Efficient Ceria–Platinum Inverse Catalyst for Partial Oxidation of Methanol
Anna Ostroverkh, Viktor Johánek,* Peter Kúš, Romana Šedivá, and Vladimír Matolin
Department of Surface and Plasma Science, Charles University in Prague, V Holesovickach 2, 180 00 Prague 8, Czech Republic

ABSTRACT: Ceria–platinum-based bilayered thin films deposited by magnetron sputtering were developed and tested in regard to their catalytic activity for methanol oxidation by employing a temperature-programmed reaction (TPR) technique. The composition and structure of the samples were characterized by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Both conventional (oxide-supported metal nanoparticles [NPs]) and inverse configurations (metal with oxide overlayer) were analyzed to uncover the structural dependence of activity and selectivity of these catalysts with respect to different pathways of methanol oxidation. We clearly demonstrate that the amount of cerium oxide (ceria) loading has a profound influence on methanol oxidation reaction characteristics. Adding a noncontinuous adlayer of ceria greatly enhances the catalytic performance of platinum (Pt) in favor of partial oxidation of methanol (POM), gaining an order of magnitude in the absolute yield of hydrogen. Moreover, the undesired by-production of carbon monoxide (CO) is strongly suppressed, making the ceria–platinum inverse catalyst a great candidate for clean hydrogen production. It is suggested that the methanol oxidation process is facilitated by the synergistic effect between both components of the inverse catalyst (involving oxygen from ceria and providing a reaction site on the adjacent Pt surface) as well as by the fact that the ability of ceria to exchange oxygen (i.e., to alter the oxidation state of Ce between 3+ and 4+) during the reaction is inversely proportional to its thickness. The increased redox capability of the discontinuous ceria adlayer shifts the preferred reaction pathway from dehydrogenation of hydroxymethyl intermediate to CO in favor of its oxidation to formate.

INTRODUCTION
Hydrogen generation from methanol is an attractive means of H₂ production for, for example, proton exchange membrane (PEM) fuel cells or hydrogen-based combustion engines because methanol is an abundant and environmentally friendly liquid fuel that can easily be transported and stored. In addition, methanol has a high atomic ratio of H/C compared with other common fuels. Catalytic partial oxidation of methanol (POM, CH₃OH + 1/2O₂ → 2H₂ + CO₂) is considered the best way to convert methanol to hydrogen because it offers the advantage of an exothermic reaction, 100% hydrogen yield, and release of carbon in the form of harmless carbon dioxide (CO₂). Among the commonly used platinum (Pt)-group catalysts, Pt is recognized to be the best monometallic catalyst for methanol oxidation. However, apart from POM, methanol on Pt also converts to side products such as HCHO, formic acid (HCOOH), H₂O, or carbon monoxide (CO). Adsorbed CO is found to be the most stable surface adsorbate among all other methanolic fragments, blocking the adsorption sites on the Pt surface. The CO oxidation reaction is restricted to the boundaries between competing domains of adsorbed CO and oxygen, leading to reaction hysteresis or even deactivation of the catalyst. The same problem of surface blocking has been dealt with in methanol electrochemistry studies and methanol fuel cell applications. Bi Metallic alloys (with Rh, Ru, Ir, etc.) or metal-oxide systems have therefore been implemented widely to overcome this issue. Particularly, cerium oxide (ceria), used as a support or promoter of a Pt catalyst, has received considerable attention for its unique ability to act as an efficient oxygen buffer because it can store and release oxygen reversibly. The low energetic cost to form an oxygen vacancy makes ceria a great candidate for an active catalyst in all Mars–van Krevelen-type oxidation–reduction reactions.

A typical (conventional) catalyst consists of a dispersed metal supported on an oxide substrate. The promoting effect of ceria is commonly attributed to an enhanced O₂ dissociation rate at the oxide or metal–oxide interface; the cooperation between oxidic and metallic components of the catalyst is then mediated by the spillover of adsorbed reactants and reaction intermediates. Another important aspect turns out to be a direct mutual interaction between the oxide and metal, which can lead to chemical or structural changes, for example, increased redox activity or enhancement of the metal dispersion and its stabilization against thermal sintering. It is often observed, however, that under realistic reaction conditions of...
elevated temperatures and the presence of reactants the nanostructured Pt becomes inevitably encapsulated by ceria.\textsuperscript{5,23,24,26}

A different approach is the so-called inverse catalysts,\textsuperscript{20,26–31} where oxide nanoparticles (NPs) are supported on a (typically continuous) metallic substrate. Such a concept may seem counterintuitive because the design of the conventional catalyst is based on maximizing the effective surface area of the metal component and, eventually, taking advantage of size-related phenomena.\textsuperscript{15,15} However, contrary to many cases of standard oxide-supported metal NPs, the participation of the oxide in the surface reaction can be active. Unlike for ideal (flat and stoichiometric) bulk oxides, the properties of oxide NPs may be influenced by defects such as oxide vacancies\textsuperscript{32–34} and less-coordinated sites at edges and corners, by strain,\textsuperscript{35} or by enhanced electronic interactions with the supporting metal.\textsuperscript{27,29,36} It has been demonstrated that oxygen vacancies present in ceria can provide distinct reactivity\textsuperscript{16,37,38} or, in turn, that the vacancies can be created by the interaction of the oxide surface with adsorbed species.\textsuperscript{33} Moreover, in the inverse configuration, the reactive defect sites present in the oxide overlayers are not covered by metal particles as in the case of a traditional metal/oxide catalyst.\textsuperscript{15}

Several reactions have been examined on ceria NPs supported on a number of (111) faces of fcc metals,\textsuperscript{16} including Pt(111).\textsuperscript{20,21,39,40} Investigations of ceria/metal model inverse catalysts have primarily focused on the CO oxidation reaction,\textsuperscript{20,21,28,29,40} water–gas shift (WGS) reaction,\textsuperscript{30,31,41} and methanol synthesis from CO\textsubscript{2}.\textsuperscript{42} Studied both under reaction conditions and for adsorption properties of some of the individual species such as CO, O\textsubscript{2}, and H\textsubscript{2}O. The typical role of ceria in metals for oxidative reactions such as CO oxidation, WGS, or POM is to adsorb and dissociate either O\textsubscript{2} or H\textsubscript{2}O, especially in the cases where this stage of the reaction pathway does not proceed (or does too slowly) on the bare surface of the respective metal.\textsuperscript{16,23,28,29,31} The insight into elemental processes of interactions of these simple molecules with ceria/metal systems is useful in understanding more complex reactions such as catalytic reforming or oxidation of hydrocarbons, alcohols, carboxylic acids and so forth. However, to the best of our knowledge, no experimental study directly addressing methanol oxidation on ceria/Pt has been published so far. In this work, we present temperature-programmed reaction (TPR) investigation of the methanol oxidation reaction on thin film Pt/ceria and ceria/Pt catalysts prepared by the magnetron sputtering deposition technique. The reactivity measurements are correlated with complementary chemical and structural information obtained by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

### EXPERIMENTAL

**Sample Preparation.** The catalyst thin films were deposited onto a naturally oxidized Si(100) wafer (0.3 mm thick, p-type, 6–12 Ω·cm resistance) held at room temperature by means of magnetron sputtering of 2” diameter CeO\textsubscript{2} and Pt targets mounted on independent magnetrons in the same preparation chamber. Sputtering was carried out in an Ar base atmosphere at a constant partial pressure of 0.5 Pa. A radio frequency (RF) magnetron (100 W RF power) was used to deposit ceria,\textsuperscript{34} whereas Pt was sputtered using a DC magnetron (20 W DC power). The growth rate of thin films under these conditions was approximately 0.5 nm/min (measured by a quartz crystal microbalance).

**Analytical Methods.** The morphology of the deposited layers was examined by means of SEM using the MIRA 3 (Tescan) microscope operating at a primary energy of the electron beam of 30 keV. XPS was used to investigate the chemical composition of the samples. It was performed in an ultrahigh vacuum chamber operating at a base pressure lower than 10\textsuperscript{−9} Pa equipped with a SPECS Phoibos MDC 9 energy analyzer. An aluminum X-ray source was used (total energy resolution ΔE = 1 eV; photon energy hν = 1486.4 eV) for all measurements.

Catalytic activity measurements were characterized by the TPR method conducted in a custom-built laboratory microreactor system. The actual reactor comprised the analyzed sample (13 × 13 mm) sandwiched between a PID-regulated resistive heater at the bottom and a silicate glass with two feeding holes and a network of channels for effective gas distribution over the sample surface at the top, forming a small microreactor cell volume. Silicon rubber sealing (100 μm thick) was placed around the perimeter of the sample to prevent leakage. The reactor cell was enclosed in a relatively massive metal block with an integrated thermocouple (K-type) to assure good thermal stability and spatial homogeneity. All experiments were carried out at a total gas pressure of 1 bar and the sample temperature ranging between 360 and 600 K; the heating rate of the temperature ramps was set to 2 K/min.

The stream of reactants containing O\textsubscript{2} + CH\textsubscript{3}OH with a mutual molar ratio of 1:2 was produced by mixing pure oxygen (Linde gas, 99.99% purity). The flow rates were adjusted using Alicat Scientific mass flow controllers. All stainless-steel tubing between the saturator and the reaction cell was heated to about 360 K to prevent the condensation of methanol vapor before reaching the sample. The product stream was sampled through a manual metering valve and continuously monitored using a quadropole mass spectrometer (QMS, Prifer Prisma 200) connected to a vacuum chamber with <10\textsuperscript{−6} Pa base pressure. A cold trap (laboratory glass condenser immersed in a Dewar flask filled with ethanol cooled to 190–200 K) was put into the line to prevent the unreacted methanol vapor from entering the vacuum chamber with a QMS. The relative molecular concentrations of the main products H\textsubscript{2} (m/z = 2 amu), CO (28 amu), and CO\textsubscript{2} (44 amu) were calculated from QMS current signals using sensitivity factors obtained experimentally by calibration using pure gases. The calibrated intensity of the He signal (4 amu) was used as a reference to calculate the probability of methanol conversion to each of the above products, which can be further expressed as a production rate in molecules·cm\textsuperscript{−2}·s\textsuperscript{−1} using the known methanol flow rate through the reactor and the exposed surface area of the sample. The lowest measurable signal is determined by the QMS detection limit and by the level of the background atmosphere in the detection chamber. When expressed in terms of the production rate, our detection limits for the three presented products are approximately 5 × 10\textsuperscript{13} cm\textsuperscript{−2}·s\textsuperscript{−1} (for H\textsubscript{2}) and 1 × 10\textsuperscript{15} cm\textsuperscript{−2}·s\textsuperscript{−1} (for CO and CO\textsubscript{2}).

### RESULTS AND DISCUSSION

**Conventional Configuration: Pt on Ceria.** The magnetron sputtering technique proved to be a very versatile and relatively simple means of deposition of multicomponent thin films on almost any type of substrate.\textsuperscript{35–47} On the other hand, layers sputter-deposited at room temperature are generally thermodynamically unstable, and therefore, they typically undergo morphological and chemical changes during the initial reaction cycle. In this section, we demonstrate this stabilization process, but in the situations where we make comparisons of different samples, only the results of the second TPR cycle measurements will be presented to provide relevant comparisons with respect to real long-term operating conditions.

We started with a conventionally designed Pt–ceria catalyst as a benchmark, comprising nanometer-sized Pt NPs (average
thickness of 1 nm) supported on a continuous CeO$_2$ substrate (9 nm thick) on an oxidized silicon wafer. In Figure 1, the Arrhenius-type plot of hydrogen, CO, and CO$_2$ yield from methanol oxidation is shown for surface temperatures between 300 and 600 K for both TPRs.

![Figure 1. Arrhenius plot of the amount of hydrogen, CO, and CO$_2$ produced from methanol oxidation on Pt NPs on CeO$_2$ in the course of the first (dotted lines) and second (solid lines) TPR cycle.](image)

The reaction rate and selectivity differ significantly between the two consecutive reaction cycles, indicating a substantial modification of the catalyst during the first TPR. XPS analysis (not shown herein) suggests that these changes are mainly of structural nature, that is, related to diffusion of the deposited material or its morphological restructuring, because only very minor or no chemical shifts were observed in the spectra of the building elements (Ce, O, and Pt) after the reaction.

The apparent activation energy ($E_a$) for hydrogen production (calculated from the slope of the Arrhenius plot) in the lower part of the temperature range (up to about 500 K) increases from 0.47 to 0.81 eV between TPR 1 and 2. Although the mutual ratio of CO$_2$ to CO concentrations is roughly equal in both cycles, their absolute values drop by nearly 1 order of magnitude in the second run. Optimally, if the surface reaction follows the POM scheme, one should detect H$_2$ to CO$_2$ with a 2:1 molecular ratio and no CO production. In the second TPR, the former is only true above $\sim$530 K, but the presence of additional CO incommensurate with the hydrogen signal indicates that some methanol molecules follow a parallel reaction channel, most likely the methanol combustion (MC) reaction (CH$_3$OH + O$_2$ → 2H$_2$O + CO). Another potential reaction, direct methanol decomposition (MD, CH$_3$OH → 2H$_2$ + CO), can be ruled out as it would contribute to the overall hydrogen signal unlike MC, where hydrogen is released as a part of water molecules (note that the water signal could not be detected directly with our setup as mentioned in the Experimental Section). More thorough discussion devoted to the details of the reaction mechanism of methanol oxidation will be provided in the next section (Reaction Mechanism).

In Figure 2, the hydrogen yield from the Pt/CeO$_2$ catalyst in the second TPR cycle is compared to the reactivity of individual components of the catalyst, that is, both pristine CeO$_2$ and Pt NPs grown directly on the wafer, as well as to a continuous sputter-deposited Pt thin film (10 nm thick). Compared with all other samples presented in Figure 2, the reactivity of pristine CeO$_2$ is negligible up to $\sim$530 K, and even at 600 K, it is nearly an order of magnitude lower. Regarding the Pt references, the activation energy for hydrogen production on pure Pt particles is lower than that on continuous Pt as could be expected because NPs feature higher concentration of surface steps and kinks, which are more reactive than in-plane Pt atoms.$^{12,14,48}$ As a result, the Pt NPs are catalytically more efficient at lower temperatures. The slightly concave character of the Arrhenius plot is likely because of the temperature-dependent concentration of the adsorbate on the substrate, which affects the flux of reactant molecules to NPs via reverse spillover. For both pure Pt samples, the ratios of CO$_2$/H$_2$ and CO/H$_2$ remain constant at 3.5(±0.3) and 0.5(±0.05), respectively, in the whole temperature span, indicating that the methanol oxidation follows the same reaction route.

Generally, our observations show that much less CO and CO$_2$ are produced on Pt/CeO$_2$ than on pure Pt; thus, despite the very similar overall efficiency of the Pt/CeO$_2$ catalyst, the main difference comes in the selectivity, which is above 500 K strongly in favor of POM in the presence of ceria. At lower temperatures, however, a significant fraction of methanol is reacted to an undesirable mixture of CO and H$_2$O as the activation energy for the hydrogen production pathway is too large. Nevertheless, this catalyst still performs somewhat better than Pt NPs alone (>$\sim$480 K) or the Pt thin film (<$\sim$600 K) so that some synergy between Pt and ceria takes place here (which will be discussed below in more detail); see Figure 2. A major drawback, however, is the large instability of the sputter-deposited Pt/CeO$_2$ system. The potential mechanisms responsible for the decay of its catalytic activity when exposed to reaction conditions might be (1) Pt deactivation by coke formation at the surface, (2) surface smoothing or coalescence of Pt NPs, or (3) encapsulation of Pt by ceria. In the following, we will address all of the mentioned phenomena.

Deactivation by carbon deposit can be easily ruled out on the basis of our XPS measurements, which did not show any additional intensity in the C 1s region; in fact, the amount of
carbon-related signal has reduced after 2 TPR cycles to about 20% of the original value, probably because of the oxidative removal of the carbon traces accumulated during magnetron sputtering.

The effect of thermally induced surface smoothing and coalescence can be actually illustrated for the pristine 1 nm Pt sample—see Figure 3a with a conventional plot of H₂ conversion rate versus temperature. For both the fresh (TPR 1) and stabilized samples (TPR 2), the oxidation starts above 400 K and the hydrogen production grows exponentially. The growth rate is, however, notably larger for the freshly deposited Pt (corresponding apparent activation energy \( E_a = 0.83 \text{ vs } 0.67 \text{ eV} \)). The higher activity at lower temperatures is commonly attributed to the fine dispersion of magnetron-sputtered Pt into NPs and to its high atomic-scale surface roughness, providing a larger effective surface area as well as higher abundance of more reactive low-coordinated Pt atoms. Above 480 K, a loss of performance is observed, most likely because of the oxidative removal of the carbon traces accumulated during magnetron sputtering.

When the same amount of Pt is deposited on ceria, the situation becomes quite different as can be seen in Figure 3b (representing a conventional plot of the hydrogen data included in Figure 1). After the first run, the catalyst has clearly undergone a substantial restructuring leading to higher efficiency at lower temperatures (<530 K), but at the same time, it lacks performance at higher temperatures at which the desired selectivity toward POM is the highest (as is already shown in Figure 1). The shifting of the reaction mechanism from water production to hydrogen production during the sample stabilization process (i.e., mainly in the final course of the first TPR) corresponds to the concept of encapsulation rather than a purely morphological change (coalescence or cracking of the thin film), whereas methanol oxidation on Pt is known to proceed via the COad intermediate, with CO₂ and H₂O being the principal products under 600 K (also confirmed by our TPR); on ceria, the mainly detected products were H₂ and CO (see Figure 5 below). The encapsulation of Pt has also been reported recently for similar platinum—ceria systems. Another supporting experimental finding in favor of encapsulation is provided by our XPS measurements of Pt/CeO₂ (not shown here), which reveal that the Pt 4f signal drops to 43% of its original value after the first TPR, whereas the Ce 3d signal gains 40%; both values remain unchanged after the second TPR. No change in the oxidation state of Pt and only a slight reoxidation of ceria (stoichiometry coefficient increases from 1.83 to 1.94; see the related discussion in the next section for details) are observed so that the sample modification is primarily because of its restructuring and not of a chemical nature (such as Pt oxidation, Pt–Ce alloying, carbon accumulation, etc.). Under the assumption that Pt NPs are uniformly encapsulated by ceria and do not change their size distribution substantially, we can estimate the thickness of the ceria overlayer. From the magnitude of the Pt signal decay and mean free path of electrons at the kinetic energy of the Pt 4f doublet (~22 Å), we obtain 18.6 Å which accounts for about 5–6 ceria monolayers. If Pt coalescence takes place along with encapsulation, the actual value would be slightly lower.

Interestingly enough, even with Pt most likely completely covered by CeO₂, the sample is still a comparable or even better catalyst (in terms of hydrogen yield) than the bare Pt and far above ceria alone. This does not seem to be in contradiction because ceria has already been reported to be more active in, for example, CO oxidation when supported on Pt despite no Pt atoms being exposed at the surface. The reactivity of such a system stems from the interplay between the oxide and metal, where the surface ceria acts as an efficient oxygen supply for the oxidation reaction and its activity is related to oxygen vacancy formation which is, in turn, promoted by the underlying Pt.

Inverse Configuration: Ceria on Pt. In light of the previous observations, we decided to revert the deposition process to grow ceria thin films on the Pt base layer (20 nm thick) while using the same oxidized silicon wafer as a substrate. We used various amounts of ceria to cover a wide range of configurations from the discontinuous adlayer to the continuous thin film with a thickness similar to the encapsulating layer as discussed above, namely, 0.2, 0.5, 1, and 2 nm.

In Figure 4, an overview of hydrogen production from methanol oxidation in the second reaction cycle is presented in the form of Arrhenius plots for all four CeO₂/Pt samples as well as...
as for reference surfaces of pristine CeO$_2$ (0.2 and 9 nm thick) and Pt (20 nm). Regardless of the ceria loading, the reaction onset for CeO$_{x}$/Pt is observed around 400 K, like that for the conventional Pt/CeO$_2$ catalyst. The irregular shapes of the Arrhenius plots reveal a change in the rate-limiting step between competitive reaction regimes. A common feature is two linear segments, first under 450 K and second above approximately 520 K. The initial slope is inversely proportional to the ceria thickness (resulting $E_a = 0.99, 0.88, 0.82$, and 0.56 eV), whereas the high temperature sections are essentially parallel for all samples ($E_a \approx 0.64 \pm 0.03$ eV).

The conversion rates for CO$_2$ and CO formation from methanol are compared in Figure 5 for selected samples only (for better clarity): 0.2 and 1 nm ceria on Pt; both reference catalysts are also included in the graph.

Analogously, as we experienced with ceria-encapsulated Pt in the previous section, the inverse catalysts outperform pure Pt, as measured by its capability to generate hydrogen by methanol oxidation, with only a little exception for the largest ceria loading (2 nm) at higher temperatures (>500 K). As the oxide thickness is increased, the hydrogen yield approaches that of pure ceria. The activity of ceria alone is rather low, but the discontinuous oxide retains the CO$_2$ to H$_2$ molecular concentration ratio close to 1:2 and a low level of CO in the whole temperature range, suggesting that it provides high preference for the POM reaction channel. The most striking observation is the huge gap of 3 orders of magnitude between the production of CO and H$_2$ on the inverse catalyst with the thinnest ceria overlayer.

XPS has been employed to characterize the composition of our catalytic layers at different stages—immediately after deposition by magnetron sputtering, after the first, and after the second methanol oxidation reaction cycle. XPS measurements were performed ex situ, that is, after transferring the samples through air (the exposure to an ambient atmosphere was minimized by keeping the transfer time within minutes).

In Figure 6, the core-level photoelectron spectra of Ce 3d, O 1s, and C 1s are shown for the 1 nm thick CeO$_2$ layer grown on continuous Pt after deposition and after the first and the second TPR run; XP spectra of other ceria/Pt samples are qualitatively similar. Commonly for all of the spectral regions shown, the major change in the surface composition happened during the first reaction cycle, whereas hardly any differences are discernible between TPR 1 and TPR 2.

The rather complex spectra of ceria in Figure 6a consist of three $3d_{3/2}$−$3d_{5/2}$ spin−orbit-split doublets ($f_1$, $f_1'$, and $f_1''$) arising from 4f-state hybridization in both the initial and the final states of 4-valent ceria (Ce$^{4+}$) in CeO$_2$. Similarly, the two additional doublets labeled $f_2$ and $f_2'$ originate from the electronic states of 3-valent ceria (Ce$^{3+}$) characteristic of Ce$_2$O$_3$. The ratio of the total areas of Ce$^{4+}$ and Ce$^{3+}$ related spectral components (after a proper fitting) may be therefore used to estimate the stoichiometry of a given ceria compound. Another way of ceria stoichiometry determination is to utilize the O 1s spectrum (see Figure 6b), which contains two CeO$_x$-related components, namely, lattice oxygen of CeO$_2$ (Ce$^{4+}$-related peak) at $\approx 529$ eV and that of Ce$_2$O$_3$ (Ce$^{3+}$ related) around $\approx 530.5$ eV.

The additional feature around 531 eV in the O 1s spectra of the as-prepared sample has been attributed to the signal from chemisorbed oxygen binding to the nearby Pt atom. After the
reaction, the CeO$_2$-related peak is strongly suppressed in accordance with the oxide reduction observed in the Ce 3d region. Furthermore, a sharp peak develops at 532.4 eV originating from the underlying natural oxide layer of the Si(100) surface, which suggests that the integrity of the deposited thin film has been disrupted. A shoulder at the higher binding energy (BE) side (approximately between 533 and 534 eV) most likely contains contributions from adsorbed OH groups and/or water molecules.

The peak assignment in the C 1s region (Figure 6c) is as follows: The components in the low BE side (284.1–284.8 eV) contain contributions from sp$^2$ and sp$^3$ hybridized carbon; the fine structure related to individual C 1s peaks originating from C–C bonds in different configurations is indistinguishable by regular XPS because of its low energy resolution; still, the integral signal of the spectral features around 284.5 eV provides a good measure for the total amount of carbonaceous deposit. The major component after the TPR is the peak at 285.1 eV, which originates from carbon in the C–H bond, whereas oxygen-bonded carbon should exhibit three components (C–O and C–O–H at ~285.5–286 eV, C=O at ~287.3 eV, and O=C=O at ~289.8 eV). It can be seen that during the methanol oxidation reaction the carbon impurities (which were probably embedded into the thin film during magnetron sputtering) have reacted off almost completely, whereas a small amount of hydrocarbon residuals remained on the surface.

The Pt 4f spectra (not shown here) confirmed that Pt remained completely in the metallic state with the 4f doublet centered at a bulk value of 71.0 eV; hence, no noticeable oxidation or alloying of Pt with cerium took place in the CeO$_x$/Pt thin films.

In Figure 7, a quantitative evaluation of all four CeO$_x$/Pt layers is made by comparing their estimated stoichiometry coefficient $x$ at each step (as prepared, after TPR 1, and after TPR 2). The stoichiometry calculation based on Ce 3d and O 1s spectra yielded very similar values; the points in the graph represent averaged data from both methods. In the inset of Figure 7, the dependence of the stoichiometry coefficient $x$ of the as-prepared ceria adlayer on its average thickness.

![Figure 6. Photoelectron spectra of the 1 nm CeO$_x$ layer on Pt before and after both TPRs: (a) Ce 3d, (b) O 1s, and (c) C 1s core-levels. The suggested peak assignments are indicated in the spectra.](image)

![Figure 7. CeO$_x$ stoichiometry coefficient $x$ of different ceria loadings on the continuous Pt thin film calculated from XPS data. Inset: the dependence of the stoichiometry coefficient $x$ of the as-prepared ceria adlayer on its average thickness.](image)
initial stoichiometry of our Pt(1 nm)/CeO$_2$ layer was estimated based on the XPS data to be 1.83. In contrast to the inverse catalysts, the conventional Pt/ceria thin film underwent a slight reoxidation during methanol oxidation to nearly perfectly stoichiometric ceria dioxide (x = 1.94). The connection between charge transfer from the metal to oxide and generation of Ce$^{3+}$ species in the inverse catalyst has already been shown, for instance, in the case of CeO$_x$/Cu(111).$^{29,30}$

Concerning the physical properties of our inverse catalysts, all as-prepared samples exhibit essentially the same relatively flat morphology with only mild granularity (approximate grain size of ∼5 nm), which matches the structure of the underlying Pt thin film (see Figure 8). However, a disordered network of tiny cracks is also visible in the bilayer with the thinnest (0.2 nm) CeO$_2$, in accordance with the fact that the amount of material is not sufficient to create a complete monolayer of ceria. After the TPR procedure, the density of cracks is preserved, but they become more apparent because of ceria layer compression, most likely caused by its reduction and coalescence. The structure of the CeO$_2$(0.2 nm)/Pt(20 nm) sample does not change with additional TPR cycles. A different morphological evolution is observed for thicker bilayers: the common behavior is the appearance of round pits within an otherwise homogeneous surface, in accordance with the emergence of the SiO$_2$-related peak in photoelectron spectra (Figure 6b). After the first reaction cycle, the average size of the pits is roughly proportional to the thickness of ceria, whereas after the second TPR, all three samples (0.5, 1, and 2 nm ceria) end up with basically the same morphology (pits up to 40–50 nm in diameter).

The above behavior can be compared with that of bare Pt; see Figure 9. The morphology of the as-deposited Pt thin film (20 nm) shown in Figure 9a is more rough than that after adding a ceria overlayer (compared with the 1st line of Figure 8). When the surface is subjected to methanol oxidation conditions, its structure changes gradually toward a more smooth surface with frequent pits with a typical diameter of 10–25 nm after 2 TPR cycles (Figure 9d), indicative of an intensive coalescence of the originally nanostructured metal surface. This process is not driven solely by temperature but is rather stimulated by the presence of the reactive environment as evidenced by the reference experiment of annealing the as-deposited Pt layer at 600 K under vacuum for an extended time of 10 h (Figure 9b), which resulted in only a mild cracking of
the layer without any discernible smoothing or coalescence. The oxygen-induced sintering of oxide-supported Pt has already been reported in the literature,58,59 the presence of methanol vapor or methanol oxidation intermediates can also play an additional role in Pt restructuring.

On the basis of the above observations, it can be concluded that with the presence of a ceria adlayer the sputter-deposited thin film of Pt is less prone to sintering during the oxidation reaction.

**Reaction Mechanism.** Without an in operando surface analytical technique, it is not possible to directly determine the particular elementary steps of the reactions, which take place at the surface of our catalysts. Nevertheless, the integral information provided by the QMS may allow us to distinguish between different overall reaction schemes. Applied to our case, the selectivity toward a particular reaction can be calculated from relative (calibrated) concentrations of H2, CO, and CO2 and correlated with the variation of the O2 signal on the reactant side of the equations (it should be reminded in this context that we were not able to measure the concentrations of water and majority of carbohydrate species directly because of the condensation or freezing of these substances in the cold trap). For instance, the two and only final products of POM are hydrogen and CO2 in a 2:1 molecular ratio; hence, any deviation from this reaction stoichiometry or the occurrence of CO in the exhaust stream would indicate the participation of alternative pathways because no surface carbon accumulation takes place as has been verified by XPS (see Figure 6c).

Let us now discuss the whole reaction scheme of the methanol oxidation process. The initial bonding of the methanol molecule to the surface happens via the dissociation of either the C–H or O–H bond to form either CH3OHad (hydroxymethyl) or CH2Oad (methoxy) adspecies, respectively. Hydroxymethyl further dehydrogenates to CO or is partially oxidized to an HCOO radical (formate), which can be oxidized again to CO2 or bound to an available Had atom to yield HCOOH or methyl formate (HCOOCH3) when reacted with an additional methanol molecule. Partial dehydrogenation of surface methoxy, on the other hand, leads to formaldehyde (HCHOad) which can be desorbed, dehydrogenate completely to COad or proceed to form methylene glycol (or methanediol, CH2(OH)2) via incorporation of water molecules. Regardless of the preceding reaction steps, adsorbed CO molecules can be either desorbed directly or first oxidized to CO2 and then desorbed (complete oxidation of methanol, COM). The whole proposed methanol oxidation mechanism is summarized in Figure 10.

![Figure 10. Reaction scheme of the methanol oxidation process. The final products are denoted with green.](image)

The reactions taking into account all of the possible products mentioned above (except the formation of HCOOCH3, which is just a consecutive step of the HCOOH branch) can be summarized by the following overall chemical equations

1. POM: CH3OH + 1/2O2 → 2H2 + CO2
2. HCHO: CH3OH + 1/2O2 → HCHO + H2O
3. MADOL: CH3OH + 1/2O2 → CH2(OH)2
4. HCOOH: CH3OH + 1/2O2 → HCOOH + H2
5. MC: CH3OH + O2 → CO + 2H2O
6. COM: CH3OH + 3/2O2 → CO2 + 2H2O

On the basis of the above scheme, the selectivity for every particular pathway has been calculated for T > 400 K (the QMS signals are too low for a reliable calculation below this temperature). The resulting set of plots is shown in Figure 11.

There is a common qualitative characteristic of the reaction pattern for all ceria/Pt samples, which can be rendered as follows: The two main reaction channels are POM (1) competing with conversion to HCOOH (4) or, eventually, its methyl ester via sequential binding to another methanol molecule (in fact, we found no evidence of HCOOCH3 in the QMS spectra although it is one of the few organic molecules that should not freeze in the cold trap). The excess of CO2 observed at the beginning of the reaction for ≤1 nm ceria has been attributed to COM (6), presumably originating from direct oxidation on uncovered Pt sites. Regarding POM, we will only consider an overall balance because our experimental data do not allow us to distinguish quantitatively whether it proceeds via the methoxy or hydroxymethyl intermediate branch. On the lower temperature side (up to approximately 430–440 K), the POM selectivity is at its maximum (it is actually the preferred pathway for a ceria thickness of <1 nm). With increasing temperature, the ratio of CO2 to H2 drops, whereas the level of CO remains low or undetectable, which gives evidence for gradual switching in favor of the reaction (4). At even higher temperatures, the main feature observed is the onset or steep rise of CO production, indicating the participation of the MC reaction (5).

Quantitatively speaking, at lower temperatures, the thinner the ceria adlayer, the more likely methanol oxidation will proceed via POM. In fact, the sample comprising ceria NPs on Pt achieved total (100%) POM conversion around 430 K (see Figure 11d). Furthermore, with smaller ceria loading, the amount of generated CO is lower despite the higher absolute reaction efficiency. The onset of CO is observed at very different temperatures (between 380 and 515 K) depending on the ceria thickness.

In hydrogen production applications, POM is the most desired pathway because it allows harvesting of all hydrogen available within the methanol molecule, whereas it generates relatively inert and environmentally friendly CO2 as the only byproduct. On the contrary, in most cases, the MC channel is the least desired one because it generates CO, which acts as a poison both for the catalyst and for our environment. The carbohydrate compounds, on the other hand, are usually easier to be removed from the product stream than CO (for instance, by further reforming or distillation) or can even be recirculated within the fuel supply provided; they act as a spectator in the catalysis of methanol oxidation. In this regard, the catalyst...
comprising ceria islands (0.2 nm) on Pt turns out to be by far the best with both the highest hydrogen production activity and the lowest absolute content of CO in the reacted gas mixture, accounting for relative concentrations as low as ~0.1% at 330 K and ~1% at 590 K (note that the CO curve in Figure 11d was multiplied 10 times to be discernible in the graph).

We also analyzed carefully other mass signals recorded during the reaction than those plotted in the above TPR graphs. Despite the fact that the majority of carbohydrate species is captured in the cold trap (so that we cannot determine the absolute concentration values), the relative comparisons of residual signals may shed some additional light on our interpretations. The cracking patterns of most simple \((C_1)\) hydrocarbon or carbohydrate molecules overlap to a large extent as they typically contain contributions from fragments such as \(CH_2\) (13−16 amu) and CO, COH, and \(H_2CO\) (28−31 amu). Additionally, higher masses (44−46 amu) are commonly observed for molecules containing a carboxyl group (−COOH). Therefore, although it is often difficult or impossible to exactly determine the abundance of particular parent molecules, an occurrence of specific functional groups can be usually distinguished. It was found (mainly based on 29 and 46 amu signals) that the relative concentration of organic compounds containing COOH moiety increases with decreasing ceria loading, more than 3-fold between 2 and 0.2 nm. This behavior is essentially temperature independent except for the thinnest ceria adlayer where an additional enhancement (up to ~60%) is seen between approximately 430 and 530 K. This clearly suggests the structural dependence of hydroxymethyl conversion to either HCOOH or CO, with more preference toward the former pathway as the amount of ceria is decreased.

In methanol oxidation to \(CO_2\) on transition metals, the most important factor determining the overall reaction rate is whether the oxidation follows a so-called indirect or direct pathway (a dual pathway mechanism first introduced by Capon and Parsons\(^{40−65}\)). The indirect pathway involves a strongly adsorbed intermediate (in this case \(CO\)) whereas the direct one proceeds through a more weakly adsorbed intermediate (here formate or adsorbed HCOOH according to our scheme in Figure 10). In practice, the preferred direct mechanism appears to be difficult to achieve for transition metals. This scenario can change fundamentally if we modify the catalyst in such a way that it will favor the oxidation of the hydroxymethyl intermediate over its dehydrogenation. Alternatively, we can also consider a “workaround” assuming that the reaction runs via the indirect path, but the generated \(CO_{ad}\) is much more efficiently oxidized to \(CO_2\) on Pt thanks to the contribution of oxygen from ceria; hence, the Pt surface is not blocked. However, the above-discussed selectivity analysis rather supports a preference for the non-CO path.

Either way, the key role of ceria in the catalytic oxidation of methanol stems from the ability of cerium ions within the oxide lattice to switch relatively easily between \(Ce^{4+}\) and \(Ce^{3+}\) oxidation states,\(^{16,63}\) driving the release and the uptake of lattice oxygen to or from the reaction environment. In other words, oxygen may not only be supplied to the reaction site through the gas phase but also from the reservoir of ceria via the Mars−van Krevelen redox process.\(^{37}\) It can thus be expected that a correlation exists between the concentration of \(Ce^{3+}\) centers and oxidation activity of the catalyst.\(^{16,27}\) Put into context of the above discussion, the increased oxidation capability of ceria is responsible for the shift of preference toward methanol (bonded as hydroxymethyl adsorbate) oxidation to either \(CO_2\) or HCOOH via the formate intermediate. As a result, the competing pathway of formate dehydrogenation to \(CO\) is suppressed.

There is good evidence for the connection between the reducibility of ceria and its catalytic activity. The deposition of Pt NPs on well-ordered CeO\(_2\) and annealing at 600 K lead to a moderate change in the ceria stoichiometry coefficient to ~1.85 as has been identified previously by resonant photoelectron spectroscopy;\(^{62}\) a similar value (1.83) was obtained from our XPS measurement of the Pt(1 nm)/CeO\(_2\) magnetron-sputtered thin film, which increased to 1.94 after the second TPR as a result of the strongly oxidative environment. The ceria layers supported on Pt presented herein are, on the contrary, almost completely reduced (stoichiometry below ~1.6) when exposed to reaction conditions. Enhanced reducibility of metal-supported ceria nanoislands has been previously demonstrated, for example, for WGS, CO oxidation, or alkane dehydrogenation reactions on CeO\(_2\)/Au,\(^{31}\) CeO\(_2\)/Cu,\(^{27,50}\) and CeO\(_2\)/Pt\(^{20,40,64}\) inverse catalyst, as well as in electrocatalysis.\(^{55}\) A fundamental insight into the interplay between ceria and the supporting metal has been provided for Cu, Ag, and Au in a recent theoretical study,\(^{56}\) concluding that the oxide–metal interaction (which is the main contribution to the generation of \(Ce^{3+}\) states) is dominated by charge transfer, which is stronger for small NPs than for the continuous thin film of ceria. In a recent review,\(^{46}\) the connection between the concentration of \(Ce^{3+}\) ions and reduced dimensionality of a very thin (2 ML)
oxide in the CeO$_2$/Pt(111) model system has been attributed to a combination of higher concentration of low coordination sites and interfacial charge transfer.

It should be noted at this point that unlike in the case of mixed layers of finely dispersed Pt within the CeO$_2$ matrix, where the unique catalytic properties are commonly ascribed to the presence of individual ionized Pt species (namely Pt$^{2+}$), in this case, we deal with two distinct (oxidic and metallic) compounds. Of major importance is the triple-phase boundary between Pt, ceria, and the reactant mixture at which the chemical communication between the surface of ceria and Pt takes place, mainly via oxygen reverse spillover from ceria to Pt. Furthermore, the triple-phase boundary can contribute to higher reactivity by providing additional OH$_{ads}$ species for the oxidation of potentially poisoning carbonaceous species.

**Long-Term Performance.** To prove a practical usability of our inverse catalyst, a freshly prepared CeO$_2$/(0.2 nm)/Pt thin film was subjected to a long-term performance (endurance) test, that is, running the methanol oxidation reaction at a few selected temperatures for an extended period of time. The result of such a test is shown in Figure 12, where the hydrogen yield is plotted versus time for three surface temperatures 440, 470, and 500 K.

![Figure 12. Endurance test of the CeO$_2$/(0.2 nm)/Pt catalyst under reaction conditions for 440, 470, and 500 K.](image-url)

In the graph, we marked the reaction onset that occurred in the course of the initial temperature ramp at approximately 405 K, which is in accordance with the start of methanol oxidation during the regular TPR cycle, see Figure 4. When the temperature was raised to 470 K, a gradual increase of hydrogen signal was registered, relatively slow in contrast to the faster transitions from one equilibrium to another because of temperature changes. Presumably, this process reflects the restructuring of the thin film already mentioned in the previous discussion. Once stabilized, the catalyst remains very reliable (as evidenced by the second section at 470 and 440 K) without any measurable performance loss even after more than 10 h of run time.

**Noncontinuous Inverse Catalyst: Ceria—Platinum NPs.** All of the above inverse catalysts were based on continuous Pt thin films in which only a small fraction of the material actively participates in the catalysis of methanol oxidation. By reducing the content of this precious metal, the hydrogen yield per Pt atom could be optimized. Going from thick (tens of monolayers or more) to noncontinuous (near- or sub-monolayer) deposits adds some complexity and opens up an obvious question whether, or to what extent, the total reactivity and the selectivity of the ceria—platinum system will be affected.

In the following, we analyze the methanol oxidation on the sputter-deposited inverse catalyst comprising 0.2 nm ceria on 1 nm Pt supported on the Si wafer. The SEM analysis of the surface reveals a substantial modification of the initial sample morphology after its exposure to the methanol oxidation environment. In Figure 13, the image of the as-prepared sample (a) is compared with the same surface subjected to 2 TPR cycles (b). No structure is resolved by SEM on the fresh surface indicating that the Pt underlayer is initially continuous with a flat morphology. After sample stabilization under reaction conditions, an aggregation of NPs is seen. At the bottom of Figure 13, a schematic depiction of the sample structure before and after the reaction has been suggested.

The TPR results presented in Figure 14a show that the reaction pattern for CeO$_2$/Pt NPs is very similar to that of the equally thick ceria on continuous Pt despite the much lower amount of Pt used and, thus, the different morphology of the catalytic layer. Hydrogen yield exhibits perfectly Arrhenian character in almost the whole temperature range (with only a small deviation above 550 K) indicating a good chemical stability of this catalyst under our conditions. At any point, the fraction of CO in the product mixture stays below 1%, which makes the CO signal practically undetectable below 500 K. In Figure 14b, the estimated selectivities for different reaction pathways are plotted for temperatures above 400 K. In comparison to the continuous inverse catalysts (Figure 11d), the maximum for POM is shifted to slightly higher temperatures, reaching 100% between ~440 and 460 K.

An image analysis of the stabilized sample (Figure 13b) gives a NP density of 5500 μm$^{-2}$ and projected relative coverage of 28%, yielding a particle mean diameter of 8 nm. The same value was obtained independently from the statistics of several direct measurements of randomly selected grains in the image. Taking into account the total thickness measurement (1 nm), we obtain an average height of the particles of 3.6 nm; thus, they can be quite well approximated by a hemispherical shape.
resulting in the effective relative surface area of the catalyst of 55%.

As can be clearly seen in the comparison plot in Figure 15, the addition of the 0.2 nm ceria adlayer brings up to 9-fold enhancement to the catalytic activity of Pt NPs (at 600 K). Yet the absolute efficiency of the discontinuous CeO$_x$/Pt is, within the region of the highest reactivity (between 550 and 600 K), about 2 times smaller compared with that of ceria on continuous Pt. However, if we take into account the effective surface area of the composite NPs (55%), we get basically the same reaction rate per actual catalyst surface. As a result, our CeO$_x$/Pt inverse catalyst achieves a turnover frequency per surface site of approximately 150 s$^{-1}$ at 600 K. Thus, apart from the above purely geometrical considerations, no discernible NP size effect seems to come into play here, so the absolute yield shall be maximized when the substrate is fully covered by the CeO$_x$/Pt bilayer. On the other hand, a slight quantitative difference can be seen in reaction selectivity, which turns out to be even more in favor of POM on this nanostructured surface than for the same ceria loading on continuous Pt, with the maximum efficiency shifted 20 K toward higher temperatures (compare Figures 11 and 14b).

With this in mind, we can conclude that the utilization of the noble metal component could be further optimized by depositing a thinner Pt layer, just enough to be continuous (or nearly so) and to remain such after the methanol oxidation reaction. The actual value of the ideal Pt thickness is thus expected to generally depend on the adhesion energy between the selected substrate and Pt, which brings an additional degree of freedom to the optimization process in the design of the ceria–platinum inverse catalyst.

**SUMMARY**

Thin films based on ceria and Pt were prepared by magnetron sputtering on the Si substrate and tested as catalysts for the methanol oxidation reaction (stoichiometric 2:1 methanol + oxygen mixture at ambient pressure) using the TPR technique in the temperature range 360–600 K.

All of the samples were subject to a stabilization process under the reaction conditions, changing both the morphology and internal structure. The conventional structure comprising Pt NPs on CeO$_2$ suffers from encapsulation of Pt by ceria; nevertheless, the consequence for methanol oxidation is positive—slightly higher H$_2$ yield and better selectivity for POM than bare Pt NPs at the higher temperature region (above 480 K).

To better understand the mechanism of methanol oxidation on ceria-covered Pt, the deposition process has been modified to produce an inverse configuration of the metal-oxide bilayer, with an oxide thickness ranging from 0.2 to 2 nm. Among all CeO$_x$/Pt inverse catalysts investigated in this study, those with a noncontinuous ceria overlayer (0.2 nm average thickness) exhibited distinct behavior, giving the best match of properties required for methanol conversion to hydrogen. The optimal working conditions in catalyzing the stoichiometric (2:1) methanol + oxygen mixture were found to be around 430 K, providing an order of magnitude higher hydrogen yield per surface area than bulk Pt and nearly 100% selectivity toward the POM reaction while generating undetectable amounts of undesired CO. At higher temperatures, a gradual switching to a competing reaction pathway leads to the production of...
HCOOH and hydrogen while keeping the level of CO byproduct very low (below 1%). The mass spectral analysis of the reaction products suggests that the methanol oxidation on CeO$_2$/Pt proceeds primarily via the initial C–H bond scission of methanol and consequent formation of hydroxymethyl and formate intermediates.

The contribution of ceria to the overall reactivity of the ceria–platinum bilayered catalyst has been attributed to high reducibility of ceria. This redox capability is strongly enhanced on ultrathin (discontinuous) ceria. The combination of such extraordinarily active oxide with the presence of surface sites of the partially uncovered Pt metal forms a very reactive triple-phase boundary, where ceria islands serve as oxygen donors to facilitate the oxidation of methanolic intermediates on the nearby Pt sites.

The same effect of ceria doping on reactivity was found to be preserved for noncontinuous Pt as well, which opens room for further optimization of the catalyst by fine-tuning the amount of Pt, its surface morphology, or the level of metal dispersion.

In the applications where the presence of byproducts other than CO$_2$ (mainly HCOOH and CO) in the reacted mixture is not an issue, an absolute turnover frequency for hydrogen of at least 150 s$^{-1}$ can be achieved at 600 K with this type of catalyst.

The suggested CeO$_2$/Pt inverse catalyst represents an excellent example of thermodynamic synergy between different components of the oxide-metal type heterogeneous catalyst as opposed to the conventional configuration of oxide-supported metal NPs, where the support often plays a passive role, or its chemical communication with the active metal strongly relies on surface diffusion (spillover).

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: viktor.johanek@mff.cuni.cz. Phone: +420-22191-2333. Fax: +420-22191-2297.*

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The financial support of the research was provided by the grant LH15277 of the Ministry of Education, Youth and Sports and by the EU (FP7 NMP project ChipCAT No. 310191).

**REFERENCES**

(28) Senanayake, S. D.; Stacchiola, D.; Rodríguez, J. A. Unique Properties of Ceria Nanoparticles Supported on Metals: Novel Inverse