Weakening the strength of CO binding on subsurface alloyed Pt(111)

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A B S T R A C T

The interaction of CO with Pt/3d/Pt(111) subsurface alloys (3d: Ni, Co, Fe) was investigated by combination of vibrational spectroscopy and temperature programmed desorption. The binding strength of CO is significantly reduced on Pt/Fe/Pt(111) and Pt/Co/Pt(111) and is sorted in the following order: Pt > Ni > Co ≈ Fe. Our analysis shows that the 3d admetal is stable in the subsurface region and CO is linearly bonded to the atop sites of the Pt(111) surface. At high CO coverage, compressed structures are obtained. At low CO coverage, the desorption activation energy of CO (~143 kJ/mol for Pt(111)) drops to 124 kJ/mol for Pt/Ni/Pt(111), and goes further down to 111 and 110 kJ/mol for Pt/Co/Pt(111) and Pt/Fe/Pt(111), respectively. The enhancement in the surface activity is attributed to the modified backdonation to the antibonding states of adsorbed CO due to the downshifted 5d-band center of Pt upon embedding 3d metals in the subsurface region.

1. Introduction

Platinum (Pt), the most electrocatalytically active anode material for proton exchange membrane fuel cells (PEMFC), readily interacts with carbon monoxide (CO). Adsorption strength of CO on the surface sites of Pt anode is large enough to poison the hydrogen adsorption significantly, which consequently deteriorates the performances of PEMFCs. The presence of small amount of CO in the fuel feedstock (~10 ppm) ends up dropping the current density and increases the overpotential of the fuel cell, via blocking the sites required for the hydrogen oxidation reaction (HOR) occurring at the anode [1]. Besides, poisoning is rather facile since the sticking probability of CO on Pt is 15 times greater than dissociative adsorption probability of hydrogen [2]. These demonstrate that the equilibrium coverage of CO on the Pt electrode surface is a vital parameter in the overall cell performance.

The key in minimizing the CO poisoning effect on the PEMFC activity is developing an anode material which interacts with CO weakly. PtRu bimetallic catalysts are known to offer higher CO tolerance [3,4] however, practical applications of PEMFC technology require more stable and cheaper anode materials that maintain their activity in CO contaminated hydrogen fuel. In principle, bimetallic catalysts can be designed to show superior properties that are not possessed by either one of the metal components [5], however engineering novel bimetallic catalyst systems that are active for a particular application is a challenging task [6]. The complications arise because of the difference in the surface and bulk composition, stress/strain, and uneven atom distributions in supported nanoparticles.

In subsurface alloys, a subclass of bimetallic systems, the admetals settle under the topmost surface atoms of the parent substrates. They can be observed in core-shell/multishell supported bimetallic nanoparticle catalysts and can be prepared under controlled environments by deposition techniques. The stabilization of admetals in the subsurface layer has been widely investigated [7,8], three dominant factors have been introduced as the origin of the stabilization: (i) atom size differences, (ii) the surface tension between the components, and (iii) their mixing energy. Any of these factors dominate in different bimetallic alloys. The enrichment of one metal in the topmost surface region, skin layer formation, is commonly observed [9]. For instance, the size mismatch effect is very asymmetric in Pt-Ni subsurface alloys and it is the dominant factor in temperature induced segregation of Pt atoms to the topmost layer, forming Pt rich skin layers [6,10]. Similarly, dissolution of the Fe layer initially present on top of Pt(111) and consequently creating a Pt skin layer has been proposed to be the reason of superior electrochemical oxygen reduction activity [11]. Geometrically stressed and electronically modified Pt skin layers have been found to possess enhanced activity towards various technologically important reactions/interactions including electrochemical oxygen reduction [12–14], oxygen adsorption [15], hydrogen adsorption [10], and many others [9,16].

Several strategies have been suggested to tune the CO-substrate interaction strength through bimetallic catalysis to minimize the active site poisoning and to promote thermal or electrochemical conversion kinetics of CO to other molecules [9,17]. Ni-Pt with Ni in the subsurface region has been found active for the CO oxidation reaction, however,

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segregation followed by the formation of NiO_x in an oxidizing environment has also been suggested as an important parameter in the oxidation activity [18]. Ru-Pt nanoparticles with a Pt skin layer have demonstrated a decent activity for the preferential oxidation of CO in hydrogen [19]. CO also is an intermediate in electrochemical CO_2 reduction. The activity of Cu-Au bimetallic systems towards electrochemical CO_2 reduction has been attributed to their unique electronic structures [20].

The d-band model which correlates the binding strength of the adsorbates with the d-band center of the substrate atoms is quite useful to realize the chemical activities of various surfaces [21]. The interaction of frontier orbitals of the adsorbate molecules with the valence electronic states of the transition metals describes the nature of surface chemical bonding. Modification of the surface electronic properties by alloying with another metal could give rise to changes in the catalytic activity [3]. Theoretically, the changes in the electrotonic properties is expected to be different in the bimetallic homogenous surface alloys compared to the subsurface alloys. In both cases, the interatomic distances might vary; however, the lateral interatomic distances between the metal atoms in the skin layer in subsurface alloys stay close to the bulk value, especially, when the admetal atomic radius is smaller than that of the host metal. In this case, metal-metal coordination effects in the electronic structure is expected to dominate over geometric effect exerted due to atomic size differences. The investigations on the Pt/3d/Pt(111) subsurface alloys through oxygen and hydrogen interaction have revealed that the subsurface admetals move the surface d-band center away from the Fermi level, thus weakening of adsorbate-surface bond [15,22,23].

The adsorption of CO on metal surfaces is often regarded as a benchmark system and understanding non-dissociative adsorption of CO in terms of site selectivity, coverage dependence, and intermolecular interactions etc. bring along atomistic strategies to modify this interaction [24,25]. Therefore, CO adsorption has been broadly studied, both theoretically and experimentally, and different explicit structures have been reported on several single crystal surfaces [24,26–28]. At the low coverage regime, CO prefers atop sites on most transition metal surfaces; however, there are some exemptions. For Pd(111) and Ni(111), CO is also found adsorbed on the bridge and hollow sites, respectively [26,28]. The formation of ordered structures rather than random structures is remarkable and shows that the CO adsorption energy has local minima for specific structures as a function of coverage.

In the present work, we investigated the interaction of CO with Pt(111) single crystal surfaces modified by embedding a monolayer of transition metals in 3d series (3d: Ni, Co, Fe) into the subsurface regions of Pt(111), by temperature programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS). We show that CO binding strength to these Pt/3d/Pt(111) subsurface alloys is reduced compared to Pt(111). Among the Pt/3d/Pt(111) subsurface alloys that we have studied, the Pt/Fe/Pt(111) and the Pt/Co/Pt(111) systems are the most effective at reducing the CO adsorption strength.

2. Experimental methods

Experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure better than 3×10^{-10} mbar. The chamber is equipped with a quadruple mass spectrometer (Hiden Analytical), FTIR spectrometer (Bruker Vector), an e-beam evaporator (Omicron), an ion source (Specs), an atomic hydrogen source (Omicron), and variable leak valves for gas introduction. A Pt(111) single crystal (round, 10 mm in diameter) was fixed on the sample holder by two Ta wires passing through holes at the sides of the crystal. The temperature was measured by a K-type thermocouple stuck to the backside of the crystal. The sample heating was performed by resistive heating and the temperature could be feedback-controlled within 95 to 1200 K.

The Pt substrate was prepared by repeated cycles of Ar^+ sputtering (1 kV, 1×10^{-6} mbar Ar) at room temperature, oxygen treatment at 600 K for 10 min in 1×10^{-6} mbar, and subsequent flash-annealing to 1100 K. After the last oxidation step, the sample was annealed up to 900 K to remove adsorbed oxygen atoms. Pt/3d/Pt(111) subsurface alloys were prepared by physical vapor deposition of 3d metals onto freshly cleaned Pt(111) surface at 640 K. A monolayer of 3d admetal was deposited in each case and the amount was calibrated and controlled by the flux monitor (detecting ionized 3d metals during evaporation) of the e-beam evaporator. The quality of the prepared Pt/3d/Pt(111) subsurface alloys was confirmed by the absence of CO desorption peaks originating from the clean Pt(111) surface.

CO adsorption was performed by backfilling the UHV chamber through variable leak valves. CO exposure was defined by Langmuir (L), ($1 \text{ L} = 10^{-6} \text{ Torr.s}$). All TPD measurements were performed up to 650 K with a constant heating rate of 3 K/s. A differentially pumped mass spectrometer placed in a stainless-steel tube housing was used to detect desorbing CO molecules. The housing has a cone with a round opening (8 mm ID) and was kept just ~ 0.5 mm above the crystal surface to minimize the collection of molecules that were desorbing from the sides and the backside of the crystal. The IRAS spectra were collected with p-polarized light at 84° grazing angle of incidence (resolution $\sim 4 \text{ cm}^{-1}$) and referenced to the spectrum obtained from the clean substrate taken at identical temperature. Temperature programmed IRAS data was recorded by raising the sample temperature with a constant heating rate of 1 K/s. Considering the time required to acquire a single spectrum, the sample temperature was changed by 13–14 K during each measurement. Temperature programmed IRAS spectra were referenced to the spectrum obtained from clean substrates taken at 120 K.

3. Results

First, CO exposure dependent TPD and IRAS results will be presented and then the prominent findings of the analysis of the data will be grouped to identify the variations in CO interactions with the Pt/3d/Pt(111) substrates.

CO TPD spectra collected from Pt(111) and Pt/3d/Pt(111) substrates are shown in Fig. 1. For comparison purposes, similar amount of CO up to 3 L was gradually exposed to surfaces at 120 K. It is accepted that 1 L exposure is enough to attain saturated coverage at 120 K, in fact, no significant change is observed between 1 and 3 L CO exposure. As shown in Fig. 1a, on Pt(111) substrate, a main desorption peak initially appears at 465 K and gradually shifts to 365 K as the coverage increases. An asymmetry in desorption profile is observed beyond 0.5 L CO adsorption, which becomes clearer at saturation point. A small peak that is attributed to CO desorbing from step edges appears at about 510 K and its peak position does not change with coverage [29].

CO TPD spectra from Pt/3d/Pt(111) are presented in Fig. 1b, 1c, and 1d for Ni, Co, and Fe subsurface alloys, respectively. Up to 0.5 L CO exposure, all surfaces demonstrated desorption profile similar to the bare Pt(111) with reduced desorption temperatures. For Pt/Ni/Pt(111), the peak observed at 405 K at low coverage regime shifts to 307 K as the coverage increases. At 0.3–0.4 L CO exposure, a peak broadening is observed, and it could be interpreted as overlap of the main and low temperature peaks. The progressive increase of the main peak saturates at 0.6 L CO exposure; however, the low temperature peak at 231 K further develops with the increase of CO exposure. Similar to the Pt(111) substrate, the peak assigned to CO desorbing from step edges at 510 K is apparent. For Pt/Co/Pt(111), the main peak for CO desorption at low coverage appears at an even lower temperature (362 K) than those of Pt(111) and Pt/Ni/Pt(111), which progressively decreases to 305 K with increasing coverage. A shoulder peak at lower temperature appears at CO exposures above 0.4 L, which develops as a broad peak at $T = 214$ K with increasing coverage. CO at the step edges desorbs at about 505 K and the peak temperature shifts to lower temperature with increasing coverage, which is different from the behavior observed in

Fig. 1. CO TPD spectra from Pt(111) and Pt/3d/Pt(111) (3d: Ni, Co, Fe) substrates. CO was adsorbed at 120 K and exposure amounts are individually provided on the figures. CO pressure represents mass spectrometer signal, (m/e)⁺ = 28 amu. Heating rate was set to 3 K/s.

the other substrates. The CO desorption profiles of Pt/Fe/Pt(111) share similarities with that of Pt/Co/Pt(111) up to ~0.5 L. There is a significant deviation above 0.5 L CO exposure, where distinct peaks at $T = 210$ K and 160 K are observed for Pt/Fe/Pt(111) whereas a broad peak was observed for Pt/Co/Pt(111). Another difference is in the desorption of CO from step edges. Desorption peak maxima found at 496 K does not change with CO coverage. In all Pt/3d/Pt(111) samples, there is a region between the main CO desorption peaks and the peak associated to CO desorbing from step edges. There could be a broad desorption feature at about 400 K which is more distinct in Pt/Fe/Pt(111).

Fig. 2 shows IRAS spectra obtained from CO adsorbed on the Pt

Fig. 2. IRAS spectra of CO adsorbed on (a) Pt(111), (b) Pt/Ni/Pt(111), (c) Pt/Co/Pt(111), (d) Pt/Fe/Pt(111) substrates. CO was adsorbed at 120 K and exposure amounts are individually provided on the figures. Spectral resolution was 4 cm⁻¹.

Fig. 3. (a) Coverage dependent stretching frequency shift of CO adsorbed on Pt(111) and Pt/3d/Pt(111) (3d: Ni, Co, Fe) substrates at 120 K. (b) Stretching frequency shift during temperature programmed IRAS of adsorbed CO on Pt(111) and Pt/3d/Pt(111) substrates. Heating rates were 0.1 K/s.

(111) and Pt/3d/Pt(111) substrates with increasing coverage. Observed peaks correspond to stretching C–O frequencies of adsorbed CO and the peak positions depend on the type of the adsorption site. The maximum CO exposure in these samples is less than 5 L. As seen in Fig. 2a–d, a single peak dispersing within 2080–2060 cm⁻¹ depending on CO exposure is observed on the Pt/3d/Pt(111) substrates whereas the spectra obtained from adsorbed CO on Pt(111) consist of two peaks. The first peak is in similar but in a slightly higher frequency regime (2105–2090 cm⁻¹), the second peak appears after 0.5 L CO exposure with a frequency centered at 1848 cm⁻¹ and blueshifts gradually to ~1855 cm⁻¹ with coverage. Blueshift and increase in the peak intensity with increasing CO coverage are observed in all samples studied. TPD and IRAS spectra of CO presented in Figs. 1 and 2 were used as benchmark data. The analysis was focused to the coverage dependent changes in the desorption temperatures, the shifts in the C–O stretching frequencies and the variations in the peak intensities.

Fig. 3 reveals the coverage dependent evaluation of the C–O stretching frequency at 120 K and subsequent frequency changes during temperature programmed desorption. Fig. 3a clearly shows the extent of the blueshift for all samples upon isothermal CO exposure. A significant redshift is observed at the initial stages of CO adsorption on Pt/3d/Pt(111) substrates relative to Pt(111), and increase in CO exposure up to 1 L is resulted in a gradual blueshift. This blueshift monotonously decreases between 1 L and 2 L. Beyond 2 L no significant shift was observed. Similar behavior is observed on all substrates. We also note that C–O stretching frequencies on Pt/Ni/Pt(111) and Pt/Co/Pt(111) are close at low coverage regime. At high coverage regime however, they were almost identical on Pt/Co/Pt(111) and Pt/Fe/Pt(111).

In Fig. 3b, temperature programmed IRAS of C–O stretching frequencies is shown. The frequencies at low temperatures represent the saturation coverage of CO (~4 L). As the temperature is raised, a redshift in the C–O stretching frequencies is observed on all substrates. On Pt(111), a redshift from 2103 cm⁻¹ to 2098 cm⁻¹ is observed as the temperature is raised from 100 K to 300 K. Above 300 K, which is close to the onset temperature of desorption (Fig. 1a), a rapid redshift towards 2081 cm⁻¹ is witnessed in the course of CO desorption. On Pt/Ni/Pt(111), a change in the stretching frequency is observed at lower temperatures (~200 K), which also coincides with the onset of CO desorption (Fig. 1b). Rapid change in the redshift beyond 200 K spans the 2088 cm⁻¹–2064 cm⁻¹ frequency regime. On Pt/Co/Pt(111), lower desorption temperature onset (Fig. 1c) is reflected in the frequency shift. The temperature induced frequency change is similar to Pt/Ni/Pt(111) but in a lower range: between 2083.7 cm⁻¹–2057.7 cm⁻¹. CO on Pt/Fe/Pt(111) demonstrates a slightly different behavior. Since there is not a clear desorption onset in the investigated temperature regime, only gradual redshift from high coverage (low

Fig. 4. (a) Adsorption coverage dependent CO TPD temperature maxima from Pt(111) and Pt/3d/Pt(111) (3d: Ni, Co, Fe) substrates. CO was adsorbed at 120 K. Integrated peak area (b) and FWHM (c) of CO TPD from Pt(111) and Pt/3d/Pt(111) substrates in low adsorption coverage regime.

temperature) regime to low coverage (high temperature) regime is observed. There could be a slight change in desorption behavior at about 250 K, that could also be linked to desorption of low temperature peaks (Fig. 1d). It is important to note that CO stretching frequencies at low coverage regime at 120 K are higher than those recorded during desorption at high temperature limit.

Since there is a coverage dependent shift in CO stretching frequencies, it is also worthwhile to investigate the coverage dependent changes in desorption temperature maxima and full width at half maximum (FWHM) obtained from TPDs. This analysis is limited to low CO coverages because broadening observed in TPDs makes the identification of the temperature maxima difficult. Fig. 4a shows decrease in the desorption peak maxima up to 0.6 L initial CO adsorption. The analysis on temperature maxima shows that CO desorption from Pt/Co/Pt(111) and Pt/Fe/Pt(111) substrates show similar behavior, whereas Pt/Ni/Pt(111) substrate lies in between. Another interesting observation is that temperature maxima obtained from Pt/3d/Pt(111) substrates approach ~ 310 K after 0.6 L CO exposure. FWHM; however, do not show the same trend.

Fig. 4b and 4c show the integrated area and FWHM obtained from CO TPDs in low coverage regime. Analysis was done up to a limited CO coverage in order to prevent complications that could be present due to initiation of asymmetric broadening. They could give fruitful information because the nature of CO adsorption, i.e., superstructure formation, islanding etc. could depend not only on the type of the substrate but also on the coverage, which could be estimated from TPD peak areas. FWHM of TPD spectra of CO adsorbed on Pt(111) and Pt/Fe/Pt(111) are much narrower than those on the other two subsurface alloy systems. FWHM obtained from the Pt/Ni/Pt(111) and Pt/Co/Pt(111) substrates nearly overlap and asymmetric broadening might have an influence even at CO exposure as low as 0.1 L on Pt/Co/Pt(111) substrate.

Peak heights and FWHM of IRAS peaks of CO are presented in Fig. 5 as a function of exposure at 120 K and higher temperature. As seen in Fig. 5a, FWHM of the peaks drops sharply for Pt/Ni/Pt(111) and Pt/Co/Pt(111) substrates within 0.2 L CO exposure, makes a dip centered at about 0.4 L and then increase steadily until reaching saturation. Similar behavior is observed on Pt/Fe/Pt(111) except the dip appears at slightly higher exposures. Fig. 5c represents the peak heights at various exposures. IRAS intensities of the adsorbed molecules should be treated with caution, they might not reflect actual coverage due to intensity borrowing phenomena [30,31]. On all substrates, the peak heights go through a maximum before they reach a saturated value. Initial increase in the peak heights could be correlated with coverage but differences at the extended exposures (after saturation) do not relate the coverage differences directly. On Pt/Fe/Pt(111), peak maximization is seen at higher exposures compared to the others. Temperature induced changes in both FWHM and the peak heights presented in Fig. 5b and 5d could further emphasize dynamic changes on the surfaces during

Fig. 5. Adsorption coverage and temperature dependent CO IRAS peak analysis. FWHM-peak height of the vibrational spectrum of CO on Pt(111) and Pt/3d/Pt(111) (3d: Ni, Co, Fe) substrates as (a–c) increasing CO exposure at 120 K and (b–d) heating with a rate of 1 K/s. Inset in (c): peak height values zoomed in low coverage region.

desorption. For Pt/Ni/Pt(111) and Pt/Co/Pt(111) substrates, The FWHM go up slightly before reaching an onset of desorption (Fig. 1b and 1c), and then narrows down while low temperature features are desorbing. Interestingly, the peak heights go up in this temperature regime. Decrease in the peak heights as desorption rate increases with temperature (due to coverage decrease) is accompanied by increase in FWHM. For Pt/Fe/Pt(111), the FWHM and peak height changes are smoother, but not featureless.

4. Discussion

The results that are obtained from the analysis of TPD and IRAS spectra of CO on Pt/3d/Pt(111) substrates are summarized in comparison to Pt(111) as follows: All three 3d metals, Ni, Co, and Fe; are stable at subsurface region up 640 K and CO desorption temperature decrease relative to the temperature on bare Pt(111) surface, indicating that the CO interaction with those subsurface alloys is weaker. At low CO coverage limit, desorption temperatures follow $\text{Pt} > \text{Ni} > \text{Co} \approx \text{Fe}$ order. Similar order is observed to a limited extent in C–O stretching frequencies of adsorbed CO determined by IRAS. Weaker adsorption of CO on subsurface alloy systems is evident from TPDs but redshifted CO stretching frequency is counter intuitive considering basic description of frequency shifts observed in internal modes of the molecules that are adsorbed on metal surfaces [31].

Dipole interactions of adsorbed CO molecules with their image dipoles on metal surfaces and the surfaces acting like a rigid wall against adsorbed CO have been suggested to justify the stretching frequency shifts compared to the gas phase. However a more realistic model introduced by Blyholder [32], based on orbital interactions, is considered to be more appropriate to explain the CO-metal surface chemical bonding [30]. CO adsorption is described by a charge transfer from 5s orbitals of CO localized on the carbon atom to the metallic states (dominated by d states) and backdonation from the metal to the $2\pi^*$ orbital of CO. Since the $2\pi^*$ orbital is antibonding, backdonation makes the C – O bond less stable due to reduced electronic charge between C and O atoms and the degree of filling of $2\pi^*$ orbital plays an important role in the adsorption strength [30,31]. The charge exchange is considered to be necessary to keep CO neutral. Consequently, adsorption on metallic surfaces causes a redshift in the stretching frequency of CO, which also depends on surface termination and adsorption site.

The structure of CO on Pt(111) is well-documented. A $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure of linearly bonded CO forms at 100 K and it is stable up to 1/3 ML within 100–150 K temperature range [29]. Above 150 K, increasing coverage leads to the formation of a $c(4 \times 2)$ structure of linear and bridge bonded CO, which appears to reach saturation at 1/2 ML CO coverage between 250–300 K temperature range [24]. Extended CO exposures can also lead to the formation of compressed structures. Increasing coverage beyond 1/3 ML at 100 K leads to appearance of diffuse LEED pattern, $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure along with faint $c(4 \times 2)$ has been observed at higher coverages. Sharper LEED patterns from $c(4 \times 2)$ structures are clearly seen as the temperature is raised to 260 K [29,33]. Vibrational spectroscopy (IRAS/HREELS) and XPS investigations show that CO preferentially adsorbs on atop sites at low coverages, and the bridge sites are occupied subsequently. IRAS data presented in Fig. 2a is consistent with the general picture of CO adsorbed on Pt(111) substrates [34]. Up to ~ 0.5 L exposure at 120 K only linearly bonded CO (2105 cm^{-1} to 2090 cm^{-1}) is visible and peaks gain intensity with coverage [35]. For further exposures bridge bonded CO (~ 1848 to $\sim 1855\text{ cm}^{-1}$) becomes visible. Both linear and bridge bonded CO peaks gain intensity unevenly due to absorption cross-section differences. The frequency of bridge bonded CO is lower because CO is closer to surface Pt atoms and the degree of overlap between orbitals is enhanced. For a perfect $c(4 \times 2)$ structure, the number of linearly and bridged bonded CO per unit cell is the same but IRAS peak intensities do not provide this information due to the difference in IR absorption intensity per molecule. Dipole coupling between linearly bonded CO gets enhanced with increasing coverage and it is the primary reason of the blueshift. On all substrates, a similar blueshift upon increasing coverage up to 1 L relative to the low coverage limit is noticed. It indicates that an identical density of CO is present on those surfaces. On Pt/3d/Pt(111) substrates bridge bonded CO is not observed. Possible reasons behind this observation will be discussed further below. Therefore, the focus will be on the changes in the frequency and the intensity of the linearly bonded C–O stretching peaks.

Isotope labelling investigations show that frequency shifts with coverage occur once the vibrational frequencies of the coupled molecules are very close [36]. As seen in Fig. 3a, C–O stretching frequency steadily blueshifts on Pt/3d/Pt(111) up to 1 L CO exposure, which suggests that CO binds to identical sites. Adsorbate induced surface segregation is a possible hypothesis; however, our findings indicate that it is not very likely. It is expected that if a part of the CO molecules is linearly bonded to the segregated 3d adatom, coupling would be weaker since the C–O stretching frequencies would be more apart. For the same reason, intensity borrowing, significant change in intensities, is not observed.

CO TPD spectra presented in Fig. 1 do not manifest a certain structure formation nor a preferential site for CO adsorption. It is however a quantitative tool, a combination of IRAS and TPD provides complementary information about many adsorbate/substrate systems. Even in the low coverage regime, CO desorption temperature shows a downshift with increasing coverage. This is a type of desorption behavior different than ordinary first order molecular desorption in which increasing coverage does not result in a shift in temperature [37]. Even at the lowest coverage, the repulsive forces between CO molecules are significant and influence desorption behavior [25]. Reduction of the sticking probably above 0.5 L is apparent in our TPD spectra.

It is also interesting to see in Fig. 4a that CO desorption peak temperature maxima has a different total shift by increasing coverage for each substrate. On the Pt(111) substrate, the temperature shift is about 100 K and on Pt/Ni/Pt(111) the shift is similar, 97 K. However, much narrower temperature shifts were observed on the Pt/Co/Pt(111) and Pt/Fe/Pt(111) substrates, 57 K and 58 K respectively. Short range coordination could be similar on Pt/Co/Pt(111) and Pt/Fe/Pt(111) since the temperature shift depends on the extent of repulsive interactions between CO molecules. At the low coverage regime, CO desorption temperatures only represents the bonding condition at which CO-metal

substrate interaction is dominant. Similar conclusion could be drawn from the analysis of IRAS data. Therefore, the modification of the surface electronic structure by embedding 3d metal could be analyzed at low CO coverage. The changes in the intermolecular interactions and dipole coupling are matters of discussion at higher coverages.

Additional CO desorption states are also apparent on Pt/3d/Pt(111) substrates above 0.5 L exposure (Fig. 1). Apart from the changes induced by repulsive interactions, new features appearing as a low temperature shoulder in TPDs require discussion. Since they are gaining intensity after certain exposure, they could be related to the formation of compressed structures that are observed on bare Pt(111) surfaces. Population of bridge or three-fold hollow site is not plausible because no associated peak was observed in IRAS data. Alternatively, it could originate from CO adsorption induced surface segregation of the substrate 3d metal.

It could be helpful to shortly review the interaction of CO with closed packed surfaces of bare 3d metals, keeping in mind that the presence of the Pt(111) substrate complicates a direct comparison. On the Ni(111) surface, the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure is stable up to 1/3 ML and $c(4 \times 2)$ and more compressed $(\sqrt{7}/2 \times \sqrt{7}/2)R19.1^\circ$ structures have also been observed. LEED and IRAS indicate that adsorption on top, bridge, and threefold hollow sites are all plausible [38,39]. TPD investigations show a desorption peak at ~ 440 K [26]. The frequency of linearly bonded CO spans between 2050 and 2058 cm^{-1} which is even lower than the stretching frequency of CO on Pt/Ni/Pt(111) substrate obtained at low coverage [39,40]. On Co(0001) surface, structures including $(\sqrt{3} \times \sqrt{3})R30^\circ$ for 1/3 ML, $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ for 7/12 ML, $(\sqrt{7}/3 \times \sqrt{7}/3)R30^\circ$ for 3/7 ML CO coverages [41] and $(\sqrt{7} \times \sqrt{7})R19.2^\circ$ for 1/2 ML compressed CO [27] have been suggested but stretching frequency of linearly bonded CO (exists for all proposed structures) has been reported below 2000 cm^{-1} . TPD data only shows desorption peaks at about 450 K [27], which is much higher than the desorption temperatures observed on Pt/Co/Pt(111) substrate. On Fe(110) bcc surfaces, $p(1 \times 2)$ for 1/2 ML and $c(2 \times 4)$ for 1/4 ML structures with linearly bonded CO geometry have been observed [38]. No peak above 2000 cm^{-1} is present in vibrational spectra. Overall comparative analysis makes us conclude that compressed inhomogeneous CO structures could be formed at high coverages despite absence of LEED patterns; nevertheless, CO is linearly bonded to atop sites of the Pt skin layer and CO adsorption induced segregation of the 3d metal is not likely.

The C–O stretching frequency change upon increasing temperature (Fig. 3b) provides information about the change in the dipole coupling in the course of thermal relaxation of the compressed CO structures and desorption. Keeping in mind the different heating rates in IRAS and TPD experiments, redshifts could be divided into two temperature regimes, except for Pt/Fe/Pt(111). A steady but monotonous redshift changes its pace after the initiation of desorption. The redshift up to the onset of desorption could be attributed to loss of dipole coupling due to dynamic relaxation of adsorbed CO molecules. For Pt/3d/Pt(111) systems this relaxation is accompanied by partial desorption. Under such circumstances the diffusion is facile and much faster than the rate of desorption. When a sufficiently high temperature is attained, the desorption rate significantly increases and much faster redshift until complete desorption is observed. It is worth noting that at the high temperature limit (low coverage limit) vibrational frequencies are lower than those obtained at 120 K for low CO exposure. This might again raise adsorbate induced or thermal segregation questions, but it could well be related to temperature differences as well. The Pt/Fe/Pt(111) system behaves different than the others. On this substrate the repulsive interactions; thus, the compressed structure formations could be different. This difference could also be seen in the widths of the desorption peaks presented in Fig. 4b. At the low exposure limit, the local neighborhood of CO on Pt/Fe/Pt(111) substrate could be similar to the Pt(111) substrate.

The FWHM and the peak heights of CO IRAS spectra give fruitful information about the changes occurring on the substrate surfaces

during adsorption and desorption. As Fig. 5a shows, the FWHM of the CO stretching peaks reach a minimum at a certain CO exposure that varies depending on the substrate. Coincidentally, the peak height goes through a maximum and settles in a constant value (Fig. 5c). Up to 0.5 L exposure, peak heights linearly increase with coverage, with no apparent distinction depending on the substrate except Pt/Fe/Pt(111). It could be argued that, up to 0.5 L exposure, CO linearly adsorbs on the atop sites without significant change in the sticking probability. The coverage will be close to 0.25 ML at which the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure is dominant on the Pt(111). Here, CO molecules are homogeneous, which is supported by the dipole coupling induced narrowing of FWHM of the peaks. The FWHM of peaks continuously narrow down along with the increased coverage up to 0.5 L. An inhomogeneous compression of CO layers is speculated beyond 1 L exposure since the peak reduces its height and its FWHM get broadened (Fig. 5a). Disorder in the CO layer on Pt/Fe/Pt(111) substrate seems to be significant judging by the trends in peak height and FWHM. It cannot be related to different the amount of CO on this substrate since integrated TPD peak areas shown in Fig. 4b represent similar coverages.

Peak heights and FWHM of the IRAS peaks could then give information about the structural changes as a function of temperature. As can be seen in Fig. 5d, the linearly bonded CO peak height on Pt(111) decreases monotonously up to the onset of desorption (~ 300 K) indicating significant structural relaxation and surface mobility. The peak height decreases steadily upon desorption, as expected. The increase in FWHM with temperature (Fig. 5b) also supports temperature induced disorder. Temperature induced structure formation can then be reflected to the trends in peak height and FWHM. For Pt/Ni/Pt(111) at 240 K, for Pt/Co/Pt(111) at 210 K, and for Pt/Fe/Pt(111) at 175 K, there could be relaxation triggered by desorption. Narrowed FWHM could be attributed to the formation more relaxed structures while increasing temperatures. This data favor relaxation rather than the formation of more ordered structures since the temperature dependent CO stretching frequency (Fig. 2b) does not change its redshifting behavior.

TPD and IRAS findings indicate that subsurface alloys reduce the binding strength of CO and it is solely related to the modification of the electronic states of the Pt skin layer. The compressed structures formed on Pt/3d/Pt(111) substrates differ from the ones on Pt(111). At the low coverage limit where the intermolecular CO interactions are limited, desorption activation energies (E_d) of CO from Pt/3d/Pt(111) substrates could be estimated by application of Redhead's analysis, which correlates E_d with TPD peak temperature, T_{max} [24,42]. Assuming that the frequency factor to be 10^{15} s^{-1} [25], E_d (extrapolated to zero coverage) of CO from Pt(111) substrate is found to be around ~ 143 kJ/mol, which is in good agreement with the literature [24,43]. E_d drops to 124 kJ/mol for Pt/Ni/Pt(111) system, and to 111 and 110 kJ/mol for Pt/Co/Pt(111) and Pt/Fe/Pt(111), respectively. It is now worth discussing the effect of the subsurface 3d atom on the Pt atoms at the topmost surface.

Addition 3d atomic layers in the subsurface region reduces the center of Pt 5d band [44]. For Ni and Co, this shift has been confirmed by valence band XPS measurements that show a clear decrease in Pt 5d electron density at the Fermi level [15]. In this picture, weaker CO adsorption on Pt/3d/Pt(111) substrates could be attributed to enhanced backdonation to $2\pi^*$ orbital of CO, which consequently leads to reduction of stretching frequency of CO linearly bonded to Pt atop site. Here, it is assumed that CO-substrate bond length does not change significantly. On the Cu/Pt(111) system, the strength of the CO-metal interaction and CO stretching frequency have been found to decrease simultaneously. This coinciding observation has been explained by suggesting that the topmost metal surface layer could be charged, and thus polarizing CO [45]. Similar activities of Pt/Co/Pt(111) and Pt/Fe/Pt(111) at the low coverage limit could be due to Pt 5d states shifted to similar energies. This hypothesis could not be proposed without involving 5s donation to metallic states. Down shifted Pt 5d-band center possibly changes the extent of 5s donation with the stabilizing effect of

backdonation. Absence of bridge bonded CO on Pt/3d/Pt(111) could be due to an extensive occupation of the $2\pi^*$ orbital, which weakens the internal C–O bond energy and results in the overall chemisorption state unstable.

5. Conclusion

Controlled weakening of the CO-substrate interaction could boost the performances of PEMFCs due to enhanced CO tolerances of Pt based catalysts. We showed that subsurface alloying on Pt(111) could significantly reduce the CO binding strength. The analysis of TPD and IRAS spectra of CO on Pt/3d/Pt(111) substrates (3d: Ni, Co, Fe) shows that 3d metal is stable in the subsurface region, leaving Pt at the surface layer, and CO is linearly bonded to atop sites of the Pt atoms. Significantly lower CO binding strength on Pt/Co/Pt(111) and Pt/Fe/Pt(111) substrates compared to Pt(111) is evident from the reduction in the desorption activation barriers from 143 kJ/mol to ~ 110 kJ/mol at the low coverage regime. Compressed structures form on all substrates at high coverages and CO–CO repulsive interactions become dominant. Lower stretching frequencies and weaker substrate interactions of CO linearly bonded to Pt/3d/Pt(111) substrates are attributed to enhanced backdonation to $2\pi^*$ orbital of CO due to lowered 5d band center of Pt.

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