20], provide reliable recipes for producing mixed metal oxides. Second, MoOₓ is produced by the oxidation of Mo overlayers in O₂ gas. As outlined above, molybdenum additives on Rh are expected to exert a catalytic promotional effect on CO dissociation, however, in our previous study MoO₃ originating form MoO₂ and MoO₃ supports was only found to inhibit the CO adsorption [19]. In the present work we extend the former investigations to a MoOₓ-Rh system capable of promoting the decomposition of CO.

2. Experimental

The experiments were performed in an ultrahigh vacuum (UHV) chamber (base pressure <5×10⁻⁸ Pa) equipped with facilities for Auger electron spectroscopy (AES), and temperature programmed desorption (TPD). AES measurements were performed with a Physical Electronics coaxial-gun single pass cylindrical mirror analyzer (CMA), while mass spectrometric and TPD data were collected by a Balzers QMS 200 quadrupole mass spectrometer. A smooth polynomial was subtracted from each TPD spectrum as a baseline correction, applied also by others [21] and care was taken to avoid the generation of any additional TPD feature by this procedure. AES was performed in the differential mode with 3 keV primary electron energy, 3 V modulation, and 1–2 µA beam current. AES data were evaluated either plotting the absolute peak-to-peak heights of main peaks (Mo: 186 eV, Rh: 302 eV, Ti: 387 eV, O: 503 eV, C: 272 eV) or Auger ratios calculated from these peaks. Work function (WF) was measured by two methods. First, it was determined by recording the cut-off energy of inelastic secondary electrons excited by the AES beam. The sample bias was ~19 V and the relative WF values were derived by an accuracy of around 0.1 eV comparing the positions of the inflexion points in the current vs. voltage curves [22] with that for the nearly stoichiometric TiO₂(110) surface. Second, sensitive non-contact WF measurements were performed in a temperature-programmed manner [23] by a Besocke type Kelvin-probe with a sensitivity of 1 meV.

The TiO₂(110) single-crystal was the product of PI-KEM. The sample was attached to a Ta plate with an oxide glue (Aremco, Ceramabond 571), and could be heated with a W filament placed behind the Ta plate. The sample temperature was measured by a chromel–alumel thermocouple, attached to the side of the sample with the same adhesive material. To avoid the fracture of titania single crystal, the heating and cooling rates during cleaning and all measurements presented here were always less than 2 K/s, regulated by a computer-controlled circuit. The duration of annealing in stepwise heating experiments was equal to or less than 1 min.

The typical cleaning procedure of titania consisted of Ar⁺-ion bombardment (1.5 keV, 1×10⁻³ A cm⁻², 300 K, 30 min) and annealing at 1000 K for 30 min. The absence of oxygen-treatments resulted in blue-colored, defective crystal. Note, that after this procedure the contribution of Ti³⁺ and Ti²⁺ signals to the Ti 2p photoemission feature was found to be below 3%, according to XPS measurements performed in another vacuum chamber. The above treatment ensured the appropriate electrical conductivity for electron spectroscopy and high enough defect-density to observe 2D-like growth of Rh-particles in extended coverage range, which allowed the estimation of surface coverage through AES measurements [24]. A monolayer (ML) Rh coverage corresponds to a Rh surface concentration, where, supposing a 2D film growth on a TiO₂(110) single-crystal, the Rh AES signal would disappear [25]. This method was verified by AES measurements, through following the growth of Rh layer on Mo multilayer which is known to obey a layer-by-layer growth mode [26], giving a well-defined break-point in the Mo AES signal intensity at 1 ML Rh coverage. It is known from previous STM investigations that the above sample treatment results basically in (1×1) bulk terminated registry, although the presence of 1–2% of defect sites (0D dots and 1D strings of Ti₂O₃ stoichiometry) cannot be excluded [27]. This surface is mentioned throughout this article as a nearly stoichiometric titania and is designated as s-TiO₂(110).

An EG/N4 e-beam evaporator of Oxford Applied Research was used for the deposition of Rh and Mo by physical vapor deposition (PVD) at a sample temperature of 300–330 K. The oxidation of molybdenum layers (0.1–1.2 ML) was performed via reaction with the titania support, or by heating in 1×10⁻⁶ mbar O₂ for 20 min at 560 or 650 K.

3. Results and discussion

3.1. Properties of Rh particles supported by mixed molybdenum-titanium oxide

In our former study it was verified by LEIS measurements that the extent of thermally assisted encapsulation of 1.0 ML thick Rh film was somewhat modified by 1.2 ML Mo pre-deposited onto the TiO₂(110) substrate [28]. Since it has been found that the TiO₂ species migrated to the Rh promotes the dissociation of adsorbed CO [2,6], to clarify the promotional effect of MoOₓ overlayer, the extent of encapsulation of Rh by MoOₓ and TiO₂ species on the Mo pre-covered titania is to be estimated. For comparison with previous LEIS data [28], the effect of heating on the surface composition of a 1.0 ML thick Rh layer...
deposited on the titania, pre-covered with 1.2 ML Mo was followed by AES, see Fig. 1. On annealing to 720 K, the Rh AES signal reduced by about 30%, and both the Mo and Ti signals enhanced, which can be explained by the encapsulation of Rh particles by MoOx and TiOx species, completing by about 700 K as proven by the disappearance of Rh LEIS signal shown in a previous study [28]. Although Rh clusters (0.4 ML) on a TiO2(110) support do not aggregate up to 700 K [29], this cannot be completely ruled out for the particles supported by the Mo-covered titania, giving a possible contribution to the Mo AES signal enhancement (Fig. 1). Above 720 K, the decay in Rh AES peak intensity accompanied by the Ti signal enhancement can partly be due to the aggregation of Rh particles. The decrease in Mo AES signal above 720 K can be attributed to an extended oxidation of Mo-deposit to MoO2 and MoO3 through redox reaction with the substrate and above 800 K to the sublimation of MoO3 to the gas phase [30]. It was found in an earlier study that above 500 K the outermost surface region loses Mo [28]. The decay in surface Mo concentration on annealing at 500–1000 K is accompanied by a 0.75 eV decrease in WF (not shown), which can also be correlated with the diffusion of Mo into the defect sites of titania lattice and with the sublimation of MoOx species. Considering the lower WF of TiOx overlayer [31], 0.6 eV, as compared with that of MoOx [19], 1.0 eV, the WF decrease above 500 K can be related to the increase of TiOx coverage on Rh particles at the expense of MoOx species.

To reveal the details of the surface chemistry of Rh particles (1.0 ML) supported by the Mo covered (1.2 ML) titania, the effect of stepwise heating was followed by CO titration, as presented in Fig. 2A. Note that CO does not desorb from the Rh-free, Mo-covered titania surface after 20.0 L of CO exposure. The molecular α-CO desorption characterized with Tp=460 and 570 K is suppressed after pre-annealing to 480 and 630 K, while a new state, designated as β-CO, showing broad feature at 700 K without pre-annealing, appears and is shifted to 730 K. The β-CO state developed with Tp=700 K can be associated with a recombinative CO desorption affected by the MoOx surface species, which was found to migrate easily to the Rh particles from the MoO2 and MoO3 supports between 330 and 600 K [19]. After pre-annealing to 630 K, the β-CO peak became asymmetric and a shoulder appeared at around 770 K. A comparison with former findings reveals that the
of MoO$_2$ phase separation occurs\cite{21}. Following the decomposition of restricted mixing (5 inactive MoO$_x$ species onto the metal\cite{19}. The above deposition of 1.2 ML Mo on the TiO$_2$(110) substrate can be inferred Rh nanoparticles supported by MoO$_2$ the CO desorption ceases after the reasoning below) the amount of desorbed CO up to 720 K pre-annealing to 1000 K removed all the CO desorption features, which is in agreement with a former observation regarding the inhibition effect of a continuous, pure TiO$_2$ layer on CO adsorption\cite{6}. The quantitative evaluation of CO desorption is presented in Fig. 2B, where it is illustrated again that the β-CO state evolved already at 330 K, reflecting that MoO$_2$ can migrate to the Rh particles at this temperature. In Fig. 3, comparison of the normalized total amounts of desorbed CO (Fig. 2) with that from TiO$_2$ and MoO$_2$ supported Rh particles\cite{19} reveals that on the Mo covered titania (designated as Ti$_1$-$x$Mo$_x$O$_2$, see the reasoning below) the amount of desorbed CO up to 720 K pre-annealing temperature is between those found for the pure oxides. For Rh nanoparticles supported by MoO$_2$ the CO desorption ceases after pre-annealing to 550 K due to the migration of a rather mobile and inactive MoO$_x$ species onto the metal\cite{19}. The above findings support that the species which cover the Rh supported by the mixed titanium molybdenum oxide have an apparent intermediate mobility between that of TiO$_2$ and MoO$_x$. Up to 550 K mostly MoO$_x$ may cover the surface and above 550 K the surface concentration of TiO$_2$ can be enhanced.

The formation of mixed molybdenum-titanium oxide following the deposition of 1.2 ML Mo on the TiO$_2$(110) substrate can be inferred from literature findings. It is established that in the interfacial reaction of Mo and TiO$_2$(110) surface a maximum oxidation state of +4 can be reached in a molybdenum deposit at 300 K\cite{30}. The similarity between the structure of rutile TiO$_2$ and monoclinic MoO$_2$ allows a limited mixing (5–6%) of these oxides, while at higher concentrations of MoO$_2$ phase separation occurs\cite{21}. Following the decomposition of Mo(CO)$_6$ and a subsequent heat treatment at 853 K in air, the formation of a substitutional near-surface alloy with a stoichiometry of Ti$_{1-x}$Mo$_x$O$_2$ ($x<0.1$) was found\cite{32}, corresponding to Mo$^{4+}$ ions embedded in the titania lattice. Although the replacement of Ti$^{4+}$ ions with Mo$^{4+}$ ions needs thermal treatment\cite{21,32}, the WF changes of the Mo-covered TiO$_2$(110) sample\cite{19} indicate that it occurs to some extent even at 420 K. Accordingly, the surface composition of support during stepwise heating (Figs. 2 and 3) can be assigned as Ti$_1$-$x$Mo$_x$O$_2$ with the remark that $x$ is increasing during the heating process.

Taking into account the desorption peak temperatures for the recombinative CO states shown in Fig. 2A, it is reasonable to suppose that from the Ti$_1$-$x$Mo$_x$O$_2$ mixed oxide below 500 K mostly MoO$_x$ migrates to the Rh, but above this temperature the overlayer formed is composed of mixed MoO$_x$ and TiO$_2$ layer. It is remarkable that the promotional effect for CO dissociation on the mixed oxide support is maximized at lower pre-annealing temperature, 630 K (Fig. 2), as on the titania-supported Rh particles, 700 K\cite{6}. This can be explained with the higher mobility of MoO$_x$ species originating from the mixed molybdenum titanium oxide as compared with that of TiO$_2$ stemming from TiO$_2$(110). Importantly, the recombinative CO desorption occurs with lower desorption peak temperature in the presence of MoO$_x$ (700 K, Fig. 2) than under the influence of TiO$_2$ (765 K,\cite{6}), meaning that in a catalytic reaction the removal of surface O and C atoms takes place with lower activation energy, allowing higher reaction rate.

To investigate the effect of temperature on the mobility of MoO$_x$ species originating from the mixed molybdenum titanium oxide, on the Mo covered (1.2 ML) titania 1 ML thick Rh layer was also formed at 200 K (not shown). It is known from XPS data that the extent of redox reaction between titania and Mo at this low temperature is the same as at 300 K\cite{28}, hence the production of similar MoO$_x$ species can be expected in both cases. A CO adsorption-desorption experiment revealed that on the layer produced at 200 K no recombinative β-CO state formed, verifying that at this temperature MoO$_x$ species could not migrate onto the Rh particles.

It is to be considered that the dissociation of CO on titania supported Rh particles was found to occur only above a threshold Rh coverage, ~0.2 ML\cite{24}, what can be related with coverage dependent structural and electronic features characteristic of the metal deposit and with metal substrate interaction\cite{33}. To reveal a possible particle size effect, the influence of Rh coverage on the decomposition of adsorbed CO was investigated on the Mo-covered titania support. In Fig. 4 it can be seen that at 1.2 ML Mo pre-coverage two molecular CO states populate, with $T_p$=420 K and with $T_p$=493 K. The apparent upward shift in the peak temperature of the latter one above 0.5 ML Rh coverage can partly be due to overlapping with the broad β-CO feature appearing at around 700 K. The formation of β-CO state begins only at a threshold coverage range, $\Theta_{Rh}=0.5–0.7$ ML. To explain this phenomenon it must be considered that the CO dissociation activity of Rh particles has been found to be correlated with the availability of highly coordinated adsorption sites which depends on the size and shape of nanoparticles\cite{34}. For CO dissociation an ensemble of metal atoms in a particular geometry capable of binding the CO molecule and its dissociation products can be an important factor\cite{35}. In other words, to bind the O and C adatoms, a minimum number of Rh atoms are needed in the Rh particles. It was found that the CO dissociation activity of alumina supported Rh particles depended on the island size, exhibiting a maximum for islands with around 1000 atoms\cite{33}, which was correlated with the presence of highly coordinated adsorption centers on Rh particles, the formation of which requires obviously a minimum number Rh atoms. In addition, it is important to emphasize, that the electronic band structure, determining the chemical reactivity of metal deposits, also depends on the number of constituent atoms of metal particles\cite{33}. These effects can contribute to the appearance of the threshold Rh coverage observable in Fig. 4, corresponding to an average Rh particle size below which the reactivity towards the CO molecule is suppressed even in the presence of a reactive MoO$_x$ moiety.

The surface processes were also followed by temperature-programmed WF measurements performed with a Kelvin-probe, see the inset in Fig. 4. This method which monitors around 7 square
millimeter area in the middle of the sample, rules out the contribution of gas desorption from the back and edge of the sample to the WF signal, which, on the contrary, may exert some influence on the TPD spectra [36]. The molecular and recombinative CO desorption states could be detected by the Kelvin-probe also as overlapping features at 1.2 ML Mo pre-deposition and 1.0 ML Rh coverage. In comparison with the corresponding, uppermost TPD spectrum of Fig. 4, the amount of molecular state seems less than that of recombinative one. This can be associated with the dipole moment of adsorbed states [23]. Accordingly, the dissociation products, O and C adatoms seems to have a larger average dipole moment than the CO molecule. Note that good coincidence was found in the shape and location of normalized TPD spectra and the negative derivative of temperature-dependent WF signals on the surfaces where molecular CO desorption prevailed, i.e. on Rh multilayers.

3.2. The effect of oxidized and pure Mo overlayers on the reactivity of Rh nanoparticles towards CO

To suppress the possible contribution of TiOx overlayer on the surface chemistry of TiO2(110) supported Rh nanoparticles, the effect of oxidized Mo overlayers on CO adsorption has also been addressed. In Fig. 5A it is demonstrated how the MoOx species produced from its elements on the top of 1.0 ML thick Rh film influences the thermal desorption of CO. The Mo coverage varied between 0.1 and 0.5 ML, and the Mo deposits were oxidized in 10−6 mbar O2 for 20 min at 650 K. A similar treatment of Mo multilayer resulted in the formation of molybdenum oxide with a high WF of 7.0 eV, attributed to MoO3 [19] and it was established that under similar conditions the oxidation number of Mo deposited on titania raised above +4 [30]. Note that a control thermal desorption spectroscopy (TDS) experiment verified that from the mixed molybdenum titanium oxide no CO desorption occurred following 20.0 L gas exposure. In Fig. 5 it can be seen that at 0.1 ML Mo coverage the MoOx suppressed the α-CO states at Tp=440 and 563 K, but generated a new, broad CO desorption feature with Tp=725 K, which can be identified as the recombinative β-CO state. The state with Tp=563 K can be ascribed to molecular CO adsorbed at on-top, while the one with Tp=440 K at bridge position [24].

![Graph](image_url)
adsorbate-adsorbate interaction can contribute to the broadening of TDS traces. At $\Theta_{Mo}=0.2$ ML the $\alpha$-states are further reduced, the $\beta$-CO is intensified and its $T_p$ is shifted to 740 K. At $\Theta_{Mo}=0.35$ ML the $\beta$-CO is eliminated, but the $\alpha$-CO with $T_p=512$ K is still present. The concerted suppression of $\alpha$-CO states at $T_p=563$ K and $T_p=544$ K reflects the bonding of MoO$_x$ species on the corresponding adsorption centers with similar probabilities, resulting in a narrow TDS feature with $T_p=512$ K at 0.35 ML Mo coverage. At $\Theta_{Mo}=0.50$ ML all CO desorption ceased, revealing a complete hindrance of CO adsorption. Although the size and shape of titania supported Rh nanoparticles was found unaltered by STM up to 700 K during the encapsulation with TiO$_x$ species [29], structural changes of Rh particles covered by MoO$_x$ cannot be ruled out on annealing. The determination of change in the particle size from CO desorption experiments is not straightforward, since different CO adsorption states develop which require different number of surface sites on Rh (Fig. 5A). However, it can be estimated that the size of Rh clusters is not changing substantially in the presence of MoO$_x$ overlayer and adsorbed CO, since the total amount of desorbed CO as a function of MoO$_x$ coverage decreases approximately linearly (Fig. 5B).

Clearly, in Fig. 5 the amount of dissociative $\beta$-CO state goes through maximum with the increase of the MoO$_x$ coverage, hence the formation of this state can be associated with the overall number of perimeter sites. The disappearance of the $\beta$-CO at $\Theta_{Mo}=0.35$ ML can be due to the coalescence of MoO$_x$ species into larger islands resulting in a strong reduction in the number of active MoO$_x$ perimeter sites. If the coalesced islands are large enough, the concentration of $\beta$-CO drops below the detection limit of TDS, but a fraction of the surface may still remain free to allow molecular CO adsorption. Note that in Fig. 2A the appearance of $\alpha$-CO following a thermal treatment at 730 K can be explained similarly, that is with the aggregation of MoO$_x$ and TiO$_x$ species, leaving enough adsorption centers for molecular CO bonding. It is important to note that the position of $\alpha$-CO desorption peaks varies only slightly with the MoO$_x$ coverage in Fig. 5A, which is indicative of a weak interaction between MoO$_x$ overlayer and rhodium, allowing a simple site-blocking effect. This mechanism was also observed for a MoO$_x$ covered Pt(111) single crystal as deduced from CO adsorption experiments [14]. On the other hand, the recombination of $\beta$-CO state reflects the presence of reactive MoO$_x$ species on Rh. Similarly, in a high pressure study [8] reactive CeO$_x$, TiO$_x$ and MoO$_x$ moieties were found to generate water dissociation even on the rather indifferent Au(111) single crystal.

To exclude any pre-annealing of the Mo-covered rhodium clusters before TPD experiments, the titania supported Rh films were covered by different amounts of Mo metal and their reactivity was tested through CO adsorption (20.0 L). In Fig. 6A it is demonstrated that enhancing the coverage of metallic Mo from 0.2 ML to 1.0 ML on a 1.0 ML thick Rh film strongly suppresses the amount of $\alpha$-CO state with $T_p=450$ K, but leaves nearly intact the other state with $T_p=545$ K. The $\gamma$-CO with $T_p=585$ K on the Mo-free titania originates from the titania-rhodium interface [24], and is eliminated at and above 0.2 ML Mo coverage. Noticeably, the $\beta$-CO with $T_p=700$ K also appears on the Mo-covered Rh particles, and it is detectable even at $\Theta_{Mo}=2.0$ ML. Its amount has a maximum at $\Theta_{Mo}=0.5$ ML (Fig. 6B), suggesting that the recombination of C and O atoms proceeds at the molybdenum-rhodium interface. Considering the unvaried and low, 700 K peak temperature for the associative CO desorption at 0.2–2.0 ML Mo coverages, it is reasonable to suppose that it originates not from the inner part of Mo islands, where the O and C atoms are more highly coordinated to Mo atoms, but from their perimeter sites where weaker binding occurs. If the O and C atom containing, 2.0 ML thick Mo layer forms 3D structures, the MoO$_x$C$_x$–Rh interface represents adsorption sites where the recombinaive CO state can still be populated. Molecular CO desorption at this coverage may be absent if the 3D structures are produced only during the heating cycle of TPD experiment.

The question arises whether the CO dissociation could be observed on Mo-covered platinum metals in previous model studies. It has been established that the oxidation state of molybdenum in a deposit can greatly influence the reactivity of a platinum metal [13]. As an extremity, a Pt(110) single crystal covered by metallic molybdenum is more reactive than the bare or MoO$_x$-covered one [14]. After exposing a Pt(110) crystal to 10.0 L Mo(CO)$_6$ at 300 K a CO TDS feature appearing at 540 K was associated with CO desorption from the Mo deposit [13]. In addition, CO desorption was detected with $T_p=575
and 600 K after saturating the Pt(110) and Pt(110)+MoOₓ surfaces with Mo(CO)ₓ. Since the latter peak temperatures are by more than 100 K higher than the Tₑₛ of molecular CO desorption for either Pt [13] or Mo [37] surfaces, the corresponding desorption states can be attributed to the recombination of C and O adatoms. Furthermore, AES proved that the surface C and O contaminants originating from the high temperature (700 K) decomposition of Mo(CO)ₓ on the same Pt(110) surface could be completely eliminated by annealing to 1000 K [14]. These observations indicate that on a Mo-covered Pt(110) surface C and O atoms recombine above 500 K and below 1000 K, that is in the same temperature region, where associative CO desorption was found from the CO-saturated Rh+Mo and Rh+MoOₓ surfaces. Accordingly, on different platinum metals the surface species produced by the oxidation of molybdenum deposits with the oxygen of dissociated CO, seems to have the potential to act as promoter in those catalytic reactions where the decomposition of CO is an intermediate step.

It is worth comparing the TDS data for CO desorption from MoOₓ and Mo covered Rh surfaces, displayed in Fig. 5 and Fig. 6. First, it is to be considered that the MoOₓ particles are reactive with CO only at their perimeter [11], [12], while the whole surface of Mo islands covering the Rh can react with CO. As a result, the inactive MoOₓ layer [14] can completely suppress the reactivity of Rh towards CO adsorption at 0.5 ML Mo coverage that is the MoOₓ species prepared can fully block the surface. On the contrary, the 2.0 ML thick Mo layer reacting with CO seems to be able to produce 3D structures, providing active reaction centers at the rhodium-molybdenum interface. It is remarkable that the temperature range for recombinative CO desorption is 800–1200 K on a macroscopic molybdenum surface [37], but from the perimeter of the nanosized, Rh supported Mo particles CO desorbs with Tₑₛ=700 K. This low temperature can be explained by the influence of the underlying rhodium and by the lowered coordination of surface Mo, C and O atoms to each other as compared with that in a 3D structure. Taking into account that on the Mo layer supported by Rh particles the CO adsorption results in O and C-atoms, on the one hand it is straightforward that the oxidation number of Mo cannot be 0 following CO exposures. On the other hand, the oxidation number of Mo must be lower than that reached by extensive oxidation in O₂ gas. Accordingly, Mo with oxidation number less than +6 is responsible for the promotional effect of MoOₓ on CO dissociation.

3.3. The impact of MoOₓ species on the surface chemistry of CO on Ar⁺-ion sputtered Rh multilayers

To eliminate completely the effect of TiOₓ(110) support on the surface chemistry of Rh, MoOₓ species was produced on Rh multilayers. To get rid of the trace amount of carbon being present in Rh multilayers after metal deposition, they were annealed to 1000 K to encapsulate them by TiOₓ, which oxidized the carbon contamination. The TiOₓ overlayer was removed by mild Ar⁺-ion sputtering [6] and the clean Rh was covered by Mo and oxidized in O₂ stream at 560 K.

In Fig. 7 the effect of annealing on the 20.0 ML thick Rh multilayer covered by MoOₓ is displayed, as followed by AES and WF measurements. The points at 300 K correspond to a 1.0 ML thick Mo deposit. The oxidation performed at 560 K caused a small change in the Mo/Rh AES ratio, but was accompanied by a significant WF enhancement of 1.3 eV. The stepwise heating between 560 and 1000 K resulted in the gradual decrease of both the Mo/Rh AES ratio and WF. Remarkably, the former quantity indicated a nearly complete loss of Mo in the near-surface region after annealing at 1000 K. This is in harmony with the evaporation of volatile MoOₓ species above 800 K [30]. The elimination of MoOₓ from the surface is accompanied by 1.1 eV WF decrease. A similar value, 1.0 eV was calculated for MoOₓ species covering completely a 0.4 ML thick, MoOₓ-supported Rh layer after annealing to 550 K [19], suggesting that the two species are similar. The high initial WF difference presented in Fig. 7, 2.0 eV, related to the WF of nearly stoichiometric titania involves a high absolute WF of around 7.0 eV, which is close to that of bulk MoO₃ [19]. High dipole moments were also found for atomically thin MoOₓ layers formed on graphene [38].

The question arises, how the thickness of a MoOₓ overlayer correlates with its WF. Well-defined MoOₓ films could be prepared on the Au(111) surface with monolayer [39] and bilayer thickness [40]. It was established that the charge transfer between a molybdenum trioxide monolayer and the supporting metal can result in the reduction of molybdenum ions, corresponding to lower WF of the MoOₓ overlayer as compared with that of bulk oxide [41]. The WF was found to depend on the MoOₓ layer thickness, being higher at higher oxide coverages. Since our MoOₓ overlayer is characterized, as shown in Fig. 7, by a WF of near to 7.0 eV, a value close to that of bulk MoO₃, it is probably composed of a bilayer.

In Fig. 8 CO desorption signals are presented for MoOₓ covered Rh multilayers saturated with CO at 300 K. It is demonstrated that increasing the coverage of MoOₓ species, the Tₑₛ of the associative CO desorption (γ-CO, 812 K), characteristic of the ion-sputtered Rh film [6], decreases gradually, manifesting in the appearance of a broad TPD feature with Tₑₛ=785 K at ΘMo=0.2 ML. At higher molybdenum coverages, ΘMo=0.5 ML and ΘMo=0.75 ML the recombinative CO desorption is characterized by peaks at Tₑₛ=742 K. Overlapping molecular CO desorption states show TDS features peaked at 588 and 540 K, which are suppressed with the enhancement of MoOₓ concentration. The development of β-CO with Tₑₛ=742 K can be attributed to the same process that was observed for Rh particles covered by MoOₓ, produced from 0.1–0.2 ML Mo (Fig. 5), namely to the MoOₓ assisted dissociation of CO. The enhanced peak temperature for the recombinative CO desorption, 742 K, as compared with 725 K observed for Rh particles (Fig. 5A) can be due to the presence of defect sites generated by Ar⁺-ion sputtering. Noticeably, the recombinative CO-desorption from a pure Mo multilayer (not shown) provides a much higher desorption
Mo\textsubscript{O\textsubscript{x}} species promotes the decomposition of carbon monoxide. The extent of promotion is maximal at intermediate, 0.2–0.3 ML Mo coverage as shown in Fig. 8B, similar to that presented in Fig. 5B for Rh nanoparticles, suggesting that the active sites for CO dissociation are located at the Rh-MoO\textsubscript{x} interface on both surfaces.

As illustrated in Fig. 8, for a Rh multilayer covered by MoO\textsubscript{x} produced from 1.0 ML Mo and exposed to 20.0 L CO, any CO desorption is completely missing. Regarding the blocking effect of MoO\textsubscript{x} species on CO adsorption, this observation is in harmony with our former findings [19] and with those for the Pt(111) [11] and Pt(110) [14] single crystals, supporting that a continuous MoO\textsubscript{x} overlayer suppresses the reactivity of platinum metals towards carbon monoxide. Noticeably, the 0.75–1.0 ML Mo coverage range (Fig. 8), where the CO adsorption is completely suppressed on the ion-sputtered Rh film, is about twice as much as that for the Rh nanoparticles (Fig. 5). This can be explained by the preferential growth of 3D MoO\textsubscript{x} particles in the atomic scale valleys of the ion-sputtered surface, which makes possible a hindered aggregation of MoO\textsubscript{x} particles at 0.75 ML Mo coverage and the formation of \(\beta\)-CO at their perimeter sites.

The question arises what might be the oxidation number of molybdenum in the MoO\textsubscript{x} species being active in CO dissociation. The characterization of ultrathin MoO\textsubscript{x} layers has been addressed by XPS on several substrates. On graphene, Mo\textsuperscript{5+} and Mo\textsuperscript{6+} ions were detected for a 0.15 nm thick MoO\textsubscript{3} layer, but Mo\textsuperscript{6+} ions prevailed at 15 nm film thickness [38], suggesting a thickness effect. The activity of Au/SiO\textsubscript{2} catalysts in the RWGS reaction increased by an order of magnitude as a result of promotion by MoO\textsubscript{x}, in which Mo was found to be in +6 oxidation state [10]. MoO\textsubscript{2} supported Au and Cu particles showed outstanding activity in the WGSR reaction and it was suggested that the oxide support, containing Mo\textsuperscript{4+} ions, was directly involved in the WGSR process [9]. A monolayer thick MoO\textsubscript{x} species was found to be reducible by extended heat treatment on Au(111) [39], resulting in a stable oxide island through a reduced metal center [12], it is reasonable to suppose that to exert a promotional effect, oxygen vacancies at the perimeter of oxide particles are needed where Mo ions with oxidation number less than the maximal +6 for Mo are present.

The present UHV study confirms the suggestion of former high pressure work regarding the promotion of CO dissociation by MoO\textsubscript{x} species on Rh particles [12]. Clearly, the MoO\textsubscript{x} overlayer is capable to generate recombinative \(\beta\)-CO state both on Rh nanoparticles and argon-ion sputtered Rh films. It has been proven that to observe the promotional influence of MoO\textsubscript{x} overlayers on CO dissociation the Rh coverage must exceed a threshold coverage of 0.5–0.7 ML. Accordingly, at the 0.4 ML Rh coverage applied in our previous work [19] the promotion of CO decomposition was not observed. In harmony with the finding of high pressure studies that to promote maximally the hydrogenation reaction of CO [3, 5], the reducible oxide nanoparticles must be present on the Rh nanoparticles at intermediate sub-monolayer coverages, it is established that the optimal MoO\textsubscript{x} concentration for CO decomposition corresponds to 0.2–0.3 ML Mo coverage (Figs. 5B and 8B), supporting that the active centers are located at the Rh-MoO\textsubscript{x} interface. The lowered peak temperature of recombinative CO desorption for the MoO\textsubscript{x} modified rhodium nanoparticles, 700 K, as compared with that for the TiO\textsubscript{x}-covered ones, 765 K [6], includes that the C and O atoms generated by CO dissociation are bonded less strongly to the surface in the presence of MoO\textsubscript{x} species. During the catalytic hydrogenation of CO, the perimeter of promoter oxide species the metal ions must pass through oxidation-reduction cycles [12]. The reduction of oxide overlayer proceeding through a reaction with adsorbed C atoms has lower activation energy if the CO desorption peak temperature is lower, predicting an easier reduction with hydrogen adatoms as well. According to the well-known volcano curve confirmed for many heterogeneous catalytic reactions, for optimal peak temperature, 950 K. Considering that in the presence of a 0.5 ML thick oxidized Mo overlayer the TDS peak characteristic of associative CO desorption is located at 742 K, that is at much lower temperature than on rhodium, 812 K, and on a molybdenum single crystal, 950 and 1050 K [37], it can be established that on a defect-rich Rh surface the peak temperature is lower, predicting an easier reduction with hydrogen adatoms as well. According to the well-known volcano curve confirmed for many heterogeneous catalytic reactions, for optimal
catalytic activity the reaction intermediates must bind to the catalyst not too strongly and not too weakly [42], which seems to be valid for the C and O atoms on the MoO₃ promoted rhodium surfaces, allowing high reaction rates in their further reactions.

Due to its low surface free energy and high surface mobility, the MoO₃ species wets rhodium well, and for this reason on MoO₂ and MoO₃ supported Rh particles the CO adsorption was found to be completely blocked by the MoO₃ overlayer at relatively moderate temperature, 600 K [19]. In the present study, the elimination of CO nanoclusters and Rh mass ratio in a catalyst to avoid a complete inhibition effect.

4. Conclusions

i) Diffusion of MoO₃ and TiO₂ species from a Mo-covered (1 ML) titania to supported Rh particles (1 ML) at 330–1000 K was confirmed by AES and CO titration experiments.

ii) The MoO₃ overlayer on a 1 ML thick Rh film generated a new recombinative CO desorption state with Tp=700 K, assigned as β-CO.

iii) On a Mo pre-covered (1.2 ML) TiO₂(110) surface the development of the β-CO needs 0.5–0.7 ML threshold Rh coverage, attributable to Rh particle size effect and geometric factors governing the CO adsorption.

iv) The β-CO state can also be formed on 1.0 and 20.0 ML thick Rh films covered by MoO₃ species prepared by the oxidation of Mo overlayers in O₂ and on Rh nanoparticles covered by MoO₃Cy species produced from pure Mo deposits by CO adsorption.

v) The amount of β-CO was maximized at 0.2–0.3 ML Mo coverage, supporting that it formed at the MoO₃–Rh interface, and that this state is associated with the enhanced reactivity for CO hydrogenation found in high pressure studies. MoO₃ hindered the molecular CO adsorption, underlining that the amount of this additive must be low for catalytic promotion.

vi) The low peak temperature (700 K) for the associative CO desorption on the MoO₃ and MoO₃Cy modified Rh particles corresponds to a low activation energy in the recombination reaction of O₂ and Cₐ atoms, which allows high reaction rates for these intermediates.

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