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Promotional Effects and Reconstruction of Pt/CeO$_x$ and Pt/SiO$_2$ Model Catalysts Produced by Electron-Beam Lithography (EBL)

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We have studied the activity and stability of EBL-fabricated Pt/CeO$_x$ and Pt/SiO$_2$ supported model catalysts during catalytic reactions. Different mixtures of $H_2 + O_2$ diluted in argon and $CO + O_2$ diluted in argon have been used in the temperature range 300–475°C. Reaction-induced morphology changes are observed for both types of samples after heat treatments in mixtures of $H_2 + O_2$ diluted in argon. The EBL-fabricated samples are stable for reproducible CO oxidation measurements for at least a period of 50 h at 400°C. Pre-reduction at 400°C is shown to be favorable for CO oxidation in rich mixtures for the EBL-fabricated Pt/CeO$_x$ catalyst, while the opposite is measured for the EBL-fabricated Pt/SiO$_2$ catalyst. Two powder samples, Pt/CeO$_x$ and Pt/SiO$_2$, have also been tested during similar pre-treatment studies. Increased activity for CO oxidation (rich conditions) is found for both types of samples after pre-reduction, compared with pre-oxidation.

Key Words: **Pre-treatment; Pt; ceria; silica; CO oxidation; electron-beam lithography (EBL); reconstruction.**

INTRODUCTION

In recent years there has been a rising interest in a new type of supported model catalysts prepared by electron-beam lithography (1–4), as a complement to other models of supported catalysts (5, 6). These supported model catalysts can be designed with regard to particle size, interparticle distances, and component (e.g., particle–support) interaction. The particle size is controllable, even though the size limit so far lies in the 10-nm range and up (1–4, 7–11). Even in this regime, there may be fundamentally new catalytic effects that can be studied compared with single crystals, foils, etc., such as spill-over effects (12) and new kinetic effects related to communicating facets of single-catalyst particles (13, 14). This size regime is sufficient to model, e.g., "aged" but still operational traditional supported catalysts. 3D-functional units can be designed to model the corresponding structures in practical catalysts (2). One example is the Pt/CeO$_x$ oxygen storage functional unit found in catalytic converters for cars (15). Ceria influences the catalytic properties of a Pt catalyst in many different ways (16); see Fig. 1. For example, it promotes oxidation reactions of CO and hydrocarbons (16–18) and thus improves the low-temperature activity of the catalyst. The pretreatment of the catalyst is then of great importance. A Pt/ceria sample that is pre-reduced (exposed to H_2 at elevated temperatures) usually shows much higher activity compared to a pre-oxidized sample (16, 17). Ceria also acts as an oxygen storage element due to the ability of ceria to change its oxidation state. During periods of lean mixtures (oxygen-excess mixture), oxygen atoms spill over from Pt to CeO$_x$ ($x < 2$) to form a more saturated CeO$_x$ ($x \to 2$), which also maintains the NO$_x$-reducing capabilities of the catalyst during oxygen excess. At subsequent periods of fuel-rich mixtures (oxygen-deficient mixture), oxygen spills back from CeO$_x$ onto Pt to participate in the oxidation of CO and hydrocarbons (Fig. 1). In this way short detours away from stoichiometric air-to-fuel ratios can be handled by the catalyst without undesired slip of CO, hydrocarbons, and NO$_x$.

EBL-fabricated supported model catalysts can be used to explore these processes and also have the advantage of being fairly easy to characterize with surface analytical tools (4).

The number of reports, found in the literature, on reaction activity (2, 3, 8, 10, 19), stability (2, 3, 8, 9, 19), and characterization (3, 9, 10) of Pt-containing EBL-fabricated model catalysts is still limited. This indicates both that this is a relatively new way to study supported model catalysts and also reflects some difficulties in using EBL-fabricated samples as model catalysts, namely, problems related to the low total surface area (in turn requiring special microreactors) and the stability of thesex samples (8).

For EBL-fabricated surfaces to work as supported model catalysts, they must be stable at reasonable operating conditions. Thermal and chemical stability of EBL-fabricated Pt nanoparticles on SiO$_2$ were studied by Wong *et al.* (2)

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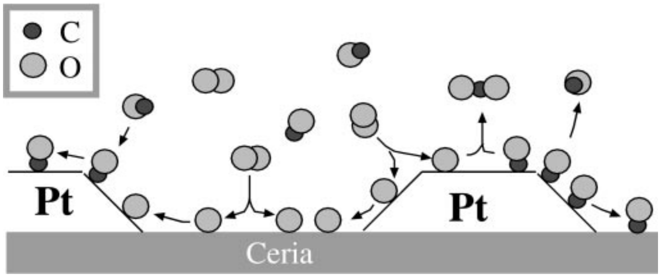


FIG. 1. A schematic picture of the interactions of CO and O_2 over a platinum particle situated on ceria.

and more recently by Eppler *et al.* (9). Wong *et al.* demonstrated massive restructuring of the initial model catalyst at $\approx 700^\circ C$ in $H_2 + O_2$ (O_2 excess) including crystallization and disintegration (of larger particles). Eppler *et al.* showed that, at 1 atm O_2 ($\approx 430^\circ C$), there is crystalline domain growth within individual Pt particles. Dean *et al.* (20) have shown that faceting of Pt films deposited on SiO_2 occurs in oxidizing mixtures above 300°C, and they observed platinum particle formation at temperatures above 450°C in certain $H_2 + O_2$ mixtures. These findings are in agreement with our present observations of reaction-induced morphology changes on EBL-fabricated Pt-containing supported model catalysts treated in $H_2 + O_2$ reaction mixtures (O/H ratio = 2) at temperatures $\leq 475^\circ C$.

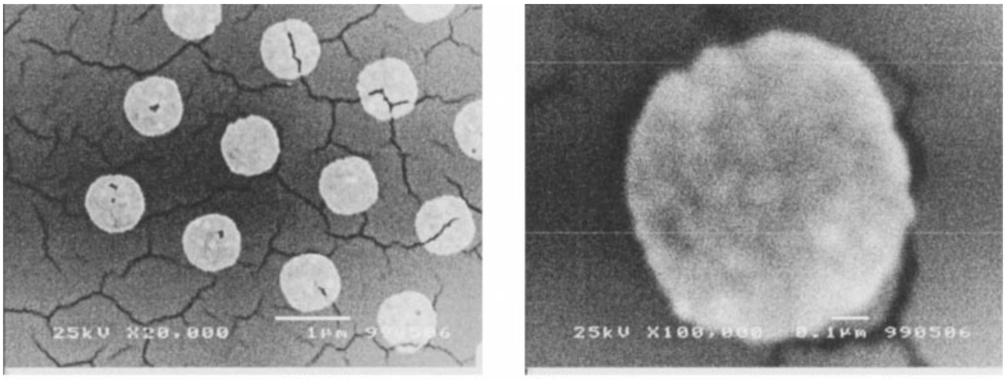
In this study we focus on the stability of EBL-fabricated Pt/CeO_x and Pt/SiO_2 model catalysts in reactive mixtures of $CO + O_2 + Ar$ and $H_2 + O_2 + Ar$ at different temperatures (300–475°C). The stability is evaluated by secondary electron microscopy (SEM) and by catalytic activity measurements. The catalytic activity for Pt deposited on SiO_2 and CeO_x, respectively, is used to measure accompanying activity changes due to, e.g., pretreatment conditions, i.e., pre-oxidizing or pre-reducing. We show that a promotional effect for CO oxidation on ceria can be observed with EBL samples and that a pre-reduced EBL-fabricated Pt/CeO_x model catalyst is more active than a pre-oxidized one, as is the case for Pt/CeO_x catalysts produced by normal wet-deposition methods. This promotional effect was not observed for the EBL-fabricated Pt/SiO_2 model catalyst. The results are compared with similar studies performed on powder catalyst samples of Pt/CeO_x and Pt/SiO_2.

EXPERIMENTAL METHODS AND PROCEDURE

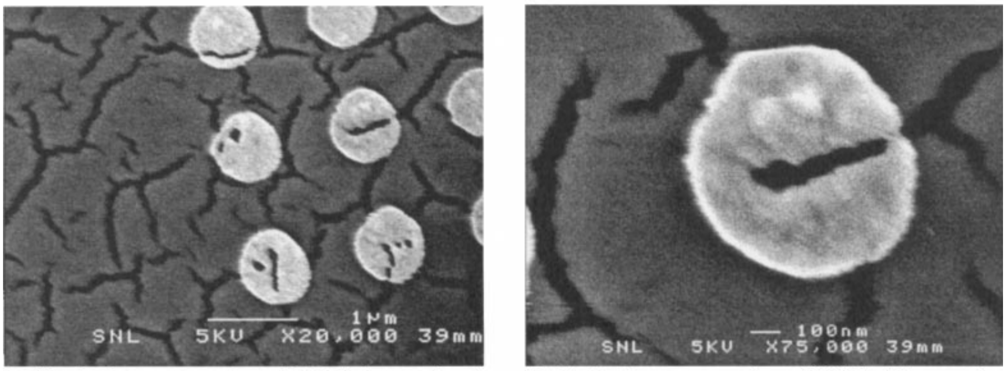
EBL-fabricated Pt/CeO_x and Pt/SiO_2 model catalysts were used; see Figs. 2 and 3. In short, the preparation procedure is as follows: A polished SiO_2 wafer is first cleaned in a reactive ion etching (RIE) oxygen plasma (250 W, 50 Torr O_2, 120 s). The support consists of Si wafers thermally oxidized (1000-Å-thick SiO_2 layer). The CeO_x support is made by evaporating a 300-Å-thick CeO_x layer on top of the SiO_2 support in an AVAC HVC-600 thin film deposition system. A ZEP-7000B resist layer (300-nm-thick) is then deposited on the support by spin coating and subsequently baked at 170°C for 20 min. A pattern is exposed in the resist in a JEOL JBX-5DII electron beam lithography system. Development of the resist is made in a methylethylketone (MEK) : diethylemalonate (1 : 1) solution for 3–5 min, and subsequently rinsed in isopropanol. Soft oxygen plasma treatment (50 W, 10 Torr O_2, 30 s) is made before Pt evaporation in the AVAC HVC-600 system. Lift-off is made in a MEK solution at 42°C in an ultrasonic bath. A more thorough description of the fabrication process is found in (21). The thickness of the Pt particles was 20 nm in this work and the geometrical total Pt surface area was estimated to be 0.4 mm^2.

A micro-flow-reactor, described in detail elsewhere (8), is used for making catalytic activity measurements at atmospheric pressure. In short, the micro-reactor consists of long inlet and outlet channels (100 mm) with very small inner diameters (0.1 and 0.2 mm, respectively). The whole reactor is situated inside an evacuated quartz tube equipped with a manometer. The total molar flow through the micro-flow-reactor is $4–6 \times 10^{-8}$ mol/s (corresponding to approximately 1 μl/s at atmospheric pressure) and is set up by two controlled leak flows. The two leak flows are (i) a capillary leak into an ultra-high vacuum chamber equipped with a quadrupole mass spectrometer and (ii) a leak seal from the reactor volume into the evacuated quartz tube. These leak flows are of the same order of magnitude (≈ 0.5 μl/s). The latter seal is present for sample exchange. The gas composition is measured with a quadrupole mass spectrometer in the vacuum chamber. The reactor acts as a tank reactor with a gas residence time of about 100 s and a short mixing time through diffusion (in the range of seconds). Heating of the reactor is accomplished by a heating coil outside the evacuated quartz tube. Heat-resistant fabric is shielding both the sample and a thermocouple, attached to the outside of the micro-flow-reactor from direct exposure to the heating coil. This setup enables temperature ramp measurements as well as steady state measurements. The response time is large, around 400 s, for a step change in the gas feed. The reactor is made of Pyrex glass, which has a melting temperature of approximately 500°C. This puts an upper limit on the working conditions for the micro-flow-reactor. The reactor can be cleaned of Pt contaminants by removing the capillary leak, washing the reactor in aqua regia, and remaking the capillary leak again by glass blowing, as described in (22). No catalytic background activity is measured in the reactor after such a cleaning procedure.

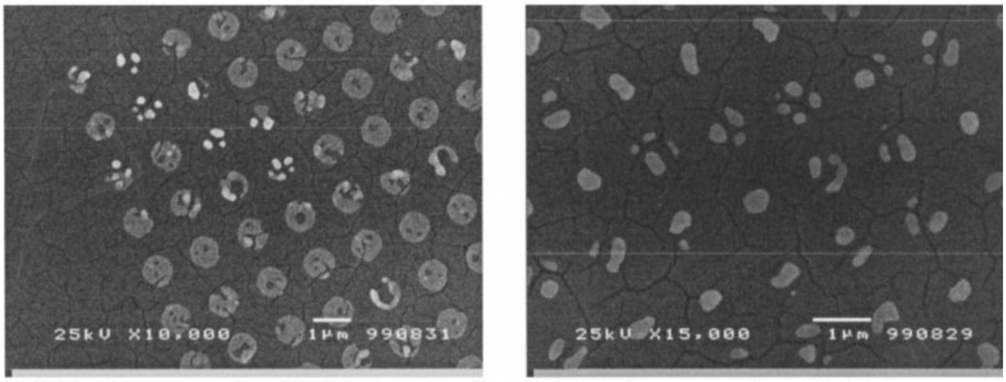
We studied reaction-induced morphological changes on EBL-fabricated supported model catalysts by treating the samples at elevated temperatures in $H_2 + O_2$ mixtures diluted in Ar. Two different mixtures were used, referred to as the "$\alpha = 0.33$" mixture (0.5% H_2 + 1.0% O_2 diluted in Ar)



Pt/CeO$_x$ heat treated at 300°C (overview) Pt/CeO$_x$ heat treated at 300°C (closeup)



Pt/CeO$_x$ heat treated at 400°C (overview) Pt/CeO$_x$ heat treated at 400°C (closeup)



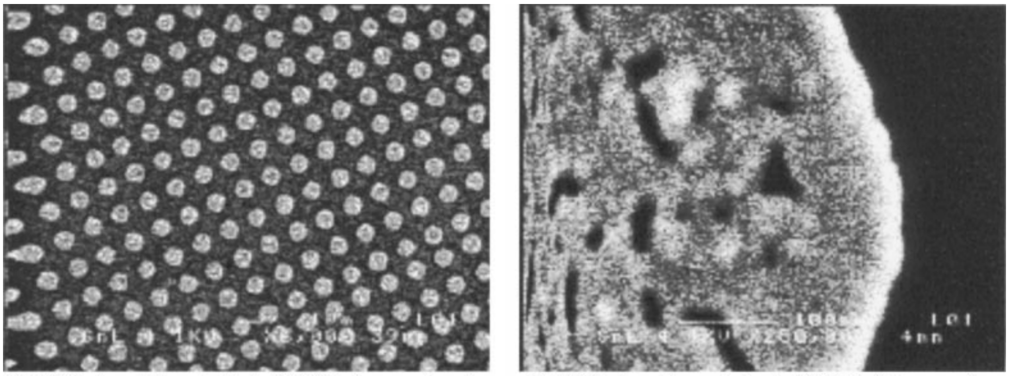
Pt/CeO$_x$ heat treated at 475°C for 10 hours (overview) Pt/CeO$_x$ heat treated at 475°C for 20 hours (overview)

FIG. 2. SEM pictures of EBL-fabricated Pt/CeO$_x$. After heat treatments in a mixture of 0.5% H_2 + 1.0% O_2 diluted in Ar ($\alpha = 0.33$) for 10 h at temperatures of 300°C (top), 400°C (middle), and 475°C (bottom), except for the bottom right picture, which has an additional 10 h in a mixture of 0.87% H_2 + 0.63% O_2 diluted in Ar ($\alpha = 0.58$).

and "$\alpha = 0.58$" mixture (0.87% H_2 + 0.63% O_2 diluted in Ar). The "α" parameter is defined as $\alpha \equiv P_{H2}/(P_{H2} + P_{O2})$. The heat treatments were made at constant temperatures and the sample was removed from the reactor and studied in SEM after each temperature. In the end (i.e., at sufficiently high temperature) this produces Pt/CeO$_x$ and Pt/SiO$_2$ samples as pictured in Fig. 2 (bottom right) and Fig. 3, respectively. These two samples have been used in the pre-treatment studies described below.

The 1 wt% Pt/SiO$_2$ and 1 wt% Pt/ceria powder samples were produced by wet-deposition methods as described elsewhere (16, 23). The BET surface area was 170 and 158 m^2/g for SiO$_2$ and ceria, respectively. The catalytic properties were tested in a flow reactor with a Balzers QMG 422 mass spectrometer.

The catalytic activity experiments consist of different pre-treatments, pre-oxidizing or pre-reducing, and subsequent catalytic activity measurement in a rich mixture of 1.05%



Pt/SiO_2 heat treated at 400°C (overview) Pt/SiO_2 heat treated at 400°C (closeup)

FIG. 3. SEM pictures of EBL-fabricated Pt/SiO_2 after heat treatment in a mixture of 0.5% H_2 + 1.0% O_2 diluted in Ar ($\alpha = 0.33$) at 400°C for 10 h.

CO + 0.45% O_2 diluted in argon. This CO + O_2 mixture corresponds to a stoichiometric number ($S = 2[O_2]/[CO]$) of 0.85. The rich CO + O_2 mixture does not reach full conversion (of O_2 to CO_2), even at 400°C for the EBL-fabricated samples. Therefore, this temperature was chosen to test the EBL-fabricated samples. The Pre-treatments of the catalysts are made at 400°C in either an oxidizing or a reducing mixture for either 15 min or 3 h (if not stated otherwise). The oxidizing mixtures are 1% O_2 diluted in Ar for EBL samples and 1.5% O_2 diluted in Ar for the powder samples. The reducing mixtures are 8% H_2 or 1.0% CO diluted in Ar for the EBL samples and 2% H_2 diluted in Ar for the powder samples. The pre-treatments are followed by an Ar flow until no trace of hydrogen or water is seen in the reaction chamber. The catalytic activity measurements are performed by setting up the CO + O_2 mixture and measure the CO_2 production versus time.

RESULTS

Figure 2 shows EBL-fabricated Pt/CeO_x samples that have been heat-treated in H_2 + O_2 reaction mixtures for 10 h at each of the temperatures 300, 350, 400, and 475°C and analyzed in SEM after each temperature. At 300°C, the H_2 + O_2 treatment ($\alpha = 0.33$) causes some depletion of Pt above the cracks in the CeO_x layer; see Fig. 2 (top). At 350°C there is little change from that observed at 300°C (not shown). At 400°C, the depletion of Pt around the CeO_x cracks grows larger and larger, but the Pt not deposited near the cracks seems to maintain its structure; see Fig. 2 (middle). At 475°C significant morphological changes occur, not only close to the CeO_x crack pattern but also away from the crack pattern. At this temperature the 700-nm Pt dots start to disintegrate into several smaller Pt particles, situated around their original location on the CeO_x support; see Fig. 2 (bottom left). After another 10 h in a H_2 + O_2 mixture ($\alpha = 0.58$) at 475°C, almost all the 700-nm Pt particles have disintegrated into groups of smaller particles; see Fig. 2 (bottom right). Similar results have been observed at higher temperatures for Pt on SiO_2 (2). The particle structure obtained through the heat treatment, as shown in Fig. 2 (bottom right), is quite different from the initial structure, as shown in Fig. 2 (top).

CO oxidation was used as a probe reaction to measure the reactivity of the Pt/CeO_x sample after each heat treatment step. The main effect is that the light-off curve goes toward higher and higher temperatures; i.e., the catalyst becomes less and less active, after each increase in temperature for the reaction heat treatment (see Fig. 4). (A somewhat increased background activity for CO oxidation in the micro-flow-reactor was also observed after the H_2 + O_2 ($\alpha = 0.33$ and $\alpha = 0.58$; 10 h each) treatment of the Pt/CeO_x sample at 475°C (not shown).)

After pre-reduction of the sample in H_2, or pre-oxidation in O_2, at 400°C, the CO oxidation activity of the sample with disintegrated original Pt islands was tested in a rich mixture of 1.05% CO and 0.45% O_2 diluted in argon ($S = 0.85$). The CO oxidation experiments were performed

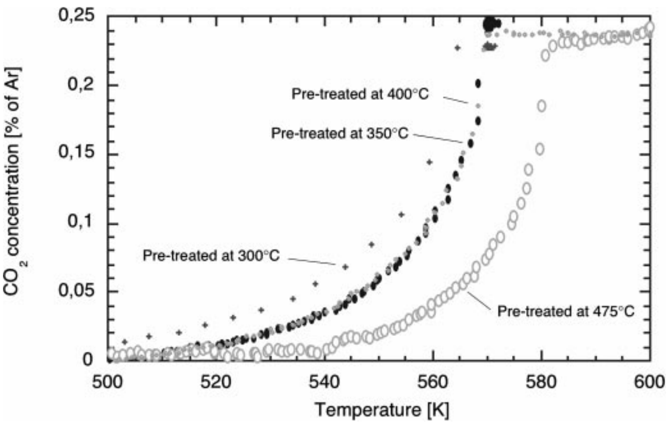


FIG. 4. The production of CO_2 during CO oxidation at $S = 4$ over the disintegrated EBL-fabricated Pt/CeO_x model catalyst during heating ramps made after different H_2 + O_2 ($\alpha = 0.33$) reaction heat treatments (300°C (crosses), 350°C (bullets), 400°C (stars), and 475°C (open rings)).

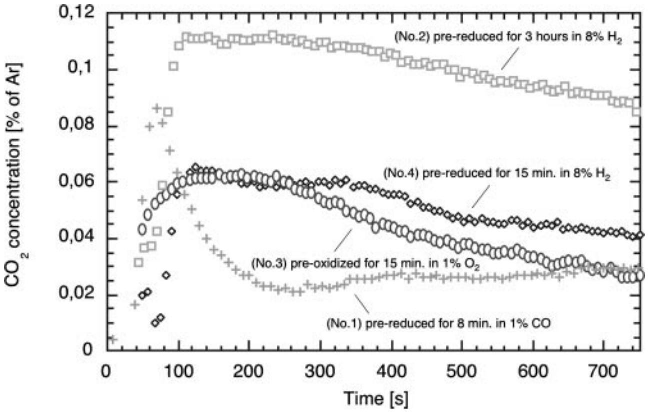


FIG. 5. CO_2 formation versus time after exposing the disintegrated EBL-fabricated Pt/CeO_x catalyst to a rich mixture of 1.05% CO + 0.45% O_2 diluted in Ar at 400°C. The trace indices mark the order in which the experiments were performed. The pre-treatments are as follows: (No. 1) reducing in 1.0% CO diluted in Ar for 8 min, (No. 2) reducing for 3 h, (No. 3) oxidizing for 15 min, and (No. 4) reducing for 15 min.

at 400°C, and the CO_2 production versus time in the reaction mixture was recorded. The CO_2 production traces for the "disintegrated Pt/CeO_x sample," after reduction and oxidation pre-treatments, respectively, are shown in Fig. 5. The trace indices (1)–(4) in Fig. 5 mark the order in which the experiments were made. The sample pre-treatments in Fig. 5 are as follows: (1) reducing for 8 min in 1.0% CO diluted in Ar, (2) reducing for 3 h, (3) oxidizing for 15 min, and (4) reducing for 15 min. We note that a long reducing pre-treatment (3 h) leads to increased catalytic activity (trace (2)) for the rich CO + O_2 mixture compared with the oxidizing pre-treatment (trace (3)). Thus, an increase in the maximum CO_2 production of over 80% is observed for the pre-reduced sample compared with that of the pre-oxidized sample (an increase from 0.06 to 0.11). The increase is minor for the shorter (15 min) pre-reduction in hydrogen (trace (4)) and only an initial increase is seen for the short (8 min) pre-reduction in 1.0% CO (trace (1)).

After approximately 50 h at 400°C during runs like the ones mentioned above, the catalytic activity starts to increase with each run for both types of pre-treatments (not shown), indicating that the Pt/CeO_x sample is not totally stable for CO oxidation experiments at this reaction temperature, at least not for a longer period of time (>50 h).

At higher temperatures (475°C), the reproducibility is lost and an increased background activity for CO oxidation is measured in the reactor after the sample is removed (not shown). This indicates that there is Pt contamination in the reactor. Reactor cleaning in aqua regia removes the measured background activity. At 300°C reproducible CO oxidation measurements have been performed in the micro-flow-reactor for this sample over much longer periods of times than 50 h (not shown).

Also for the powder samples a significant increase in activity was observed for the pre-reduced Pt/CeO_x sample compared with the pre-oxidized one. The light-off temperatures were 115 and 170°C, respectively.

EBL-fabricated samples with Pt deposited on SiO_2 instead of CeO_x were also heat-treated in a $H_2 + O_2$ ($\alpha = 0.33$) reaction mixture for 10 h at each of the temperatures 300, 350, and 400°C and then analyzed in SEM after each temperature. The 700-nm particles remain intact at 300 and 350°C, and reproducible CO oxidation measurements were performed at 300°C (not shown). At 400°C the 700-nm Pt particles are still intact, but surface roughness and holes in the metal are observed; see Fig. 3.

For the Pt/SiO_2 sample the opposite trend is, surprisingly, observed with regard to how different pre-treatments affect CO oxidation (compared with the Pt/CeO_x sample). Higher activity is measured for the pre-oxidized sample than for the pre-reduced sample; see Fig. 6. The trace indices in Fig. 6 mark the order of the experiments and the pre-treatments are as follows: (1) reducing for 3 h, (2) oxidizing for 15 min, (3) oxidizing for 15 min, (4) reducing for 3 h, (5) oxidizing for 15 min, (6) reducing for 15 min, and (7) oxidizing for 15 min. The pre-reduced sample seems to be re-oxidized in the rich CO + O_2 mixture, and the time for re-oxidation depends strongly on the pre-reduction time, as can be seen in Fig. 6. Fairly reproducible runs can be made for long periods of time (>50 h) at 400°C in CO oxidation mixtures (including pre-treatment mixtures), as can be seen from Fig. 6.

For the powder samples (Pt/SiO_2) the pre-reduction was found to be somewhat beneficial for the activity. The light-off temperatures were 209°C (pre-reduced) and 225°C (pre-oxidized).

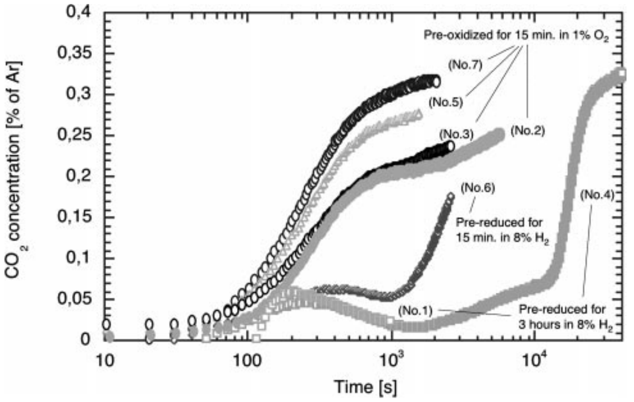


FIG. 6. CO_2 formation versus time after exposing the disintegrated EBL-fabricated Pt/SiO_2 catalyst to a rich mixture of 1.05% CO + 0.45% O_2 diluted in Ar at 400°C. The trace indices mark the order in which the experiments were performed. The pre-treatments are as follows: (No. 1) reducing for 3 h, (No. 2) oxidizing for 15 min, (No. 3) oxidizing for 15 min, (No. 4) reducing for 3 h, (No. 5) oxidizing for 15 min, (No. 6) reducing for 15 min, and (No. 7) oxidizing for 15 min.

DISCUSSION

Many of the most intensely studied reactions connected with automotive emission control, namely, oxidation of CO and C_3H_6 (17), and continuous reduction of NO_x by hydrocarbons in lean mixtures (24), occur at temperatures well below 400°C for Pt-containing catalyst systems. Other processes like NO_x storage (25) have the operating window at temperatures around and above 400°C. Reproducible catalytic activity measurements have been made during a period of 50 h at 400°C for the EBL-fabricated samples (both the Pt/CeO_x and Pt/SiO_2). Thus, these catalysts can be used to study several aspects of the practically important reactivity under realistic reaction conditions. A much higher thermal stability, of temperatures up to $\approx$730°C, have been observed for Pt-containing EBL-fabricated samples in vacuum, 1 atm H_2 (2, 9), and in 1 atm of Ar (26). This higher stability temperature in non-oxygen atmospheres allows the use of characterization methods, which often requires temperatures above 400°C, e.g., CO-TPD and TPR experiments.

The disintegrated Pt/CeO_x sample has been heat-treated at 475°C in mixtures of $H_2 + O_2$ diluted in argon for tens of hours before the long-term CO oxidation measurements started. The increasing activity with time for the Pt/CeO_x sample after 50 h in the reaction mixture at 400°C indicates that the sample is not long-term stable at this temperature. This is perhaps not so surprising, considering that the morphological changes start already at and below 400°C for the fresh Pt/CeO_x sample (see Fig. 2 (top and middle)). The stability problem at 400°C is most likely due to reshaping of the catalyst structure during reaction conditions, forwards closer to equilibrium (Wulff) shapes, and obviously with a favorable structure for CO oxidation efficiency. The latter can, e.g., be a change in the relative amount of different (*hkl*) facets, and/or edge sites on the Pt particles, and/or Pt–CeO_x edge sites. It is less likely that so-called catalytic etching (27) occurs at 400°C, and this is supported by Dean *et al.* (20) (see discussion below). In contrast, there is at 475°C an increase in background activity in the reactor after the treatment in mixtures of $H_2 + O_2$ diluted in Ar ($\alpha = 0.33 \leftrightarrow$ O/H ratio $= 2$ and $\alpha = 0.58 \leftrightarrow$ O/H ratio $= 0.7$ for 10 hours each), indicating Pt contamination of the reactor walls possibly due to catalytic etching at this higher temperature. The latter is supported by the fact that the total geometrical area of the Pt particles was reduced by a factor of 4, compared with the "fresh" sample, and that the overall CO oxidation activity decreased, indicating a loss of Pt surface area, after the $H_2 + O_2 +$ Ar treatment at 475°C. When we were searching for platinum particles on the CeO_x support, away from the original platinum array structure, some particles were found but only a small number. According to the measurements made by Dean *et al.* (20), our reaction conditions fall close to, but not within, the region (temperature and O/H ratio) for which they observed catalytic etching on a Pt film deposited on SiO_2. In a $H_2 + O_2$ mixture (O/H ratio $= 2$) at 510°C they found formation of platinum particles in a region close to and around the location of the catalytically etched platinum film. This was not observed in O_2 or H_2 mixtures alone at this temperature. Below this temperature, at O/H ratios $= 2$, they only found faceting of the Pt film when exposed to either O_2 or $H_2 + O_2$ mixtures (what they call thermal etching).

The Pt/SiO_2 sample seems to be more stable for CO oxidation at temperatures of 400°C, compared with the Pt/CeO_x sample, and showed only small variations in activity with time, even after 50 h in the reaction mixture. However, there seems to be a slow drift toward higher activities with each run, even for the Pt/SiO_2 sample after 50 h in the reaction mixture at 400°C.

Pt catalysts containing ceria have been shown by many authors to have a higher activity toward CO oxidation in rich conditions, especially if the catalyst is pre-reduced prior to the activity measurement, compared with a pre-oxidized catalyst (16–18, 28), and significant Pt/ceria interaction has also been demonstrated by CO-TPD (29). We have verified that this is also the case for EBL-fabricated Pt/CeO_x supported model catalysts and we have observed the same qualitative behavior for powder samples for similar reaction conditions. Consequently, relevant catalytic studies at fairly high reaction temperatures (400°C) can be performed with this new type of supported model catalysts made by electron-beam lithography. It can be noted that a rather long reduction time is required at 400°C in a mixture of 8% H_2 diluted in Ar to observe this positive effect on CO oxidation in rich conditions.

For the Pt/SiO_2 catalyst the opposite trend was observed compared with that of the EBL-fabricated Pt/CeO_x sample, namely, that the catalyst was more active when pre-oxidized compared with when it was pre-reduced. This is contradictory to what, e.g., Mergler *et al.* (28), have observed on Pt/SiO_2 supported catalysts and to what we observe for the powder samples in this study, namely, a small activity increase in rich conditions with a pre-reduced Pt/SiO_2 catalyst compared with a pre-oxidized catalyst. At present, we do not have a satisfactory explanation for this behavior seen in Fig. 6 for the Pt/SiO_2 catalyst. An initial delay in the oxygen signal of 30–60 s is observed for the pre-reduced samples compared with the pre-oxidized samples. This delay in oxygen signal is also detected for a similar experiment without the sample present. There is a 6-h delay before the activity is regained on the pre-reduced (3 h) sample. The cause for this is still not known. Lamber and co-workers (30, 31) have identified a Pt–Si phase (platinum silicide) on supported Pt/SiO_2 catalysts after prolonged heating at 570°C in H_2. After treatments in hydrogen at 500°C, the platinum particles behave as metallic platinumbased on the infrared spectra of CO chemisorbed on Pt/SiO_2, and a change is only observed above 500°C. They suggest that oxidative decomposition of platinum silicide at lower temperatures (400°C) might decorate the metal particles with silica species. Niehaus and Comsa (32) and Keck and Kasemo (33) have shown that ppm impurities of Si in bulk Pt segregate to the surface in the presence of O_2, forming a SiO_2–$PtSi_xO_y$ compound. The difference between the results for Pt/SiO_2 EBL samples and those for the samples used by Lamber *et al*. could be the following: In our case we use an oxidized silicon wafer (a 100-nm-thick SiO_2 film on Si) while Lamber *et al*. (30) used SiO_2 support either oxidized from bulk SiO or etched from quartz membranes. SiO_2 on Si as a thin film may allow diffusive transport of Si through the thin SiO_2 film (at sufficiently high temperature), and thus Si could then interact with Pt. A possible explanation for the hampering effect on CO oxidation observed for the EBL-fabricated Pt/SiO_2 sample at reducing pre-treatments would be the formation of platinum silicide from SiO_2 but the temperature at which we perform our experiments (400°C) seems to be too low for this to occur (30, 31).

CONCLUSIONS

We have shown that EBL-fabricated supported model catalysts can be used to study practically important reactions under realistic reaction conditions. The EBL-fabricated model catalysts have been shown to be stable for at least a period of 50 h during CO oxidation at 400°C. A promotional effect of CeO_x was observed in agreement with observations on powder samples. Further pre-reducing pre-treatments were observed to increase the activity, compared with oxidizing pre-treatments, for the Pt/CeO_x sample, in accordance with similar measurements performed on a conventional powder Pt/CeO_x catalyst. For Pt/SiO_2 the pre-oxidized pre-treatment was found somewhat more beneficial, which is opposite to what was observed for the powder Pt/SiO_2 catalyst. The cause of the latter is discussed but yet open.

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