CO Adsorption on Pt Nanoparticles in Low E-fields

Studied by ATR-IR Spectroscopy in a Microreactor

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Abstract
The adsorption of carbon monoxide (CO) on platinum (Pt) nanoparticles under influence of a low electrical field (E-field) is studied. The adsorption of CO is monitored by attenuated total reflection infrared (ATR-IR) spectroscopy, while an external electrical field is applied over the microreactor. Linearly (on top; CO\textsubscript{L}), bridged (2 fold hollow; CO\textsubscript{B}) and multiply (3 fold hollow; CO\textsubscript{MB}) adsorbed CO species were found on the Pt nanoparticles. In a sequence of adsorption experiments the integrated ATR-IR intensity of the absorption band of the linearly adsorbed CO\textsubscript{L} was found to reach steady state values after an initial decrease, which is attributed to a loss of Pt surface area due to sintering of the Pt metal nanoparticles. The application of electrical fields result in changes in the ratio between linearly adsorbed CO, on top of Pt, versus CO adsorbed on multiple Pt atoms.

Keywords: ATR-IR, CO adsorption, E-field, Microreactor, Infrared
1. Introduction

CO adsorption on group VIII metal catalysts has been intensively studied over the years, because of the relevance of CO as a probe of the available amount of adsorption sites on surfaces of catalysts. CO is also important in the catalytic conversion for pollution control\(^1\)-\(^2\) and often used as model reactant for commercially industrial processes, including naphtha reforming, (de)hydrogenation, and oxidation reactions\(^3\)-\(^4\). The electronic properties of the metal catalyst surface play a vital role in the reactivity. The charge on the surface of the catalyst is generally influencing the adsorption and reactivity of CO\(^5\). Baker and coworkers demonstrated nicely, using a solid-state charge-based microreactor, that a negative charge on the surface of the Pt catalyst increases the activity for CO oxidation, while a positive charge decreases the activity for CO oxidation\(^6\). Effects of the work function of the metal catalyst on the reaction rate are reported by Vayenas and co-workers\(^7\)-\(^9\). H. J. Kreuzer reported calculations of the adsorption of chemical species on metal surfaces\(^10\) in the presence of weak electrical fields, where at fields below \(~1\times10^8\) V/cm atoms and molecules polarize, leading to drastic changes in the adsorption properties of molecules on surfaces. This is due to the distortion of the binding orbital, which leads to new bonding properties\(^10\).

Here we present a study on the influence of a weak electric field on the adsorption of CO in a home-built microreactor. In order to generate the required field strengths we fabricated microstructures similar to field emitter tips. The sharp curvature of the microstructures integrated in the gas flow channel of the microreactor enhances the local E-field. CO is used as a probe molecule for our newly developed microreactor, in which we are able to vary an external E-field over the microreactor and simultaneously monitor the catalyst interface with Attenuated Total Reflection (ATR) infrared (IR) spectroscopy.
2. Experimental section

2.1 Fabrication of the ATR-IR microreactors

The main device used in this study is a microreactor designed for simultaneous application of an external (E-field) and in situ ATR-IR. A schematic representation of the microreactor is shown in Figure 1(a). Details of the fabrication and choices of the materials for this microreactor have been described elsewhere. In brief, the E-field is applied via Cu/TiSi2 contacts (Cu/green bars in Figure 1(a)) to the top and bottom electrode. The bottom electrode, fabricated from a double side polished p-type (500 µm thickness, 5-10 Ω cm resistivity, Okmetic Finland) Si(001) wafer, acts as total internal reflection element for the ATR-IR measurements. On the top electrode, fabricated from a double side polished p+ -type silicon (500 µm thickness, 0.01-0.02 Ω cm resistivity, Okmetic Finland), cylindrical pillars are micromachined. The interspace between the top of the micropillars and the ATR-IRE surface is ~ 2 µm. The width and length of the channel are 1.8 and 4.4 cm, respectively, leading to a total microreactor volume V of ~1.3 x 10^-2 cm³. The SiO2 layer terminating the ATR-IRE crystal (colored in orange in Figure 1(a)) is defined by dipping the ATR-IRE containing wafer in 1% HF for about 25 min (after photolithography and prior to thermal bonding), during which the initial ~ 2 µm SiO2 layer is locally thinned down to 140 nm ± 40 nm.

2.2 Coating of the gas flow channel with Pt nanoparticles

Commercially available Pt nanopowder from Sigma-Aldrich (with an average particle size < 50 nm) was suspended as received in n-hexane (Sigma Aldrich, > 99.00% purity over molecular sieve). The Pt nanoparticle suspension was prepared by adding 50 mg Pt nanopowder to 1 mL of n-hexane (which would be enough to fully cover the entire bottom electrode with a ~ 50 nm layer of Pt particles), followed by vigorous ultra-sonication for 3 h. The microreactor was coated three times subsequently by flowing the 50 mg/mL Pt nanoparticles in n-hexane suspension through the microreactor flow channel, and dried overnight under 10% oxygen/helium (O2/He) mixture.
(99.999% purity from Praxair) with a flow of ~30 µL/min (with a mass flow controller of Brooks, model 5850/BC).

2.3 Electrical characterization of the Pt coated microreactors

Subsequent to the coating with Pt nanoparticles the electrical response of the microreactors was investigated. A Keithley 2410 power supply programmed via a home-written Labview script was used to apply the voltage pulses and to record the electrical response in the form of I(V) curves.

2.4 Pre-treatment of the microreactors

A pre-treatment to remove any trace of n-hexane from the deposition process and to reach a stable IR signal was performed prior to ATR-IR microreactor experiments, consisting of four cycles of CO chemisorption and subsequent CO oxidation with total flows of 30 µL/min of CO (99.97% purity) and premixed 10% O₂/He mixture (99.999% purity), respectively (all gases from Praxair). During these pre-treatment cycles, no E-field was applied to the microreactor. After these pre-treatment cycles, 30 µL/min of hydrogen (99.99% pure H₂ from Praxair) was flown through the microreactor for 1 h. Gas flows (i.e. single composition and from premixed compressed gas cylinders) were controlled with mass flow controllers from Brooks (model 5850/BC). All experiments are performed at room temperature.

2.5 CO adsorption/oxidation cycles

CO (99.97% purity, Praxair) was flowed (30 µL/min) for 210 minutes followed by a premixed 10% v/v O₂/He (99.999% purity, Praxair) mixture (30 µL/min) for 360 min to remove the adsorbed CO, thereby preparing the surface of the Pt nanoparticles for the next CO adsorption experiment. These experiments (CO adsorption and subsequent oxidation), hereafter termed as an “adsorption cycle”, were performed during the application of respectively ± 5 V, ± 15 V and ± 25 V over the microreactor in subsequent experiments, keeping the top electrode connected to earth as indicated in Figure 1(a). To verify the influence of the external E-field over the deposited Pt catalyst, a “reference
“experiment” without E-field was performed between every two adsorption cycles with a flow rate of 30 µL/min.

2.6 ATR-IR measurements

During each experiment in situ ATR measurements were carried out in a Fourier Transform Infrared (FT-IR) spectrometer, Tensor 27 (Bruker Optics) with a MCT D316/6-L detector cooled with liquid N₂ and a resolution of 8 cm⁻¹ & 256 co-added scans. The microreactor was positioned in a home-designed ATR cell, which consists of four concave polished mirrors mounted on a metal holder with electrical connectors. ATR-IR spectra are measured against a background in He, and are shown baseline corrected.

3. Results

3.1 Coating the gas flow channel of the ATR-IR microreactor with Pt particles

A representative Scanning Electron Microscope (SEM) image of the deposited Pt nanoparticles on the ATR-side (bottom electrode in Figure 1(a)) after fracturing a freshly coated ATR-IR microreactor into small pieces with a diamond dresser is shown in Figure 1(b). The inset shows an image of the deposited Pt nanoparticles at higher magnification. Figure 1(c) shows a SEM image after coating a diced, flat Si substrate with the Pt nanoparticles, following a procedure similar to the one described in the experimental section 2.2. Figure 1(d) shows a SEM image of the Pt nanoparticles in a manually cleaved microreactor after 20 E-field CO adsorption/oxidation cycles. Energy dispersive X-rays spectroscopy reveals a Pt coverage of ~ 0.14 µg/mm² (assuming a penetration depth of ~ 5 µm for the electron beam used in EDX).

The images in Figures 1(b)-(d) show Pt particles on the bottom-electrodes (confirmed by the SEM image of the backscattered electrons, EDX spectroscopy, and X-ray photo-electron spectroscopy, XPS, not shown) with a bimodal size distribution. Large particles with diameters of 100 to 150 nm are observed, as well as small particles with diameters around 10 nanometers. Moreover,
smaller Pt particles of diameter < 10 nm are also observed in Figures 1(b)-(c), while in Figure 1(d) these smaller Pt particles are less frequently observed. In addition, in Figure 1(d) the coalescence of Pt particles shows up as neck-formation between two adjacent particles (see open yellow ellipse). For the top electrodes with pillars, similar coalescence was observed.

3.2 Electrical characterization of the microreactors

I(V) curves are recorded for the Pt nanoparticle-coated microreactor with a premixed 10% O₂/He mixture flow through the microreactor. The results are plotted as Fowler-Nordheim graphs, i.e. ln(J/E²) vs. 1/E^{11, 12}, in Figures 1(e) and 1(f). Figure 1(e) is measured with the E-field directed downwards (from the top electrode with the pillars towards the bottom ATR-IRE electrode), while Figure 1(f) is measured with the E-field directed upwards. The current density in Figure 1(e) was calculated using only the total area of the flat micropillar top surfaces (~0.4 cm²), i.e. the surface area where the gap between top and bottom electrode is 2 µm^{11, 12}. The total geometric surface area of the ATR-IRE flat electrode in Figure 1(f) was 7.9 cm².

3.3 CO adsorption ATR-IR measurements

Pre-treatment results.

ATR-IR measurements during a single pre-treatment cycle (no applied E-field) of the microreactor are shown in Figure 2(a). Infrared absorption peaks develop during adsorption at initially 2068 cm⁻¹, shifting to 2050 cm⁻¹ with increasing surface coverage at 1840 cm⁻¹ and multiple bands are observed from 1730 to 1620 cm⁻¹, with a maximum at 1708 cm⁻¹. The absorption band initially observed at 2068 cm⁻¹, which shifts to 2050 cm⁻¹ with increasing surface coverage can be assigned to linearly adsorbed CO (hereafter referred to as CO_L). The absorption band at 1840 cm⁻¹ can be assigned to bridging CO (CO_B) and the bands around 1708 cm⁻¹ are ascribed to a combination of multiply adsorbed CO (CO_MB). The weak maximum at 1656 cm⁻¹ is attributed to the presence of water in the CO feed and is corrected for in the inset of Figure 2(a).
The ATR-IR spectra in Figure 2(b) were collected after 210 min, at the end of each of the CO adsorption steps during the pre-treatment cycles (in absence of any E-field). Note the decrease in the intensity of the CO absorption bands after the subsequent pre-treatment cycles.

**CO adsorption/oxidation cycles in a weak external E-field**

Integrated intensities (after correction for the presence of water in the CO feed) of the CO absorption bands in subsequent adsorption cycles are displayed in Figure 3. The integration boundaries for all the CO$_x$, CO$_B$ and CO$_{MB}$ are 2110 – 1900, 1900 – 1750 and 1750 – 1600 cm$^{-1}$, respectively. The integrated intensity is shown from $t = 0$, the moment that the CO flow through the microreactor is started, over a time lapse of 200 minutes. Figures 3(a), (3c) and 3(e) show the integrated intensities of the CO$_x$, CO$_B$ and CO$_{MB}$ absorption bands, respectively, in a subsequent set of adsorption cycles for increasing values of an E-field applied in the downwards direction, while Figures 3(b), (3d) and 3(f) show the integrated intensities of the CO$_x$, CO$_B$ and CO$_{MB}$ absorption bands, respectively, in a subsequent set of adsorption cycles for increasing values of an E-field applied in the upwards direction.

In Figure 3(a) and 3(b) the integrated intensity starts to rapidly increase after a few minutes and levels off to a constant value after ~80 minutes. This constant value is higher in the first two experiments (with applied voltages 0 and – 5 V) in Figure 3(a) and has similar values for the other experiments in Figures 3(a) and 3(b), i.e. at ~ 0.6 of the y-axes for the total integrated area of CO$_x$.

Two reference measurements (i.e. without E-field, see experimental section 2.5) are performed prior to the application of $V = -15$ and $V = -25$ in Figure 3(a), see 0V (-15) and 0V (-25). Note that a reduction pre-treatment with H$_2$ was carried out between the experiment resulting in Figure 2(b) and the experiments shown in Figure 3 (see experimental section 2.4). No changes in the ATR-IR spectra were found during these reduction experiments.

The signal-to-noise ratio in Figures 3(c)-(f) is much lower, due to the lower peak intensities of the CO$_B$ and CO$_{MB}$ absorption bands. In Figures 3(c)-(f) the integrated intensities start to increase immediately from $t = 0$ and seem to level off to a constant value around $t = 100$ min. Note that in the
experiment with 25 V applied over the microreactor the increase in the integrated intensity in Figures 3(d) and (f) is significantly larger than at lower potentials.

In between every CO adsorption cycle in which an E-field was applied an adsorption cycle without an applied E-field (i.e., 0 V) was performed as reference. ATR-IR absorption spectra at \( t = 200 \) min of these reference measurements are shown in Figure 4. The broad and strongly asymmetric CO absorption band has initially a maximum at 2052 cm\(^{-1}\) (after 0 cycles, only pretreated), which shifts to \( \sim 2080 \) cm\(^{-1}\) after 20 CO adsorption cycles, accompanied by a \( \sim 25\% \) decrease of the integrated signal.

Figures 5(a) and 5(b) present IR spectra including CO and CO\(_{2}\) absorption bands measured (in between \( t = 150 \) and 155 min) in presence of different E-fields in the downwards and upwards direction. In Figure 6 we plotted the time averaged (from \( t = 150 \) to 210 min.) CO\(_{L}\)/CO\(_{B}\) and CO\(_{L}/CO_{MB}\) ratios of the integrated peak areas as a function of the applied potential (see Figure 3). For the applied negative potentials (0 to -25 V) the CO\(_{L}/CO_{B}\) and CO\(_{L}/CO_{MB}\) ratios decrease slightly with increasing field strength, while for positive potentials (0 to 25 V) a significant decrease in the CO\(_{L}/CO_{B}\) and CO\(_{L}/CO_{MB}\) ratios is observed with increasing field strength.

4. Discussion

4.1 Coating the gas flow channel of the ATR-IR microreactor with Pt particles

From the SEM image of the ATR-IRE of a fractured microreactor in Figure 1(b) it can be observed that the Pt nanoparticles are homogeneously distributed over the entire surface forming square clusters. This square distribution pattern, where each square has a width-of about 16±6 \( \mu \)m, can be attributed to the presence of the pillars with pitch (i.e., pillar diameter + pillar-to-pillar interspace) dimensions of 20 \( \mu \)m at a distance of only 2 \( \mu \)m on the opposite top electrode during the drying process of the Pt suspension in \( \eta \)-hexane, as a consequence of which capillary forces act during the drying process. The successful deposition of Pt nanoparticles with \( \eta \)-hexane as a solvent in the
microreactor is related to its low surface tension, since similar Pt functionalization experiments with water or ethanol as solvent within the microreactor failed.

4.2 Electrical characterization of the microreactors

The Fowler-Nordheim (FN) plots in Figures 1(e) and 1(f) reveal linear behavior at low 1/E values, which is indicative of E-field driven electron emission. The onset field strength for field emission can be extracted from the intercept with the 1/E axis in Figures 1(e) and 1(f). A higher 1/E value is needed to start electron emission from the flat surface in Figure 1(e) compared to electron emission from the micropillars in Figure 1(f). The relatively sharp edges of the pillar tips locally enhance the E-field, leading therewith to a lower onset E-field value for electron emission from the pillared top electrode. From Figures 1(e) and 1(f) the calculated onset values for electron emission correspond to application of ~ -4 V and ~ 1 V over the microreactor, respectively.

It is clear from FN plots that below E-field emission (i.e. < 1 and -4 V) the reactor surface becomes polarized and electron field emission does not yet occur at a significant rate. We have estimated that electron emission happens above 1 V and -4 V in the upward and downwards potentials. This emission is expected to occur within a small part of the microreactor, where the distance between the top of the micropillars and the ATR-IRE surface is the smallest, namely 2 µm.

4.3 CO adsorption ATR-IR measurements

In Figures 2(a) and 2(b), the assignments of the CO absorption peaks at 2068-2050 cm⁻¹, 1840 cm⁻¹, 1708 cm⁻¹ to linear (CO₁), bridging (CO₂) and other multiply-bonded (CO₃) CO, respectively, is in accordance with literature¹⁷,¹⁸. The weak absorption at 1656 cm⁻¹ (for which is corrected in the inset of Figure 2(a)) is most likely due to the presence of water¹⁹,²⁰. The exact structural assignment of the adsorption configuration for the 1708 cm⁻¹ absorption band remains unclear, but likely candidates are a long 2-fold bridge (which could for instance occur between 2 adjacent ridges of the
missing row reconstructed (110) surface) or CO molecules σ-bonded to one Pt atom and σ or π bonded to a second one\textsuperscript{17, 18}.

An interpretation for the red-shift from 2065 cm\(^{-1}\) to 2050 cm\(^{-1}\) in \textbf{Figure 2(a)} needs further investigation as no clear conclusion can be drawn from the recorded IR measurements. An increase in dipole-dipole interaction strength would show up as a blue-shift in the spectra, which we would expect. The increasing dipole-dipole interaction is, however, apparently compensated by another effect in our measurements. A higher degree of back-donation to the π* CO orbitals would result in a red-shift. A possible reason for this higher degree of back donation could be co-adsorption of water, which is present as impurity in the CO feed as indicated by the absorption at 1656 cm\(^{-1}\). Water adsorbs via the oxygen and is able to donate electrons to the Pt. As a consequence, the back-donation from Pt to CO increases, leading to a red-shift. Co-adsorbing water is indeed reported to cause a red-shift of \(\approx 20\) cm\(^{-1}\) in the CO\(_{L}\) absorption peak\textsuperscript{19, 20}.

The successive ATR-IR measurements during CO adsorption in \textbf{Figure 2(b)} reveals a continuous decrease in the intensity of the CO\(_{L}\) band (see cycle 3 and cycle 4), followed by a further (\(~40\%) drop in the total ATR-IR intensity in the subsequent experiments in \textbf{Figure 3} (compared to the initial intensity in \textbf{Figure 2}), most prominently visible in \textbf{Figure 3(a)} as a decrease in integrated intensities. More precisely, the decrease in integrated intensity is clearly observable in the first two adsorption cycles in \textbf{Figure 3(a)} (ca. 20\% of the integrated signal). After these two cycles the integrated CO\(_{L}\) absorption intensity in \textbf{Figures 3(a) and 3(b)} levels off around a value slightly above 0.6 (see, y axis-total integrated area). We assign this decrease in intensity in \textbf{Figures 2 and 3(a)} to a decrease in available adsorption sites during the experiments as a consequence of particle restructuring during CO and/or O\(_{2}\) exposure. For the reference measurements 0V, 0V(-15) and 0V(-25) performed in between two E-field measurements (see \textbf{Figure 3(a)}) a similar decay is observed, supporting this particle restructuring during the CO/O\(_{2}\) exposure. Furthermore, CO\(_{L}\) ATR-IR absorption spectra in \textbf{Figure 4} show significant changes between 0 and 20 cycles. The absorption maximum is blue-shifted from 2052 cm\(^{-1}\) in the first spectrum to 2080 cm\(^{-1}\). A blue-shift for the CO\(_{L}\) absorption band for larger
Pt particles compared to smaller ones is well documented\textsuperscript{21}. This shift is consistent with our ripening interpretation and in good agreement with the observed decrease in the total integrated signal in Figures 2 and 3(a), which strongly suggests that this ripening mechanism leads to a lower surface area for CO adsorption. Indeed, clearly ripened particles are observed after 20 CO adsorption/oxidation cycles in Figure 1d. Besides ripening, the blue-shift of the CO\textsubscript{L} peak in Figure 4 could also be explained by partial oxidation of the Pt nanoparticles. CO adsorption on slightly oxidized Pt surface will result in a blue-shift of the CO\textsubscript{L} IR band relative to CO adsorption on a clean Pt surface\textsuperscript{21, 22}. Note that due to the lower signal-to-noise ratio in Figures 3(c) to (f) it is not possible to observe a similar decay in the integrated intensities after the first experiments.

Enhanced particle restructuring in CO and/or O\textsubscript{2} pressure was observed and documented before\textsuperscript{24-31}. CO induced changes in the surface morphology of Pt nanoparticles are observed by infrared spectroscopy\textsuperscript{24}, scanning tunneling microscopy\textsuperscript{25, 28, 31}, environmental transmission electron microscopy\textsuperscript{29}, and grazing incidence small-angle X-ray scattering\textsuperscript{27} and are attributed to an Ostwald ripening mechanism (migration of atoms)\textsuperscript{25, 27, 28} or Smoluchowski ripening (particle migration)\textsuperscript{28}. In Ref. 26 O\textsubscript{2} induced ripping of Pt nanoparticles is attributed to an Ostwald ripening process, while in Ref. 31 enhanced ripping is observed when both CO and O\textsubscript{2} are present. Whether in the present study the loss of surface area should be attributed to Ostwald ripening, Smoluchowski ripening, or both\textsuperscript{32}, cannot be answered with the data at hand. The observed neck-formation (see Figure 1(d)) could originate from both processes individually and from a combination of the two ripening mechanisms.

For CO\textsubscript{b} and CO\textsubscript{MB}, an increase in the peak height is observed in Figures 5(a) and 5(b) at 25 and – 25 V. The highest intensity growth is revealed in Figure 5(b) for an applied potential of 25 V along with a red-shift to 1700 cm\textsuperscript{-1} as the applied E-field increases. To assess possible CO dissociation effects caused by high applied electrical potentials, in Figure SI-1 we compare the integrated CO\textsubscript{MB} as a function of time at different electrical potentials. No changes in oxidation time are observed for -25 V, 25V and 0V, suggesting that similar amounts of CO species (CO\textsubscript{L}, CO\textsubscript{b} and CO\textsubscript{MB}) are adsorbed on Pt nanoparticles. Therefore, possible dissociated CO might be minimal.
This shift is attributed to an increase in the bond strength due to a reduce $\pi$ back donation when the electron density on the Pt lowered by the application of the electrical potential. Significant loss of surface area is endorsed to a loss of IR intensity during CO exposure cycles. The effects flatten off after $V = -5$ (see Figure 3), and thus any change in the IR ration in Figure 6 cannot be attributed to the loss of surface area, since the integrated values stayed constant after the measurement at - 5 V. Thus, changes in the $\text{CO}_\text{L}/\text{CO}_\text{B}$ & $\text{CO}_\text{L}/\text{CO}_\text{MB}$ ratios are assigned to the application of the E-field. These results indicate that the electronic modification of the platinum nanoparticles can be caused by the application of the electrical field, particularly at positive potentials, were a pronounced decrease in both ratios is observed. A change in the electronic structure of the (supported) metal particles influences the adsorption geometry of adsorbed CO as a consequence. Similar lowering of the $\text{CO}_\text{L}/\text{CO}$ bridging ratios are observed (see Figure 6) for alkali-promoters during a catalytic chemical reaction, e.g. Pt/SiO$_2$ and Pt/Zeolites. In these studies, the integrated intensity ratio of the $\text{CO}_\text{L}/\text{CO}$ bridging drops significantly, suggesting an increase in the electron density on the metal atom with increasing alkalinity of the support. Our results are in agreement with J. T. Miller et al., who reported a shift to lower frequency and a decrease in the linear to bridging ratio as the alkalinity of the support increases. For CO, a decrease in the binding energy of the Pt valence orbitals would result in a better overlap of the 5d--$\pi^*$ orbitals this leading to more $\pi^*$ electron density, a weaker C--O bond and a shift in the IR bands to lower energy. Likewise, their theoretical calculations predict a shift from linear to bridge-bonded CO when there is a better overlap of the 5d--$\pi^*$ orbitals. It is important to note that effects in the adsorption geometry of the molecule (i.e. increases of the $\text{CO}_\text{B}$ and $\text{CO}_\text{MB}$ integrated areas) due to an increase in temperature are unlikely. For such temperature effects a sharp drop (or increase) in the $\text{CO}_\text{B}$ or $\text{CO}_\text{MB}$ integrated area in Figure 3 are expected at higher temperatures ($\sim 100^\circ\text{C}$).

In short, by controlling the applied potentials to the ATR-IR microreactor, the adsorption geometry of $\text{CO}_\text{MB}$ can be tuned. Therefore possible applications to increase selectivity during a catalytic chemical reaction can be expected.
5. Conclusions

We have studied the influence of the presence of low strength E-fields on CO adsorption on supported Pt particles \textit{in situ} by ATR-IR in a sequence of CO adsorption/oxidation cycles. A decrease of the ATR-IR intensity of the CO$_{L}$ absorption band is observed in subsequent CO adsorption/oxidation cycles. This observed decrease in the ATR-IR intensity is caused by a coarsening effect during the experiment and is not directly influenced by the direction or the magnitude of the applied E-field. Drops in the CO$_{L}$/CO$_{B}$ and CO$_{L}$/CO$_{MB}$ ratios are found. Excitingly, by combining ATR-IR spectroscopy with an E-field, new insights are generated regarding controlling the adsorption geometry of the tested adsorbate.

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Figure captions

**Figure 1.** (a) Schematic representation of the microreactor used in this study. On the top electrode of $p^+$-type Si 15 µm high micropillars are micromachined (note that the microdevies are not drawn to scale). On the bottom electrode, which acts as an ATR-internal reflection element, 140 nm SiO$_2$ (orange) is grown. (b)-(d) SEM images of (b) the bottom electrode of a fractured freshly coated microreactor (the inset shows a higher magnification); (c) a coated Si wafer, and (d) a bottom electrode of coated microreactor after having been subjected to CO adsorption studies. In (d) an example of coalesced particles is outlined by the ellipse. (e)-(f) Fowler-Nordheim plots extracted from the I(V) measurements for the Pt nanoparticles coated microreactors in 10% O$_2$/He mixture. In (e) the E-field is directed downwards (from the top towards the bottom electrode), while in (f) the E-field is directed upwards. The dotted lines are linear fits.

**Figure 2.** (a) ATR-IR spectra recorded during CO adsorption without an applied E-field. The inset shows a 100x magnification of the signal from 1900 to 1600 cm$^{-1}$ after correction for water absorption, by subtraction of the last spectrum (with the water signal) of a completed adsorption/oxidation cycle. (b) ATR-IR spectra recorded at 210 min during CO adsorption pre-treatment cycles.

**Figure 3.** Integrated intensities of the CO$_L$ (a-b), CO$_B$ (c-d) and CO$_{MB}$ (e-f) absorption bands in subsequent adsorption cycles (Sequence: 0 V, -5 V, -15 V, -25 V (in (a), (c) and (e), field downwards), 0 V(1), 0 V(2), 5 V, 15 V, 25 V (in (b), (d) and (f), field upwards)). The legend in (a) is also valid for (c) and (e), the legend in (b) for (d) and (f). Note: (a) Integrated intensities of the CO$_L$ IR bands without applied E-field (i.e. V = 0) prior to V = -15 and V = -25 (0V(-15) & 0V(-25)).

**Figure 4.** ATR-IR CO absorption spectra after 200 min. exposure to CO of the reference measurements (i.e. measurements without E-field, V = 0) performed within two CO adsorption cycles in which an E-field was applied.
Figure 5. ATR-IR CO$_B$ and CO$_{MB}$ absorption spectra during the application of a negative potentials in (a) at $V = -5, -10, -15, -25$ and during the application of a positive potentials in (b) at $V = 5, 10, 15, 25$. The plotted spectra are time averaged from $t = 150-155$ min, close to the end of CO adsorption step.

Figure 6. CO$_L$/CO$_B$ and CO$_L$/CO$_{MB}$ ratios as a function of the applied potential. This calculation based on the averaged results in Figure 3. The ratios averaged after ~80 minutes.
Figure 1

(a) Schematic diagram of the device.

(b) SEM image of the samples with dimensions.

(c) SEM image of the surface at 20 nm resolution.

(d) SEM image highlighting specific features.

(e) Graph showing LN(J/E^2) vs. E^1 for an E-field downwards.

(f) Graph showing LN(J/E^2) vs. E^1 for an E-field upwards.
Figure 2
Figure 3

E-field downwards

(a)

(b)

E-field upwards

(c)

(d)

(e)

(f)
Figure 4
Figure 5
Figure 6

![Graph showing the relationship between CO and CO\textsubscript{MB} with applied potential (Volts).]
Graphical Abstract
Supporting information

CO adsorption on Pt nanoparticles in low E-fields studied by ATR-IR spectroscopy in a microreactor

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1. Following CO adsorption experiments from Figure 3 (see main text).