High low-temperature CO oxidation activity of platinum oxide prepared by magnetron sputtering

V. Johánek*, M. Václavů, I. Matolínová, I. Khalakhan, S. Haviar, V. Matolín

Department of Surface and Plasma Science, Charles University in Prague, V Holešovičkách 2, 180 00 Prague 8, Czech Republic

A R T I C L E   I N F O

Article history:
Received 10 September 2014
Received in revised form 9 December 2014
Accepted 19 March 2015
Available online 25 March 2015

Keywords:
Platinum oxide
Reactivity
Carbon monoxide
Oxidation
Fuel cell
Magnetron sputtering

A B S T R A C T

CO oxidation on platinum oxide deposited by magnetron sputtering on flat (Si) and highly porous (multi-walled carbon nanotubes, MWCNT) substrates were examined using X-ray photoelectron spectroscopy, scanning tunneling microscopy, temperature-programmed desorption and temperature-programmed reaction in both UHV and ambient pressure conditions. Platinum in the freshly deposited thin film is present entirely in the 4+ oxidation state. The intrinsic CO oxidation capability of such catalyst proved to be significantly higher under approx. 480 K than that of pure platinum, presumably due to the interplay between metallic and cationic platinum entities, and the reaction yield can be further enhanced by increasing effective surface area when MWCNT is used as a support. The thermo-chemical stability of the platinum oxide, however, has its limitations as the thin film can be gradually thermally reduced to metallic platinum (with small residuum of stable Pt^2^+ species) and this process is further facilitated in the presence of reducing CO atmosphere.

1. Introduction

Besides other applications such as dielectric or ferroelectric films for micro- and nano-electronics, or optical materials, platinum and its oxides have been commonly used as a catalyst in chemical and electrochemical applications. In proton exchange membrane fuel cells (PEMFC) highly dispersed platinum is often used as a chemically active material incorporated into one or both fuel cell electrodes. It has been speculated that due to oxidizing environment during fuel cell operation the platinum may exist in the form of an oxide rather than metal. Since active catalytic material such as platinum is (both in practical applications and model studies) often deposited on an oxide support, the oxygen can also be diffusively interchanged with the substrate. In particular, this phenomenon can be expected on the commonly used cerium oxide (ceria), which exhibits quite unique properties attributed to its high oxygen storage capacity [1]. Thus ceria acts as an oxygen buffer which can be easily reduced and re-oxidized [2], readily changing ionization or oxidation state of the adsorbed species or layers and/or inducing a local charge transfer.

Since the reactivity of metallic and oxodic form of platinum is generally different [3,4], the performance of a Pt-based fuel cell may be sensitive to the oxidation state of platinum or the presence of oxygen within the catalyst volume. One of the reactions determining performance and lifetime of hydrogen- or methanol-fueled PEMFC is oxidation of CO, commonly present in hydrogen produced by hydrocarbon reforming (in hydrogen-fueled FCs) or being a by-product of methanol reforming (in methanol-fueled FCs), respectively.

Several types of platinum oxides have been reported so far. Pure crystalline compounds, including tetragonal PtO [5–9], cubic Pt₃O₄ [9,10], Pt₅O₆ [10,11], Pt₃O₆ [10], and PtO₂ [9] where the latter exists in two crystal modifications – α-PtO₂ [7,8] with hexagonal structure and orthorhombic β-PtO₂ [10,12,13]. Non-stoichiometric amorphous phases of platinum oxide (α-PtO₃) have also been prepared [14–17].

As a noble metal, platinum is relatively difficult to be bulk oxidized directly. Oxidation process can be, however, facilitated by electrochemical means or by reactive sputtering, where either oxygen plasma induces formation of an oxide film on a pristine platinum surface [18] or the platinum is sputtered away from a target in a mixture of oxygen and a noble gas (usually argon) using magnetron and deposited onto a solid substrate; in this technique the resulting composition of the oxide is determined by the deposition rate, the gas composition and pressure, and substrate temperature [7,15,19].
2. Experimental

Samples of platinum oxide thin films supported on various substrates (multi-walled carbon nanotubes (MWCNTs) supported on Si(1 1 1) wafer, oxidized Si(1 1 1), and Ta polycrystalline foil) were prepared using reactive DC magnetron sputtering from a Pt target (99.95%) in pure oxygen atmosphere (Linde Gas, purity 5.6). Deposition was carried out with substrates at room temperature and $4 \times 10^{-1}$ Pa pressure of O$_2$. We used Advanced Energy MDX500 power supply in power regulating mode, the applied power was 15 W yielding discharge voltage of about 480 V. The samples were placed 90 mm away from the 2"-diameter target. At these conditions the average deposition rate of 3 nm/min was achieved. In every run more substrates of the same type were placed in the magnetron simultaneously in order to produce a set of identical samples to be subjected to different experimental procedures.

The surface morphology of the samples was imaged by means of scanning electron microscopy (SEM; TESCAN-MIRA microscope) operated at 30 keV of primary electron beam energy.

X-ray photoelectron spectroscopy (XPS) was performed with an Al X-ray source ($h\nu=1486.6$ eV, energy resolution $\Delta E = 1$ eV) and the SPECS Phoibos MDC 9 energy analyzer. All the XPS experiments were done in an ultrahigh vacuum (UHV) experimental chamber operating at base pressure $<10^{-7}$ Pa.

The reactivity tests at atmospheric pressure were done using a home-made microchip reactor system. The gas composition is mixed using digital mass flow controllers, analysis of the gas composition is done by a Pfeiffer Prisma 200 series quadrupole mass spectrometer placed in a UHV chamber into which a small part of the product gas mixture is sampled through a metering valve. For CO oxidation experiments a CO+O$_2$ mixture (3 sccm CO+7 sccm O$_2$) was diluted in an inert buffer gas (He, 30 sccm) to form a total pressure of 1 atmosphere inside the reactor. The design of the microreactor is specific in that the reaction chamber is formed by a flat sample at the bottom and a quartz glass cover with gas feeding holes and channels for better distribution of the gas flow at the top. The space between the two plates is retained by a 100 $\mu$m thick silicone rubber sealing placed around the sample circumference. Heating of the sample is computer controlled using a PID regulator.

The temperature-programmed desorption (TPD) and low-pressure temperature-programmed reaction (TPR) experiments were performed in another UHV system ($<10^{-8}$ Pa base pressure) equipped with Pfeiffer PrismaPlus quadrupole mass spectrometer placed in a differentially pumped nozzle in order to separate background contribution from the molecules desorbing directly from the sample. In this apparatus the platinum oxide surface was exposed by pure carbon monoxide via a simple collimated gas dosers aimed directly at the sample surface. The samples were inserted into the UHV chamber immediately after the oxide deposition and used in experiments without any prior treatment.
3. Results

3.1. High pressure reactivity

Platinum oxide (PtO₂) deposited by magnetron sputtering with thickness in the order of a few tens of nanometers generally exhibits relatively flat continuous morphology demonstrated by the SEM image in Fig. 1a (Pt oxide grown on oxidized Si(1 1 1) wafer), virtually independent of the substrate type as was verified by comparing to MWCNTs supported on Si (Fig. 2a), Ta polycrystalline foil (Fig. 6a), and a graphite foil (not shown therein); the eventual irregularities of the as-deposited thin film originate from the substrate itself as in the case of Ta substrate, compared to the perfectly homogeneous layer formed on Si (Fig. 1 a).

Immediately after the preparation the MWCNT and Si supported catalysts were transferred into the atmospheric-pressure reactor and subjected to a steady flux of mildly oxygen rich (3:7) CO + O₂ mixture diluted in helium buffer gas. Reaction rate of CO oxidation was calculated consistently for all the samples from the partial pressure of the generated CO₂ (measured by the QMS calibrated against a reference gas of known composition), taking into account the flow rates of the individual reactant gases per sample unit area (approx. 1 cm²).

In order to obtain high reaction rate it is generally convenient to deposit the catalytic material on a large specific surface area substrate, such as nanostructured porous surfaces or carbon nanotubes. In Fig. 3 we compare ambient pressure CO oxidation reactivity of PtO₂ thin films sputtered simultaneously on a bare Si wafer and a MWCNT covered Si wafer. Reaction curves in Fig. 3 measured under the same experimental conditions follow the same shape which confirms that the behavior of the MWCNT and SiO₂/Si supported PtO₂ layers with respect to CO oxidation is qualitatively identical, and that the substantially higher absolute values of CO₂ formation rate (per unit of the Si wafer surface) of the MWCNT supported catalyst is most likely due to its high specific surface area. By taking into account the diameter of the nanotubes (200–300 nm), their typical spacing (600–800 nm) and the deposition depth (3–5 μm) the effective surface area of the catalyst can be estimated to about 5–8 times the projected area, which is in a good agreement with the reaction rate enhancement of the MWCNT sample in Fig. 3.

With this in mind, the high pressure reactivity study of the PtO₂/Si system only will be further presented and analyzed in this section. Unlike on the highly complex MWCNTs, the catalyst film thickness and surface area is well defined on the planar Si substrate and better accessible to surface science techniques. The thickness of the platinum oxide on Si was estimated to 40 nm based on the deposition rate measurement by a crystal microbalance monitor placed near the substrate.

The evolution of the CO oxidation rate with temperature during both ascending and descending branches for the PtO₂/Si system presented in Fig. 3 is shown again in the inset of Fig. 4, in which natural logarithm of the CO₂ production rate is plotted against inverse temperature (Arrhenius plot). The heating rate was set sufficiently low at 2 K/min in order to provide quasi-equilibrium conditions such that each point of the TPR measurement can be considered isothermal.

The initial part of the sample heat-up (up to about 480 K) follows an exponential growth giving a linear Arrhenius plot (curve sections labeled (1) in Fig. 4). The onset of CO₂ production is observed at approx. 440 K. Around 480 K the TPR curve starts to deviate and then continues as a different exponential above 530 K, yielding the second linear part of the Arrhenius plot (marked (2) in Fig. 4). In fact, the latter consists of two linear sections with slightly different slopes, with an elbow around 560–565 K. The reactivity data of PtO₂ are directly compared with those measured with a pure Pt magnetron sputtered thin film deposited on the same substrate (open symbols), which exhibits linear behavior across the whole

![Fig. 2. SEM image of (a) as-deposited PtO₂ on multi-walled carbon nanotubes (MWCNTs), (b) PtO₂/MWCNT after two cycles of high-pressure CO + O₂ TPR to 575 K; image size 1500 nm × 1500 nm.](Image)

![Fig. 3. Temperature-programmed high-pressure CO oxidation, comparing reaction rates on PtO₂/MWCNT/Si (black) and PtO₂/Si (gray).](Image)
temperature range, suggesting that the metallic surface remains stable under our experimental conditions.

SEM images of the Si and MWCNT supported catalysts obtained after the high-pressure CO oxidation cycle are shown in Figs. 1c and 2b, respectively. Both images reveal very similar morphological changes leading to formation of irregular supported particles with lateral size of approx. 20–50 nm. A solely thermal modification of the silicon-supported layer by annealing to 575 K in vacuum is presented in Fig. 1b. The same surface was also imaged by AFM, see Fig. 1d. A comparison of height profiles before and after the annealing obtained by AFM (bottom of Fig. 1d) clearly demonstrates a substantial roughening of the initially flat surface (approx. 0.7 nm) to the final roughness of about 2 nm with numerous pits over 5 nm deep.

Another PtO\textsubscript{x}/Si sample with the same properties as above was exposed to pure CO gas (diluted in He with 7.5% relative concentration), representing an extreme case of oxygen-lean reaction conditions, and heated with a constant rate of 10 K/min. As can be seen in Fig. 5, the CO\textsubscript{2} signal sets off at 440 K and exhibits a sharp maximum at 462 K, dropping to nearly zero when the surface temperature reaches 470 K. The steep onset of CO\textsubscript{2} production might indicate a self-accelerated reaction due to a light-off by the reaction heat, inducing both increase of intrinsic reaction rate and the rate of surface reactant circulation. As the temperature is further ramped up the production of CO\textsubscript{2} starts to gradually increase again. On the contrary, the descending TPR branch (as well as the complete second TPR cycle, not shown herein) exhibits a catalytic activity only in the high temperature region (525–575 K).

4. Low pressure studies

4.1. XPS

The low pressure studies were performed with PtO\textsubscript{x} thin films deposited onto a metallic substrate (polycrystalline tantalum foil) for practical reasons, considering that the layer is thick enough to suppress the role of the supporting material. According to ref. [8] the platinum oxide was expected to grow as an amorphous PtO\textsubscript{2} phase, given our preparation conditions during reactive sputtering. The composition of the oxide was verified by XPS (Figs. 7a and 8a), while the morphology of the as-deposited thin film was imaged by SEM, see Fig. 6a. The bottom spectra in Figs. 7a and 8a (300 K) present Pt 4f and O 1s photoelectron peaks of as-prepared PtO\textsubscript{2}/Ta; all peak positions for Pt 4f doublet are quoted in terms of the 4f\textsubscript{5/2} peak in this paper. Shirley method was used for background subtraction, the peaks were fitted using asymmetric Gaussian–Lorentzian product functions, except for the PtO\textsuperscript{2-} related doublet where we used a convolution of Doniach–Sunjic with Gaussian. For the Pt 4f spectra constraints of constant doublet separation and constant ratio between both doublet components for all chemical states of Pt were applied.

The Pt 4f doublet at 73.7 eV corresponds to the 4+ oxidation state of platinum [20] which can be assigned to PtO\textsubscript{2} or Pt(OH)\textsubscript{4} according to available literature data [19,21]. The presence of the platinum tetrahydroxide is correlated with an appearance of an O 1s component at 531.5 eV [22] while the peak at 530.0–530.1 eV is matching the binding energy of lattice oxygen in stoichiometric PtO\textsubscript{2} [18,22]. Thus the freshly deposited thin film (or, to be more accurate, its outer layer probed by XPS) consists of a mixture of both tetrahydroxide and dioxide phases (with the average mutual ratio of about 12:88). The incorporation of hydroxyls into the layer is probably due to the exposure of the freshly prepared sample to ambient conditions during its transfer between the chambers, presumably formed by catalytic dissociation of water molecules present in air [23], while residual water remains at the surface in molecular form as is evidenced by the occurrence of the third O 1s peak at 533.0 eV [24]. The hydroxyls are presumably located at the surface, hence the bulk composition of the PtO\textsubscript{x} thin film is assumed to be much closer to PtO\textsubscript{2} than what is determined by XPS.

The sample was then heated in vacuum stepwise up to 825 K with 50 K increments and measured by XPS after each step. Thermal evolutions of the Pt 4f and O 1s spectra are shown in Figs. 7a and 8a, respectively. The layer remains intact up to 375 K. Upon further heating the surface water disappears and the platinum starts to gradually reduce its oxidation state from 4+ to both 2+ and 0 – see the metallic Pt peak emerging at 71.1 eV. The Pt 4f peak at 72.2 eV appearing at higher temperatures corresponds to 2+ oxidation state of platinum [17,20] and can be, together with the corresponding O 1s peak at 531.5 eV, attributed to PtO or Pt(OH)\textsubscript{2} since PtO and platinum hydroxides are indistinguishable by XPS due to very similar peak positions [18,25,26]. The composition is nearly stabilized above 625 K with Pt being prevailing surface compound and a small quantity (a few percent) of residual Pt\textsuperscript{2+} cations.
In Figs. 7b and 8b the intensities of the individual fitted components of Pt 4f and O 1s spectra, respectively, are plotted versus temperature. Apart from the above described behavior, a slight intermittent water signal re-appears in O 1s region around 700 K which will be discussed further.

After finishing the above thermal treatment the sample was checked again by SEM, see Fig. 6b.

4.2. TPD/TPR

Other two freshly deposited PtO$_x$/Ta samples (prepared together with the previous one) were successively moved to the TPD vacuum chamber through a fast-entry loadlock. Both samples were heated linearly: the first one in vacuum (<10$^{-7}$ Pa) while the second was exposed to a steady flux of CO with the partial pressure in the gas stream of 1 × 10$^{-3}$ Pa during heating.

In Fig. 9 thermal desorption spectra of the magnetron deposited PtO$_x$ sample are presented. The first desorbing product is hydrogen with a desorption maximum at 340 K, the wide feature at higher temperatures originates from the fragmentation of water. Water as the major compound recorded exhibits a very broad unresolved feature starting at 390 K and an intensive double peak with maxima at 675 K and 730 K. The double character of the latter desorption feature is presumably due to hydroxyl bonding to surface sites with two different types of coordination on the polycrystalline Pt/PtO$_x$. A relatively sharp molecular oxygen peak is centered around 745 K.

As the proper mass spectrometer calibration and gas sensitivity correction the oxygen balance during the decomposition process can be calculated. From the integration of 32 amu signal (O$_2$) in the 650–810 K range we obtained the average density of O per surface unit 250 nm$^{-2}$. Integration of 18 amu signal (H$_2$O) in the 590–780 K range yields the value of 780 nm$^{-2}$ of O, giving the total of 1030 nm$^{-2}$. Assuming the deposited thin film consists of the structure close to a hexagonal oxide phase α-PtO$_2$ which has in-plane Pt–Pt distance 3.10 Å and inter-planar distance of Pt layers 4.16 Å, this figure corresponds to oxygen content in a 36 nm thick layer of PtO$_2$. This value is in a very good agreement with the thickness determined independently by crystal microbalance monitor during thin film deposition (40 nm). Within the accuracy of our measurements this agreement also supports the above rendered idea that, under our experimental conditions, the oxide layer is thermally reduced in its entire volume.

The TPR results of CO interaction with PtO$_x$ are shown in Fig. 10. In comparison to the above TPD, both water and oxygen peaks are shifted to lower temperatures (oxygen peak still being positioned near the trailing edge of the main water feature, at 670 K) which is likely a result of the reducing CO environment. Instead of the broad low temperature desorption feature of H$_2$O a distinct peak around 450 K is observed. Indeed, the most prominent are CO (28 amu) and
CO₂ (44 amu) mass signals. The CO₂ production sets off at 440 K and reaches its maximum around 540 K. The complementary drop in the CO intensity reflects the consumption of CO from the gas stream hitting the surface.

Immediately after removing from the TPD chamber the sample was inspected by SEM, see Fig. 6c.

5. Discussion

5.1. Thermal decomposition

The XPS analysis of the thermal decomposition process (Figs. 7 and 8) clearly shows the gradual reduction of the deposited film initially containing platinum only in the Pt⁴⁺ oxidation state (in the form of both dioxide and tetrahydroxide) which starts above 425 K. Until about 600 K only a relatively weak desorption from the surface is seen by TPD (Fig. 9) suggesting that the initial changes
within the layer are predominantly of an internal nature. The disappearance of water O 1s XPS signal around 400 K is probably the result of splitting off of H2O held at the surface by the platinum hydroxide (a process reported at 380 K in [21,27]) and its consequent partial desorption (reported at 420 K in [21]) – notice the slight onset of water signal at this temperature in our TPD. The reduction of the mixed oxide/hydroxide layer is presumably accompanied with diffusion processes altering its depth profile. The thermally induced changes are initiated by a surface segregation of Pt(OH)2, which was reported as the least stable compound among the present group of platinum hydroxides and oxides [21].

The local increase of Pt(OH)2 at the surface explains why the Pt4+ related Pt 4f signal remains stable at 425 K when the PtO/Pt(OH)2 signal already starts to grow at the expense of PtO2. The reduction from 4+ oxidation state follows, exhibiting maximum of Pt2+ related signal at 575 K and is nearly completed at 625 K when the layer comprises primarily of metallic Pt with a small amount of bi-valent Pt (PtO and possibly Pt(OH)2) which remains stable all the way up to 825 K. The oxygen leaves the surface mainly as water (see Fig. 9) during this stage although some CO and CO2 (a few percent of the total amount of desorbing products) were also detected (mainly in the 400–550 K region), probably being a result of oxygen recombination with surface carbon impurities.

Above 625 K the PtO2-related oxygen intensity in XPS is strongly reduced while both PtO/Pt(OH)2 and H2O signals exhibit a temporary increase indicating a further diffusion of O and OH toward the surface, which corresponds with the onset of a massive water desorption observed by TPD (640–760 K). A plausible explanation is that the thermodynamically more stable dihydroxyl is decomposed at this point and the OH species accumulate at the surface, recombine to H2O and thermally desorb. This leads to the final decrease of the total XPS O 1s intensity, leaving majority of platinum in metallic form (Fig. 7b) with only some residual PtO which further diminishes with increasing temperature. Between 725 and 775 K the XPS intensity of all oxygen components vanishes completely, again being in a perfect accord with our TPD data revealing a distinct desorption of molecular oxygen with the maximum at 745 K which overlaps with the trailing edge of the water desorption peak, as well as with TPD of high-coverage O on Pt(1 1 1) and Pt(1 0 0) surfaces exposed to atomic oxygen [28]. It was also demonstrated in [21] that at 700 K it is adsorbed O only that is left on the surface of the previously oxidized platinum and, furthermore, that a thin platinum oxide layer (which remains at the surface in the final stage of thermal decomposition) possess extra stability compared to bulk PtOx due to adhesion to the underlying metal surface [29,30].

Accompanying phenomena of the thermal reduction of the mixed platinum oxide/hydroxide layer is its restructuring into irregular islands clearly visible in SEM (Fig. 6b), already registered on PtO2/Si (Fig. 1b). Since even the highest applied annealing temperature of 825 K is too low to induce such a massive surface restructuring of the already reduced Pt [31] it has to be due to the removal of lattice oxygen and thus occurs in the course of the decomposition process.

5.2. CO oxidation

The onset of CO2 production which is seen around 440 K in both low (Fig. 10) and high pressure (Fig. 5) of CO, indicating the beginning of the reduction process, coincides with the appearance of metallic Pt 4f signal in photoelectron spectra (Fig. 7). High pressure reaction of the CO+O2 mixture was detected to occur around 440 K as well.

The linear parts (1) and (2) of the Arrhenius plot in Fig. 4 reflect the stability regions of the CO oxidation, while the non-Arrhenian transition region between 480 and 530 K indicates a change of the reaction conditions due to the reduction of the PtOx layer. As was shown by comparison of annealing in vacuum (Fig. 9) and in a gas flux containing CO (Fig. 10) the presence of CO facilitates reduction of platinum oxide (shifting the TPD peaks effectively by 80–100 K in 10−3 Pa of CO). Thus, with CO the transformation between fully oxidized and almost completely metallic phase can be expected to complete near 500 K, considering the virtual disappearance of oxygen monitored by XPS (Fig. 8) at about 600 K in vacuum. Accordingly, the CO oxidation activity of the PtOx sample drops around 500 K to reach the activity of the pure magnetron-sputtered platinum.

The apparent activation energy (0.78 ± 0.05) eV for CO oxidation in the low temperature range (440–480 K) calculated from the TPR data corresponds well with most literature data obtained experimentally or theoretically on more open or less coordinated platinum crystallographic faces [4,32–34]. The activation energy increases to (0.96 ± 0.03) eV in the high temperature region, just slightly below the value measured on Pt/Si (1.07 ± 0.02) eV (compare to 0.98–1.05 eV reported on Pt(1 1 1) [35,36]).

The irreversible nature of the catalyst modification is seen from the descending part of the TPR curve achieved during the sample cool-down (see inset of Fig. 4) which can be fitted with a single exponential, as well as the fact that the subsequent TPR run under identical conditions (not shown herein) followed the same shape.
as the descending branch. SEM images (Figs. 1 and 3) confirm that, along with the composition change (reduction), variation of morphology occurs during the reaction. The formation of a cracked granular structure can be well explained by reduction of the film volume due to removal of lattice oxygen.

It is commonly agreed that on metallic platinum surfaces CO oxidation proceeds via Langmuir–Hinshelwood (LH) mechanism [4,35,37,38]. In this case, oxidation of surface bound CO molecule is allowed only if two neighboring free Pt sites for dissociative adsorption of O2 are available, making the adsorption of CO and O2 competitive process. Adsorbed CO tends to block Pt surface, partly due to its stronger bonding to Pt and partly due to the fact that O surface diffusion is slow compared to CO diffusion.

In contrast, on bulk-oxidized platinum the CO bonding is much weaker, CO diffusion is suppressed [39], and oxygen is already available at the surface and can be further supplemented via diffusion from the oxide volume. It makes platinum oxide potentially more active for CO oxidation at lower temperatures as compared to metallic Pt despite its lower intrinsic reactivity [40]. The limiting factor determining the overall turnover frequency on PtOx is, in turn, the short residence time of CO molecule on the surface.

In our TPR experiment no CO2 was detected under 400 K but it started to appear above 400 K, simultaneously with the beginning of oxide reduction as detected by XPS. It suggests that co-existence of both (oxidic and metallic) phases is responsible for the enhanced low-temperature reactivity, where oxidized Pt serves as an oxygen supply to promote oxidation of CO adsorbed preferentially on metallic Pt. Since the rate-limiting step of oxygen dissociative chemisorption on Pt does not come into play here the oxidation activity is significantly higher than on pristine platinum at the same temperature.

The TPR with pure CO presented in Fig. 5 provides evidence that the enhanced reactivity of platinum oxide is not driven by the consumption of lattice oxygen, in other words, the platinum oxide serves primarily as a catalyst not as a reactant. In the absence of gaseous O2 there are only two potential sources of oxygen – lattice O of the platinum oxide (or, to some extent, hydroxide), and O from CO, the latter requiring activation of CO molecule leading to its dissociation. The relatively abrupt cutoff of the CO2 production between 462 and 470 K suggests that the stock of oxygen needed for this particular reaction channel is limited, which is only true for the lattice oxygen. A quantitative analysis of this process shows that the amount of CO2 that evolves from the surface as the result of PtOx reduction by pure CO (calculated from 44amu mass signal time integral) is over three orders of magnitude lower than the total amount of CO2 produced during the CO + O2 TPR. Hence, it rules out the possibility that the higher low temperature oxidation activity of the oxidized versus metallic Pt is due to the irreversible consumption of lattice oxygen.

The further, much less intensive CO oxidation above 470 K proceeds exclusively, or at least substantially, through reaction of CO with O adsorbed on Pt as a product of CO dissociation since the only available oxygen is that carried by CO. Assuming the C–O bond scission is the rate-limiting step of the CO2 generation in this case, the above interpretation is consistent with the literature data of model studies of CO interaction with less densely packed platinum surfaces, reporting CO dissociation temperatures in 473–548 K range [4,41–43]. Generally, the heat of CO chemisorption on Pt increases with metal surface density [44] and lower activation energy for C–O bond activation is observed on less coordinated surface sites of Pt as CO is known through the literature to dissociate exclusively on step or kink sites on platinum, probably via production of platinum binary carbonyl precursor [41]. Thus on our highly corrugated reduced surface we can expect to see the secondary reaction onset near the lower temperature side of the above range.

Since the total amount of oxygen in our PtOx layers is not sufficient to account for the quantity of generated CO2, it is important for the sustainability of the reaction that the oxygen stock is continuously replenished. We suggest that this happens via Mars–Van Krevelen redox process [45] in which platinum surface is continuously locally reduced and reoxidized, typically accompanied with roughening of the catalyst surface [46]. The platinum caticonic sites are assumed to play a crucial role here due to their high affinity for oxygen and the forementioned weaker bonding to CO (locally preventing CO poisoning). The redox equilibrium is retained until a threshold temperature for direct thermal decomposition is reached, i.e., when oxygen diffusion rate through the PtOx thin film exceeds CO + O recombination rate at the surface.

Indeed, the stability driven by the Mars–Van Krevelen process depends on the partial pressure of oxygen which needs to be above the so-called dissociation pressure of the platinum bulk oxide at a given temperature [30]. As the temperature is increased the excess oxygen leaves the surface in the form of O2 without taking part in the reaction and the oxide layer is reduced gradually to metallic platinum. This chemical state is irreversible under our reaction conditions (mildly oxygen rich). Under oxygen-lean conditions, on the other hand, PtOx reduction accelerates as soon as CO oxidation ignites and the oxide layer is simultaneously reacted away and thermally decomposed very rapidly as in Fig. 5.

SEM inspection of various PtOx thin films deposited on different substrates after high-temperature exposure to CO-containing gas stream showed a massive roughening of the originally smooth oxide layer, compare Fig. 1c with a for Si, Fig. 2b with a for MWCNT (high-pressure experiments), and Fig. 6c with a for Ta substrate (low-pressure experiment). The observed change of PtOx thin film morphology is consistent with the previous finding that the oxide has undergone a major (if not complete) reduction during the reaction, however the fine details of the texture differ from the result of purely thermal process (compare Fig. 6b and c; see similar result in [54]). The observed difference could be due to the increased surface mobility during the oxide reduction accompanying Mars–Van Krevelen process [45,47].

6. Conclusions

In this work, both model and real catalysts based on PtOx were examined under realistic reaction conditions and correlated with characterization of the same compound under UHV. Magnetron sputtered PtOx thin film exposed to ambient air comprises of a mixture of platinum dioxide and tetrhydroxide (the latter presumably accumulated near surface), hence all the platinum is initially present in ionic form with exclusively 4+ oxidation state. Upon heating it undergoes structural phase transition through a lower oxidation degree (Pt4+) all the way to fully reduced metallic platinum with only small amounts (a few at.%) of stable Pt2+ residuum. This process is accompanied with a significant roughening of the

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“[41] It should be mentioned, though, that the oxidation/reduction transitions of the surface can be, in general, reversible with a significant hysteresis [3,47]. With increasing coverage of Oads, the binding energy of chemisorbed oxygen rapidly decreases due to repulsive lateral O–O interactions and the surface-oxide formation may become favorable [48]. It was demonstrated that during CO + O2 reaction at high pressures on Pt(1 1 1) [49], Pt(1 1 0) [3], and Pt(1 0 0) [50] under strongly oxygen-rich conditions and sufficiently large oxygen partial pressures the metal surface can spontaneously restructure and reoxidize, switching to significantly higher reaction rate. Several research groups also reported reversible chemical bistability on Pt [48] (or, more specifically, on Pt(1 1 1) [38] and Pt(1 0 0) [51]) which exhibits switching between metallic and oxidic surface phases. The oscillatory behavior of CO oxidation reaction was ascribed to a reversible CO-blocking mechanism, or by formation of non-reactive oxides on polycrystalline Pt [52]. However, this scale of re-oxidation requires much higher Pox /P2O ratio [53] than we used in our experiment.”
surface. The reduction process is facilitated in the presence of CO which consumes lattice oxygen from the thin film to form CO₂.

On pure platinum, CO₂ is generated through Langmuir–Hinshelwood (LH) mechanism between adsorbed CO and O, which is produced by dissociation of O₂ and/or CO, depending on the fraction of oxygen in the reaction mixture. The rate limiting step is oxygen molecule dissociation which is at lower temperatures rather limited due to the surface blocking by adsorbed CO. On partially reduced platinum oxide, on the other hand, the CO oxidation is governed by bifunctional mechanism where CO adsorbed primarily on a metallic platinum site reacts with oxygen bound to a catonic Pt center which continuously re-oxidizes through Mars–van Krevelen process, resulting in significantly higher reaction rate at low temperatures (below ca. 475 K). Thus, under sufficient partial pressure of oxygen, the PtO thin film remains stable and is capable of permanently providing higher CO oxidation reactivity at lower temperatures than conventional Pt-based catalysts, unless its temperature is increased to a point where it thermally decomposes.

From practical point of view, such bifunctional catalyst where co-operation of oxidic and metallic phases take place offers a great level of tunability, facilitated by the use of very versatile and straight-forward magnetron sputtering technique. In relation to fuel cell applications, platinum-oxide-based compounds can contribute to high tolerance for CO (which is a vital parameter for PEMFC catalysts) especially considering typical working conditions of PEMFCs (relatively low temperatures) at which PtO₂ is capable of providing high efficiency for CO oxidation. It was also demonstrated under realistic conditions that the absolute CO₂ yield can be further enhanced significantly by using a highly porous support such as MWCNT without negatively altering catalytic properties of the active component.

Acknowledgements

This work is a part of the research programs no. KAN100400702 financed by the Czech Academy of Science, and the projects #204/11/1183 and 13-10396S financed by the Czech Science Foundation. M.V. also acknowledge the support of the 202/09/H041 project of the Czech Science Foundation.

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