CO Adsorption and Oxidation at the Catalyst−Water Interface: An Investigation by Attenuated Total Reflection Infrared Spectroscopy

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Adsorption of carbon monoxide and oxidation of preadsorbed carbon monoxide from gas and aqueous phases were studied on a platinum catalyst deposited on a ZnSe internal reflection element (IRE) using attenuated total reflection infrared (ATR-IR) spectroscopy. The results of this study convincingly show that it is possible to prepare platinum metal layers strongly attached to an IRE, which are stable for over 3 days in aqueous-phase experiments. It is shown that ATR-IR spectroscopy is a suitable technique to study adsorption and catalytic reactions occurring at the interface of a solid catalyst in an aqueous reaction mixture, even with an extreme low-surface-area catalyst. Clearly, ATR-IR spectroscopy allows for a direct comparison of reactions on a catalytic surface in gas and liquid phases on the same sample. CO was found to adsorb both linearly and bridged on the platinum metal layer when adsorbed from the gas phase, but only linear CO was detected in aqueous solution, although with 5 times higher intensity. Oxidation of preadsorbed CO on platinum occurs in both gas phase, wetted gas, and aqueous media and was found to be 2 times faster in the aqueous phase compared to gas-phase oxidation because of a promoting effect of water. Moreover, during oxidation at room temperature, CO_2 adsorbed on Pt/ZnSe was detected in both gas and aqueous phases.

Introduction

Vibrational spectroscopy plays a key role in studies of adsorption and catalytic reactions at metal surfaces. Infrared spectroscopy has long been used as a sensitive technique for detection of adsorbed species at the metal−gas interface. However, also many catalytic reactions take place at a metal−liquid interface, e.g., the catalytic removal of nitrate from drinking water. It is important to be able to examine the interface by infrared spectroscopy to gain insight in adsorption and reaction mechanism. However, infrared spectroscopic studies at the metal−liquid interface have not yet received much attention, although recently some papers have shown the clear difference between adsorption in gas and liquid phases, as will be reviewed below.[1−4]

Normally, liquids are strong absorbers of infrared radiation; therefore, transmission infrared spectroscopy is not suitable to apply unless the path length is very short, i.e., in the order of a few micrometers. Attenuated total reflection infrared (ATR-IR) spectroscopy, however, is ideally suited for studying molecular vibrations at the solid−liquid interface because the evanescent wave is restricted to the region near the interface, thereby minimizing the contribution from the liquid.[5] The restriction of the infrared radiation to the interface is especially important when water is used as a solvent, because water is a very strong absorber in the mid-infrared region. ATR-IR have for a long time been used as a analytical tool to study the solution composition and to study the protein structure in biochemistry.[6]

On the other hand, the application of ATR-IR to study adsorption and reactions at the solid−liquid interface has only recently started.[1,2,7−11]

In the earlier applications of ATR-IR to study the solid−liquid interface, the technique was used to study the goethite−aqueous interface where the oxide particles were suspended in water.[11] The signal intensity varied because of the aggregation of the suspension.[8]

More stable signals can be obtained by depositing a very thin solid layer on an internal reflection element (IRE). In that case, it is essential that the thickness of the layer does not exceed the penetration depth of the infrared radiation (i.e., less than 1 μm). This approach was first introduced by depositing an Al_2O_3 film on the IRE by sputtering, to study adsorbed species at the Al_2O_3/ water interface.[10] However, it was not possible to examine adsorption for longer periods than 3 h because the Al_2O_3 layer became continuously thinner during water exposure.[10]

In addition, in the field of heterogeneous catalysis, ATR-IR was applied to study reactions with supported catalysts in organic solvents (cyclohexane or dichloromethane)[7,9] Supported and unsupported model catalysts were prepared by physical vapor deposition.[7] Recently, adsorption of CO on Pt/Al_2O_3 from aqueous solution examined with ATR-IR was reported.[1,2] In one study, the adsorption and oxidation of CO over Pt/Al_2O_3 was investigated in several solvents including water.[2] In another study, CO adsorption on Pt/Al_2O_3 was investigated in relation to the water−gas shift reaction and methanol reforming.[1] Clear spectral differences were observed between the adsorption from gas and liquid phases,[1,2] and the reaction order for the water−gas shift reaction and methanol reforming was reported to be influenced by the presence of water.[1]

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In addition to supported catalysts, ATR-IR was used to compare CO adsorption from gas and aqueous phases on thin platinum and palladium films.[12] Adsorption was performed from aqueous solution, and subsequently, infrared spectra were collected after removing the liquid by flushing. A comparison was only possible for the palladium film because the platinum film was unstable in contact with water, whereas palladium films were more resistant.[13] The stability of thin metal layers used as catalyst films for ATR-IR is generally a problem in aqueous phase, especially in the case of platinum.[12–14] The interaction of monolayers of water (D_2O) and CO was examined on single-crystal platinum [Pt(100) and Pt(111)] by infrared reflection absorption spectroscopy.[3,4] In both cases, the electronic properties of adsorbed CO were found to be altered by the presence of water.

On the other hand, in electrochemistry, the use of thin metal layers combined with infrared spectroscopy has been applied. Electrochemical studies combined with infrared spectroscopy at the solid−liquid interface are mainly done by RAIRS (reflection absorption infrared spectroscopy) and not ATR-IR. In electrochemistry, several studies reported the use of RAIRS to study the electro-oxidation of CO on platinum.[15,16] However, in RAIRS, the catalyst (e.g., a platinum film or electrode) is placed in close contact with the prism, thereby displacing the liquid during IR measurements, to ensure a short path length through the liquid and having the catalyst film in the infrared beam; during the reaction, the catalyst is pulled back from the prism and exposed to the solution.[15,16] Although in electrochemistry many publications appeared on RAIRS, the main disadvantage of this technique is that the sample has to be put very close to the IR window, which does not allow rapid transport of adsorbing/reacting molecules in the liquid. In contrast, with ATR-IR, it is possible to follow the reaction *in situ* without the need to displace the solution because the catalyst film is in contact with the IRE. Nevertheless, the combination of electrochemistry and ATR-IR has only been applied by one group to study the electro-oxidation of CO over platinum, but only very poor spectra for adsorbed CO were reported.[17]

In conclusion, the application of ATR-IR allows for mimicking operating conditions of liquid-phase catalytic reactions, without introducing additional mass-transfer limitations. Moreover, experiments can be performed in both gas and liquid phases on the same sample, offering the possibility to clarify the effect of the solvent and water in particularly on the spectral properties and reactivity of adsorbed species on metal surfaces. It is the objective of this work to prepare and investigate a stable thin platinum layer at an IRE and show the possibilities for *in situ* ATR-IR examination of adsorption and reactions occurring on a stable platinum layer in both gas and aqueous solution. As a first step toward examination of catalytic reactions on unsupported catalysts in aqueous phase, adsorption and oxidation of preadsorbed carbon monoxide on a platinum layer are examined in dry and wetted gas as well as in aqueous solution.

Experimental Procedures

Thin-Film Preparation. The thin catalyst film was prepared by evaporating a solution containing 0.05 mg of platinum prepared from dihydrogen hexachloroplatinate (0.088 mg of $H_2PtCl_6 \cdot 6H_2O$/

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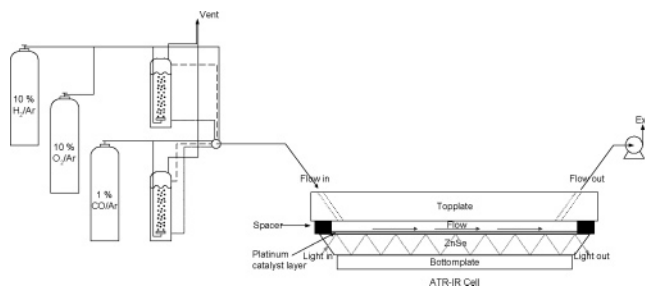(13) Zhu, Y.; Uchida, H.; Yajima, T.; Watanabe, M. *Langmuir* **2001**, *17*, 146.
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Figure 1. Schematic presentation of the experimental setup with gas supply, saturators, and FTIR spectrometer equipped with the home-built ATR-IR cell.

mL H_2O) (Alfa Aesar) on a ZnSe Internal Reflection Element (IRE, 45°, 50 × 20 × 2 mm, 25 reflections of which 13 are at the catalyst interface, ICL). The solution was left to evaporate overnight at 273 K in air followed by drying at 398 K for 2 h in flowing synthetic air and subsequent reduction in 50% H_2/N_2 at 498 K for another 2 h (flow rate of 30 mL min^{-1}, heating and cooling ramp at 1 K min^{-1}).

The catalyst is denoted Pt/ZnSe, and the same layer was used throughout all experiments to ensure identical conditions for intensity comparison. Nevertheless, it is possible to reproduce the reported results when other platinum layers were prepared. After each adsorption and oxidation experiment, the sample was heated to 398 K in synthetic air to remove any adsorbed species and subsequently reduced in 50% H_2/N_2 at 398 K (flow rate of 30 mL min^{-1}, heating and cooling ramp at 1 K min^{-1}).

***In Situ* ATR-IR Spectroscopy.** ATR-IR spectra were recorded at room temperature (294 K) with a Tensor 27 (Bruker) infrared spectrometer by averaging 100 scans with a resolution of 4 cm^{-1}. Infrared spectra were recorded using a home-built stainless-steel flow-through cell as shown in Figure 1.

The gap between the polished steel topplate and the IRE was 0.3 μm (created by the spacer); the length and width of the exposed area of the coated IRE was 40 × 10 mm, respectively. The total volume of the cell was 120 μL. After the cell was assembled in the IR spectrometer, it was purged with gaseous argon followed by a reducing gas flow for 2 h (10% H_2/Ar) to remove surface oxygen and background spectra were taken unless otherwise indicated.

Gas flow was regulated by flow controllers (Brooks 5850 TR), while liquid was flown over the catalyst by means of a belt pump mounted downstream (Watson Marlow 503s). Water (Q2 water, prepared by use of the Millipore Milli-Q water treatment system from Amphotech Ltd.) was provided from two separate glass saturators (bubble tanks), where water could be saturated with carbon monoxide, hydrogen, or oxygen at room temperature (294 K). For experiments performed in a wetted atmosphere, gases (Ar, CO, and O_2) were moistened with 2.5 vol % water (calculated on the saturation at room temperature and 1 atm pressure) in the two glass saturators. A schematic presentation of the experimental setup is shown in Figure 1.

After purging the sample compartment with dry nitrogen for 2 h (during the reduction in 10% H_2/Ar, gas), the cell was flushed with argon, while the background spectrum was recorded. When experiments were performed in aqueous solution, the cell was flushed with hydrogen-saturated water, while a background spectrum was recorded. All flow rates used in the experiments were 5 mL min^{-1} for both gases and liquid.

Results

Characterization of Thin-Film Model Catalyst. An atomic force microscope was used to characterize the catalyst layer. The catalyst layer consisted of platinum clusters up to 30 nm as shown in Figure 2. Dispersion of the platinum was calculated to be between 3 and 4%, assuming a particle size of 30 nm, resulting in a surface area of 0.015 m^2. The catalyst layer prepared by evaporation was found to adhere to the IRE in such way that
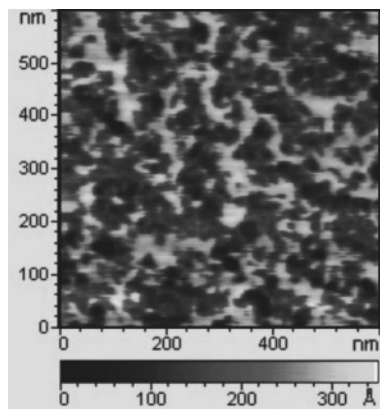
Figure 2. AFM image of the prepared platinum layer on IRE.
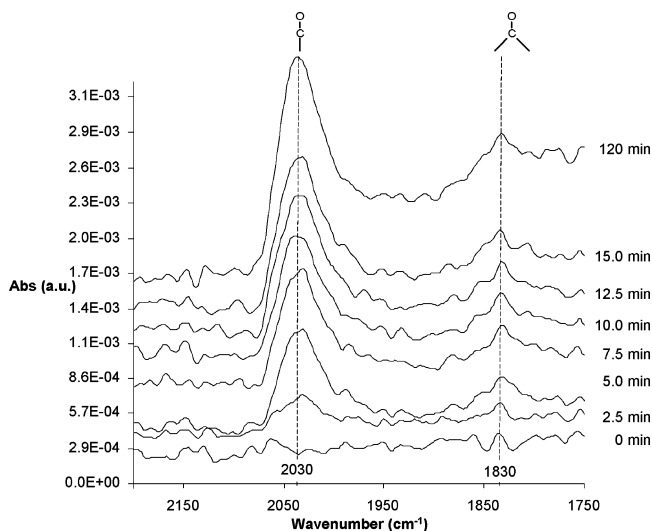
Figure 3. ATR-IR spectra as a function of time, showing the region of CO adsorption on Pt/ZnSe, while dry CO was flown (1% CO/Ar).

no loss of the IR signal was observed when water was flown over the layer for over 3 days. The film was sufficiently transparent for the ATR experiments, because it caused transmission of ca. 15%.

Adsorption of Dry CO on Pt/ZnSe. After reduction (see the Experimental Procedures), 1% CO/Ar was introduced into the cell. Figure 3 shows the ATR-IR spectra obtained during the flow of carbon monoxide over Pt/ZnSe. During CO flow, no gaseous CO was detected but only adsorbed CO was found with a distinct asymmetric infrared peak at 2030 cm^{-1} (width at half-height of about 50 cm^{-1}) and a small broad peak at 1830 cm^{-1}. The intensity leveled off in time, and a saturation value was reached after about 30 min. During adsorption, the peak positions remained constant.

Adsorption of Wetted CO on Pt/ZnSe. To examine whether water has an influence on the adsorption of carbon monoxide on the Pt/ZnSe catalyst, CO adsorption was performed in a wetted atmosphere. After the background measurement, argon moistered with water was flown over and adsorbed water on Pt/ZnSe was observed (not shown).

Subsequently, wetted 1% CO/Ar (2.5% H$_2$O) was introduced into the cell. Again, two bands developed at 2030 and 1830 cm^{-1} (not shown). When CO was adsorbed from wetted gas, the observed intensities were comparable to the adsorption from dry gas as shown in Figure 8. Peak positions and widths for adsorbed CO remained constant during adsorption.

ATR-IR of Water. Figure 4a shows the ATR-IR spectrum of water. Liquid water is characterized by two strong peaks in
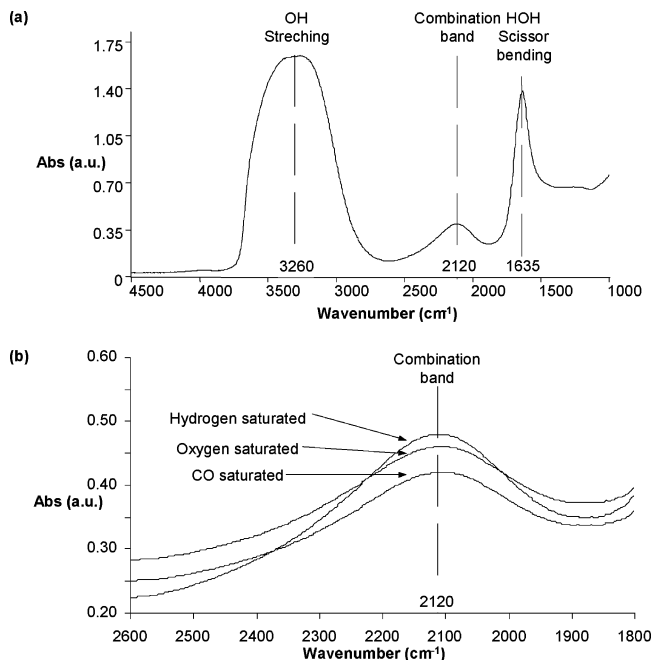
Figure 4. ATR-IR spectra of (a) pure water on a clean ZnSe IRE and (b) saturated with different gases in the region of the combination peak.

the same spectral region as the strong vibration−rotation peaks of water vapor. Similar to water vapor, a broad peak at 3260 cm^{-1} corresponding to O−H stretching and a peak at 1635 cm^{-1} from the scissor bending were detected. However, in the case of liquid water, additional weaker near-infrared peaks (300−900 cm^{-1}) have been reported, which have no corresponding peaks in water-vapor spectra.[18] An effect of these peaks can be found in the mid-infrared region, where a combination of the scissor bending at 1635 cm^{-1} and a very broad libration peak in the near-infrared region is detected as a broad and weak peak at around 2120 cm^{-1} (Figure 4a). Clearly, this peak is located in the same region as the adsorption peaks for linear- and bridge-adsorbed CO on Pt.

Figure 4b shows the ATR-IR spectra of water saturated with respectively H$_2$, CO, or O$_2$ in the region of the combination band. It is seen that the intensity of the peaks changed because of the type of dissolved gas. In comparison to H$_2$-saturated water, the intensity of the combination band decreased and broadened when saturated with CO and O$_2$.

Because, during the experiments, water is saturated with different gases, it is necessary to include the change in the peak intensity of the combination band, in the data analysis. The effect of dissolved gases can be treated by the subtraction of a scaled background chosen by a fit to the spectrum of the sample to obtain a corresponding water spectrum in the infrared region where CO adsorption was detected (2200−1750 cm^{-1}).

Adsorption of Carbon Monoxide on Pt/ZnSe from the Aqueous Phase. Subtraction of the scaled background from the spectra of adsorbed CO on Pt/ZnSe resulted in the spectra shown in Figure 5. An asymmetric infrared peak at 2030 cm^{-1}, developed in time when an aqueous solution saturated with CO was flown over the sample. With an increasing coverage, the peak position shifted from around 2020 to 2030 cm^{-1} at the saturation level. The width at half-height was found to be between 50 and 55 cm^{-1}, similar to gas-phase experiments. However, no bridged adsorbed CO could be detected at 1830 cm^{-1}, which can be due

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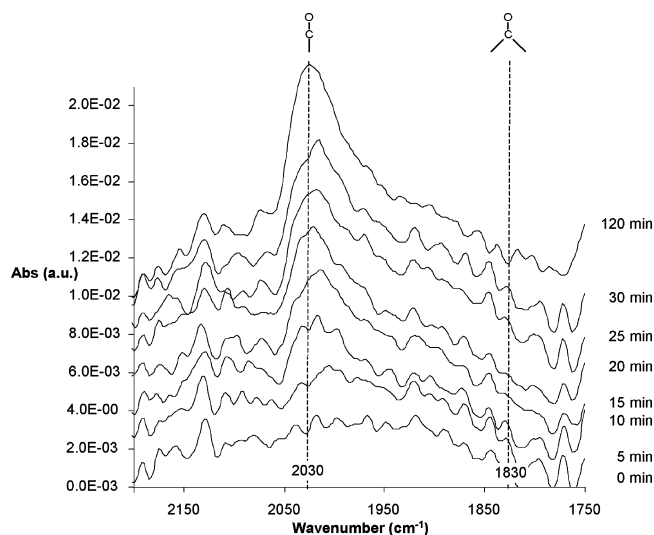
Figure 5. ATR-IR spectra as a function of time, showing adsorbed CO on Pt/ZnSe, while water saturated with CO was flown (0.035% CO/H$_2$O).

to either the lower signal-to-noise ratio or the absence of bridged CO. When adsorbed from aqueous solution, it took approximately 1 h to approach the saturation level and the intensity kept increasing slightly as for adsorption in a wet atmosphere (Figure 8). Moreover, the intensity was around 5 times higher for adsorption from the aqueous phase compared to adsorption from dry or wetted gas. After oxidation of CO (*vide infra*) and drying of the sample, adsorption of CO from dry gas resulted again in a 5 times lower intensity compared to adsorption from aqueous solution, illustrating the stability of the sample.

Oxidation of Preadsorbed Carbon Monoxide on Pt/ZnSe. Figure 6 shows the ATR-IR spectra collected during oxidation of preadsorbed CO on Pt/ZnSe by flowing dry 10% O$_2$/Ar. Both linear- and bridge-adsorbed CO peaks decreased during oxidation, while simultaneously a sharp peak developed at 2340 cm^{-1} (close to the gas-phase signal for CO$_2$ at 2340$-$2360 cm^{-1}).

Oxidation of preadsorbed CO from wetted gas was performed in wetted 10% O$_2$/Ar over Pt/ZnSe (not shown). Again, both peaks for linear- and bridge-adsorbed CO decreased, while a peak developed at 2340 cm^{-1}.

Figure 7 shows the ATR-IR spectra collected during oxidation of preadsorbed CO in aqueous solution. When oxygen-saturated water (0.5% O$_2$/H$_2$O) was flown over the Pt/ZnSe catalyst, first a shift in the peak position of linear-adsorbed CO on platinum, from 2030 to 2035 cm^{-1} occurred within 5 min, while the intensity remained constant. After the shift in the peak position, adsorbed CO disappeared and a peak at 2340 cm^{-1} evolved.

Discussion

This study convincingly shows that it is possible to prepare platinum metal layers strongly attached to an IRE, which are stable for many hours in aqueous-phase experiments. Especially in water, the stability of metal layers was reported to be a major problem.[12-14] In previous studies, the metal layer was prepared by sputtering, while in the present study, a chemical route was chosen. Deposition of the layer by evaporation of a solution containing a platinum precursor, followed by calcination and reduction treatments, obviously leads to a stable metal layer.

CO Adsorption. When Pt/ZnSe was exposed to CO, in dry gas, wetted gas, or water, distinct peaks developed in all cases around 2030 cm^{-1}, which can be assigned to linearly adsorbed CO on platinum metal particles. In addition, small bands

developed at 1830 cm^{-1} when adsorbed from either dry or wet gas, which can be assigned to bridged CO. In general, CO stretch frequencies vary between 2000 and 2100 cm^{-1} when adsorbed in linear geometry onto platinum metal surfaces, although mostly between 2050 and 2090 cm^{-1}.[19-22] Stretch frequencies for CO adsorbed in bridged geometry are normally found between 1750 and 2000 cm^{-1}.[19-22] The high linear/bridge ratio as observed for the Pt/ZnSe sample indicates the presence of large metal particles,[23] in agreement with the AFM picture (Figure 2). However, normally large platinum metal particles show CO absorption frequencies above 2065 cm^{-1},[23] while in this study, a much lower peak position is found (2030 cm^{-1}). These results might be explained by an alloying of Pt with ZnSe from the IRE as a result of the preparation method of the sample that includes calcination at 398 K and reduction at 498 K. This alloying could alter the platinum electronic properties in such a way that a unique adsorption is created, which is different from pure platinum layers or single crystals. Unfortunately, no techniques are available to investigate this hypothesis. Characterization techniques, such as XPS, LEIS, and SEM-EDX will not be able to distinguish Se signals of the crystal from Pt$-$Se alloys.

Interestingly, the observed integrated intensity of the linear CO band increased with a higher water content on the sample (Figure 8), while no shift in the peak position was detected. The intensity change was found to be reproducible on the same sample by alternating dry and wet experiments, indicating sample stability under the applied experimental conditions. A slight increase in intensity was found from dry to wet gas, but a 5 times higher intensity was observed when CO was adsorbed from the aqueous phase compared to the gas phase.

A comparison of CO adsorption on Pt/Al$_2$O$_3$ from gas and aqueous phases showed a clear red shift of up to 35 cm^{-1}, both in our laboratory (to be published) and in the literature.[1,9] The shift in infrared frequency is a complex matter and involves several factors such as the dipole moment, adsorption geometry, and metal$-$CO bond length and strength.[4] The interaction of monolayers of heavy water (D$_2$O) and CO has been examined on single-crystal platinum [Pt(100) and Pt(111)] by IRAS.[3,4] In both cases, the spectral properties of adsorbed CO were found to be altered by the presence of water. A clear red shift was observed for the frequency of both linear and bridge CO adsorbed on platinum, which was explained by a combination of increased π-back-donation from Pt to CO and a change in the CO dipole moment.[3,4] Changes in intensity of the infrared peaks have, however, not been discussed in the literature to the best of our knowledge. Possible causes for this higher intensity could be (1) an increase of the number of adsorption sites, (2) a higher coverage, (3) a change in the penetration depth, and (4) a larger extinction coefficient.

An increased number of adsorption sites, because of disintegration of platinum particles when exposed to water, can be excluded as an explanation for the increased intensity, because the experiments showed that the results are reproducible in both gas and liquid phases when performing repeating dry and wet experiments on the same sample. Further, the intensities leveled off in time in all cases (Figure 8). CO is well-known to adsorb strongly on platinum, and full coverage is easily reached in the
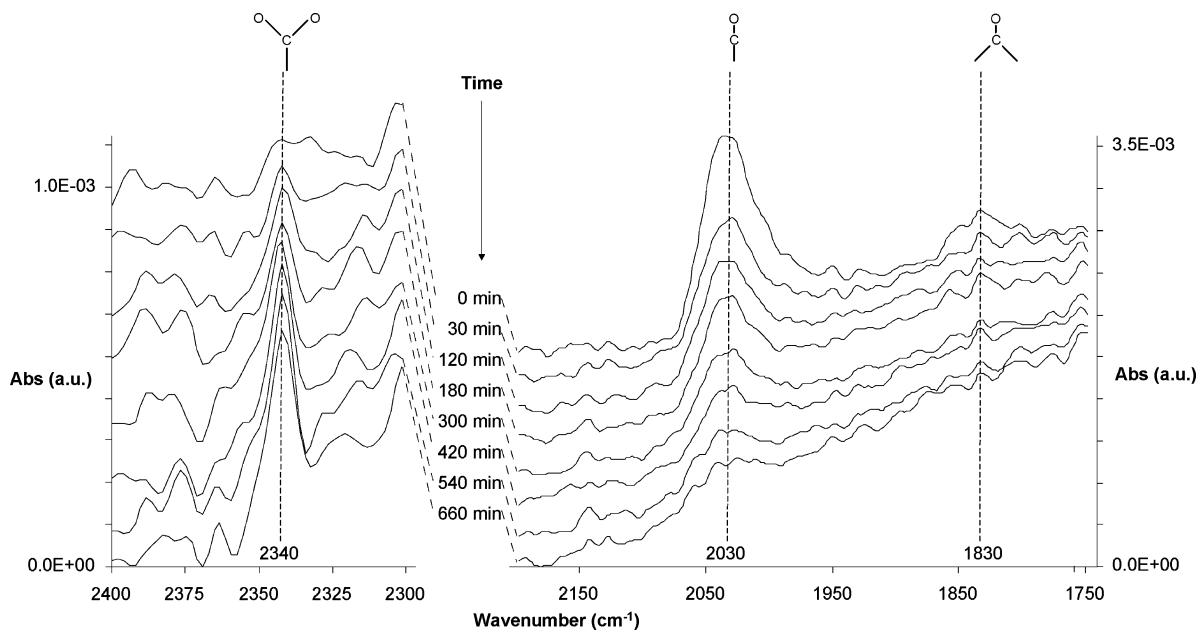
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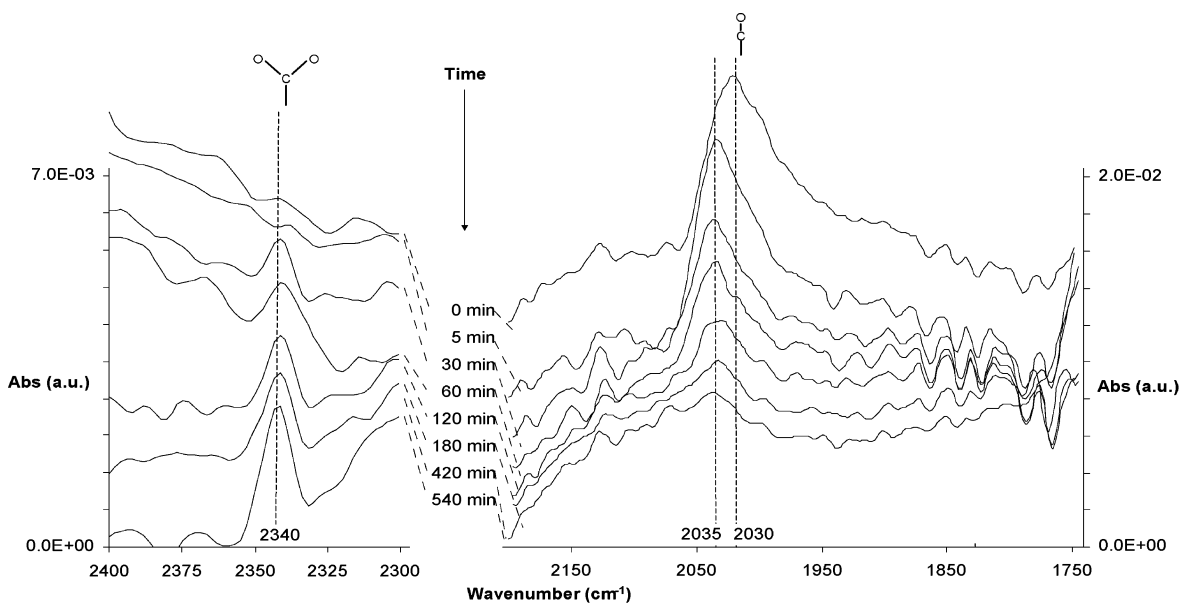(20) Kuhn, W. K.; Szanyi, J.; Goodman, D. W. *Surf. Sci. Lett.* **1992**, *274*, L611.

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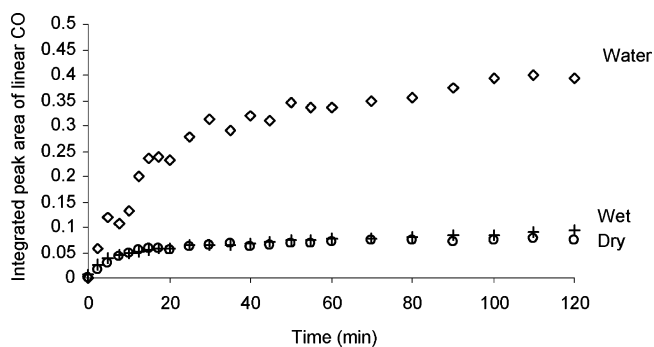
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Figure 6. ATR-IR spectra as a function of time, while flowing dry gas-phase oxygen (10% O_2/Ar) over Pt/ZnSe with preadsorbed CO.

Figure 7. ATR-IR spectra showing adsorbed CO and CO_2 on Pt/ZnSe, while oxygen saturated water was flown (0.5% O_2/H_2O).

Figure 8. Integrated peak areas of linear CO adsorbed on Pt/ZnSe, when CO was adsorbed from either dry (O) or wetted (+) gas or CO-saturated water (◇).

gas phase at 1 atm. For this reason, CO is often used for determination of metal dispersion.[24] It seems therefore impossible that adsorption of CO from the aqueous solution would lead to

a 5 times higher monolayer coverage on the platinum particles compared to gas-phase adsorption.

The penetration depth (d_p) of the ATR light can be calculated according to

$$d_p = \lambda_1/2\pi(\sin^2\theta - n_{21}^2)^{1/2}$$

The refractive index ratio is given by $n_{21} = (n_2/n_1)$, where n_2 is the refractive index of either the gas or water and n_1 is the refractive index of the IRE. λ_1 is the wavelength in the IRE and is given by $\lambda_1 = (\lambda/n_1)$. The penetration depth is higher in the aqueous phase ($d_p = 690$ nm at 2000 cm^{-1}) compared to the gas phase ($d_p = 550$ nm at 2000 cm^{-1}), because of the difference in the refractive index.[1] First, the penetration depth increased by a factor of 1.25 only, which is much less than the factor of 5 observed in the intensity of the CO band. Second, the platinum

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layer was probed by AFM to be around 30 nm thick, which is much smaller than the penetration depth of the light in either the gas or water phase. As a result, the change in the penetration depth cannot change the number of sites that is being probed in these samples and thus cannot account for the increase in intensity when CO is adsorbed from aqueous solution.

Finally, it was reported that the addition of water does not change the extinction coefficient of adsorbed CO when water vapor was added to adsorbed CO on Pt/Al$_2$O$_3$.[25] This is in agreement with our present results, because hardly any change in the intensity was observed between CO adsorption from dry or wet gas. An increased intensity of the infrared peaks when adsorbed from aqueous media was previously reported for CO adsorption on palladium supported on a germanium IRE, but no explanation for this phenomenon was given.[12] On the basis of the results of this study, we suggest that the observed intensity change can be attributed to a higher extinction coefficient of the CO stretch vibration caused by the presence of water in the liquid phase. In this situation, the adsorbed CO molecules are fully surrounded by polar water molecules that will affect the dipole moment of the CO molecule, which in turn is reflected in the larger extinction coefficient. It would be expected that a change in the dipole moment of the adsorbed CO molecule would also result in a shift of the peak position. However, because the overall shift is a complex matter involving both the dipole moment and back-donation, as discussed above, it might be speculated that these factors cancel out in this specific case of Pt/ZnSe.

CO Oxidation. When oxygen was flown over Pt/ZnSe containing preadsorbed CO, a decrease in the intensity of adsorbed CO was observed in dry gas, wet gas, and the aqueous phase, accompanied by the development of a peak with an increasing intensity at 2340 cm^{-1} (Figures 6 and 7), which is about 9 cm^{-1} lower than gas-phase CO$_2$. Moreover, the ATR-IR technique is very sensitive to adsorbed species, while free reactants and products are very difficult to observe. For example, in our experiments, gas-phase CO could not be observed in any experiment. In electrochemistry, the peak at 2340 cm^{-1} is normally assigned to trapped CO$_2$ at the interface between platinum and water, formed by the oxidation of adlayer CO during a potential sweep.[16,26] In the gas-phase, however, CO$_2$ was reported to desorb from Pt(111) at temperatures above 95 K.[27] In our experiments, nevertheless, a flow of CO$_2$ at room temperature over reduced Pt/ZnSe yielded the exact same peak at 2340 cm^{-1}, which could not be removed by flushing with inert gas. Moreover, nothing was detected when CO$_2$ was flown over a clean ZnSe IRE. It is clearly surprising to find CO$_2$ adsorbed on platinum at room temperature. On the basis of the literature and our experiments, it seems reasonable to assign the peak at 2340 cm^{-1} to adsorbed CO$_2$. However, it also seems that the Pt/ZnSe sample does not contain pure platinum metal particles, because then no adsorption of CO$_2$ in the gas phase should have been found at room temperature. In addition, Pt/ZnSe also showed extremely low linear CO stretch frequencies for CO adsorption on large pure Pt particles (*vide ante*). Both observations suggest a chemical modification of the platinum particles by the interaction with the ZnSe IRE, for example, via alloy formation or strong SMSI effects. This could alter the platinum electronic properties in such a way that a unique adsorption and reaction behavior is created, which is different from pure platinum layers or single crystals. Unfortunately, as said above, at present, no techniques are available to investigate this hypothesis. Nevertheless, this
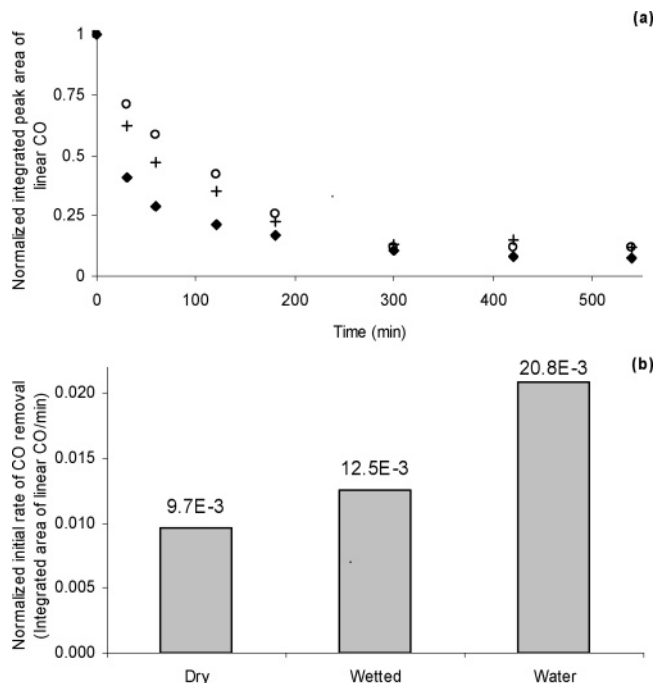
Figure 9. Normalized integrated peak areas of linear CO on Pt/ZnSe during oxidation (a) from either dry (○) or wetted (+) gas or CO-saturated water (◇) and (b) normalized initial oxidation rate in the three media.

result immediately illustrates the extreme sensitivity of ATR-IR for adsorbed species and enables the detection of adsorbed CO$_2$ on low-surface-area Pt/ZnSe at room temperature, which was not reported before.

The normalized integrated peak areas for linear CO during the oxidation of carbon monoxide in the three different media are shown in Figure 9. Remarkably, the initial rate of oxidation, defined as Δ (normalized integrated peak area for linear CO) per minute, was found to increase from dry gas (9.7×10^{-3}), to wetted gas (12.5×10^{-3}), to aqueous solution (20.8×10^{-3}) (Figure 9b). The larger observed oxidation rate cannot be attributed to the increased extinction coefficient, because the data were normalized. Consequently, the data show an enhancement of the CO oxidation rate induced by the presence of water.

Further, when oxidation was performed in aqueous solution, the peak for linear CO first shifted to a higher wavenumber (from 2030 to 2035 cm^{-1}) before it started to lose intensity. Similar shifts in the peak position have been reported for gas-phase oxidation of CO on Pt/Al$_2$O$_3$.[28] In that study, the authors attributed the blue shift to an electronic effect of adsorbed oxygen atoms close to the adsorbed CO molecules. In the present study, the blue shift is not observed in dry or wet gas-phase experiments but only in solution. In addition, the CO oxidation rate was also remarkably enhanced in excess of water, while wet gas only had a moderate influence. Interestingly, in the literature, DFT calculations have been published indicating that, during CO oxidation in water over Pt(111) and PtRu(111) surfaces, the dissociation of water is favored over PtRu(111) surfaces, while it is found to be more difficult on Pt(111).[29] The increased water dissociation contributes to the bifunctional mechanism proposed for CO oxidation in solution.[30,31] Because, in the present study, the spectral phenomena of both adsorbed CO and CO$_2$ on Pt/

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ZnSe suggest a chemical modification of the platinum particles via for example alloying with the ZnSe IRE, it could be speculated that the increased oxidation rate is also caused by an enhanced water dissociation because of this alloy formation. Nevertheless, in the absence of oxygen, no CO oxidation is observed, indicating that the observed increased oxidation rate must be the overall result of a complex interaction between water, CO, and oxygen on the Pt/ZnSe surface.

Conclusion

This study convincingly shows that ATR-IR spectroscopy can be applied to study the CO adsorption and reaction on extremely low-surface-area Pt/ZnSe samples in dry gas, wet gas, as well as aqueous solution. As such, ATR-IR spectroscopy allows for a direct comparison between adsorption and reactions in gas and liquid phases. For the first time, it is shown to be possible to prepare a catalyst film that is stable in aqueous solution for over 3 days. The layer was found to adhere strongly to the IRE during aqueous flow, and consequently, the catalyst layer could be used repeatedly.

Even though no change in infrared frequency for adsorbed CO was detected when comparing adsorption in gas and aqueous phases, the properties of CO considerably changed. The integrated peak area of linearly adsorbed CO on Pt/ZnSe was found to increase drastically in the aqueous phase compared to adsorption from the gas phase. Moreover, the presence of water promoted CO oxidation, most likely by a complex interaction of water, CO, and oxygen and the Pt/ZnSe surface. Finally, the oxidation product CO_2 was found to be adsorbed on the Pt/ZnSe surface at room temperature in dry, wetted, and aqueous phases, giving rise to an infrared peak at 2340 cm^{-1}. All observations suggest a chemical modification of the platinum particles by the interaction with the ZnSe IRE, for example, via alloy formation or strong SMSI effects.