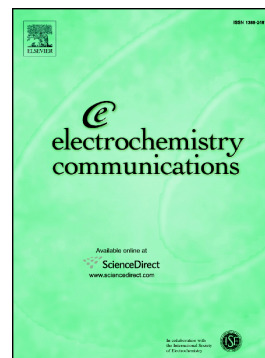# Accepted Manuscript

Mechanistic aspects of glycerol electrooxidation on Pt(111) electrode in alkaline media

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Mechanistic aspects of glycerol electrooxidation on Pt(111) electrode in alkaline media

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Abstract

Glycerol electrooxidation reaction (GEOR) in alkaline media was studied on the Pt(111) electrode with *in situ* FTIR and electrochemical methods. Cyclic voltammogram profiles display strong electrode deactivation after the first potential scan. Chronoamperometric pulses demonstrate that the deactivation is a result of the reaction intermediates yielded during the faradaic process. *In situ* FTIR shows evidence that the strongly adsorbed intermediate formed during GEOR is an acyl species which remains present on the surface within the potential window studied.

Keywords

Glycerol; Pt(111); Electro-oxidation; *in situ* FTIR; Alkaline media

1   INTRODUCTION

The understanding of catalytical oxidation mechanism of glycerol on metal surfaces and its transformation into value-added chemicals has become economic and environmentally interesting since the glycerol market has been flooded by glycerol arising from the growing biodiesel production [1].

On Pt surfaces [2–6], as well as on other metal catalysts [7–10], the electrooxidation of glycerol has shown a propensity to formation of diverse products such as glyceric acid, glycolic acid, glyoxylic acid, oxalic acid, tartronic acid, dihydroxyacetone, glyceraldehyde, among others. However, fundamental studies of glycerol electrooxidation onto Pt electrodes were mainly performed in acidic media, despite the higher electrooxidation rates when employing alkaline electrolyte [9,11,12]. Consequently, there is still no clear understanding of the mechanism of the glycerol oxidation reaction in this medium. Conventional spectroscopic

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techniques such as *in situ* FTIR are commonly employed to gather information about the nature and the bonding site of adsorbates formed during the glycerol electrooxidation reaction (GEOR), which can contribute significantly to elucidate the reaction mechanisms [13].

In this work, the reaction intermediates of GEOR on the Pt(111) electrode are analyzed by using electrochemical and FTIR techniques. The results may contribute towards a fundamental understanding of the mechanism of degradation of platinum electrocatalysts.

2   EXPERIMENTAL

Electrochemical and spectroscopic techniques are described elsewhere [14]. Briefly, spectroelectrochemical experiments were performed with a Nicolet Magna 850 spectrometer equipped with a MCT detector. The potential dependent set of spectra was acquired by increasing the potential in steps of 0.1 V. Spectra shown are composed of 100 interferograms collected with a resolution of 8 cm^{-1}. The reference spectrum was taken at 0.05 V. Single crystal preparation and surface treatments are described in [15]. Special care was taken in the stability of the voltammograms in the blank solution, which guarantees the cleanliness of the experimental system.

3. RESULTS AND DISCUSSION

Figure 1 displays the cyclic voltammogram of Pt(111) in 0.1 M NaOH in the presence and absence (inset) of glycerol. In the presence of glycerol, a high current density peak related to GEOR centered at 0.83 V is present during the positive and negative scans. It must be highlighted that there is a significant difference in peak currents for the positive and negative scan directions in the first scan (ca. 25 and 6 mAcm^{-2}, respectively) and that the currents for the subsequent cycles are significantly lower and show low hysteresis, as well as a slight decrease in the electrode activity.

The dramatic electrode deactivation after the first sweep, and the steady electroactivity decrease cycle after cycle has an amazing similarity with the results reported for ethanol electrooxidation reaction on the same surface and experimental conditions [16]. Busó-Rogero *et al.* [16] have suggested that acetaldehyde polymerization on the electrode surface causes its progressive deactivation upon cycling, whereas the negligible currents recorded at E > 0.9 V are related to the formation of an adsorbed OH layer. In fact, the results displayed in Figure 1 can open a new subject of discussion in electrocatalysis of alcohols in alkaline media since the previous published behavior leads us to suggest that it is not a particular characteristic of one oxidation mechanism reaction but a general behavior of small alcohol molecules.

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Figure 1: Voltammetric profile of glycerol electrooxidation on Pt(111) in 0.1 M glycerol + 0.1 M NaOH: scan rate: 10 mVs^{-1}. Inset: 0.1 M NaOH; scan rate: 50 mVs^{-1}.

Regarding the remarkable electrode deactivation, the effect of different adsorption times at 0.1 V on the first sweep are shown in Figure 2(a). Only small differences are observed in the intensity of the peak current density at 0.83 V. The small loss of the electrode activity as a function of adsorption time does not follow that observed when the electrode is subjected to successive potential scans. Even at potentials lower than those in which alcohol oxidation takes place, the interaction of small organic molecules with platinum surfaces can lead to dehydrogenation and/or cleavage of the C–C bond, producing strongly adsorbed species [13]. The results suggest that, despite the decrease in current density, the species which are formed at 0.1 V remain on the surface (at least) until the electrode reaches a suitable potential to start GEOR. These species have minor influence on the decrease of peak intensity. This contrasts with the effect of the species which are formed in the positive scan of the first cycle, which are probably responsible for the electrocatalytic activity decrease.

In order to evaluate the former assumption, we performed a cyclic potential step experiment by pulsing the potential between 0.1 and 0.83 V successively. The potential signal perturbation and the current-time transient response can be visualized in Figure 2(b) and (c), respectively. The current-time transient curves decay rapidly in the first few seconds, regardless of the time of adsorption at low potentials. As observed for the cyclic voltammogram results, the strong electrode deactivation behavior is also present in the subsequent potential step cycles. The intense decrease of the transient current density from the first to second cycle can be related to the formation of strongly adsorbed species which are formed only during GEOR [16,17]. These species hinder, significantly, the overall oxidation [18] by the blockage of platinum surface [16].

Fig.2-here

Figure 2: (a) Positive scan (1st cycle) of electrooxidation of 0.1 M glycerol + 0.1 M NaOH for different adsorption times at 0.1 V on Pt (111); scan rate: 50 mV s^{-1}; (b) potential signal

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protocol used in chronoamperometric experiments; (c) transient current response recorded from signal perturbation illustrated in (b).

With the aid of *in situ* FTIR, we scrutinized the GEOR mechanism. Figure 3(a) displays the potential-dependent set of spectra for GEOR. In general, the spectra follow the potential-current profile as seen in Fig. 1. At low potentials, no characteristic spectral features are observed until ca. 0.5 V, where two dominant broad positive bands roughly centered at 1600 cm^{-1} and 1400 cm^{-1} appear and remain present during the negative scan. The assignment of those peaks to a single adsorbate or product is not straightforward because the number of species that can be formed from GEOR is quite high [9,19]. The glycerol molecule can be analyzed as having at least two active centers for coordination to metal surface sites: the oxygen of an alcohol group and its α-carbon. In this sense, glycerol can initially adsorb through the coordination of one lone pair oxygen orbital or through the α-carbon atom. Both possibilities can yield many possible surface bonding configuration as GEOR intermediates, namely: η^1(O)-aldehyde, η^2(C,O)-aldehyde, acyl, alkoxyde, α-oxo η^2(C,O)-aldehyde, bidentate carboxylate, among others [20,21], whose vibrational spectra lie in the range of 1100-1750 cm^{-1} and are representative of final products, for instance, of glyceric acid, glycolic acid, glyoxilic acid, oxalic acid, tartronic acid, dihydroxyacetone, glyceraldehyde, etc. [9,10].

In relation to the lack of strong adsorbates at low potentials, it is evidenced the absence of CO stretching modes (ν(CO)) which would be expected to appear at ca. 2040 cm^{-1} and 1880 cm^{-1} [3,5,22]. Carbon monoxide is generally accepted as the main poisoning species formed in acidic media at potentials as low as 0.1 V from dissociative alcohol adsorption and during the oxidation process at higher potentials [5,22,23]. Our data show that the CO stretching mode displays a weak feature when the reaction reaches the highest reaction rate (at 0.85 V) and remains until 0.5 V in the negative sweep, justifying the higher activity when results are compared with those obtained in acidic media [2,5,19,24]. Moreover, the concomitant presence of the band in 2345 cm^{-1} with the ν(CO) stretching mode at high potentials support the ability of Pt(111) to oxidize glycerol to CO_2 from adsorbed CO, but to a lesser extent than observed in acidic media [4]. The appearance of ν(CO_2) stretching mode in alkaline media is indicative of the strong change in the interface pH since the carbonate species (CO_3^{2-}) cannot be further produced due to the depletion of OH$^-$ in the thin layer configuration [25].

It is clear that the reason why the strong Pt(111) surface deactivation occurs after the first positive potential excursion resides on the formation of strongly adsorbed glycerol

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residues other than CO, the latter responsible for the main bands seen in Fig.3(a). We can observe that the bands at 1585 cm^{-1} and 1400 cm^{-1} begin to appear approximately at the same potential (ca. 0.5 V), corresponding to the reaction onset. Concomitantly, the negative featured bands at 2720 cm^{-1} and 1895 cm^{-1}, attributed to OH$^-$ species in solution [16], are the consequence of their consumption – and not readily replenished due to the thin layer configuration – as adsorbed OH reactant-pair of GEOR.

Fig.3-here

Figure 3: (a) FTIR-in situ potential-dependent spectra of 0.5 M glycerol in 0.1 M NaOH on Pt(111) as function of the increasing potential steps from 0.05 to 0.9 V; (b) contour plot built from (a); FTIR spectrum for 0.9 V (c) and intensity band profile of chosen wavenumbers (d). The reference spectrum was collected at 0.05 V vs. RHE.

At first glance, the appearance of the 1400 and 1585 cm^{-1} bands together could be correlated with the formation of carboxylate-containing species whose bands are attributed to the asymmetric and symmetric carboxylate ν(OCO) stretching modes, respectively [10,26]. In fact, the band at 1400 cm^{-1} is assigned to symmetric stretch ν(OCO)$_s$ of twofold carboxylate species coordinated to the surface [27]. However, the 1585 cm^{-1} band could not be assigned to the asymmetric stretching mode of the bidentate carboxylate species since it would be forbidden by the surface selection rule [26–28]. This would suggest that both bands can be originated from different adsorbed species. With the aid of a contour plot, a selected spectrum at 0.9 V and the intensity band profile of chosen wavenumbers (Fig.3b-d, respectively), we can observe that as the potential is made more positive, the signal of the 1400 cm^{-1} band vanishes in a potential region where the GEOR reaches its maximum current density (ca. 0.8V) and a new band at 1360 cm^{-1} emerges apparently at the expense of the 1400 cm^{-1} band, while the 1585 cm^{-1} band does not alter its intensity over the negative scan, regardless the applied potential. The appearance of the 1585 cm^{-1} band during polyol adsorption under aqueous environment was not reported previously and a clear-cut assignment about its origin is not straightforward.

Under UHV environment, spectroscopic studies of decomposition of small aldehydes and alcohols showed that the process can occur through the formation of acyl intermediates which were identified by the loss feature of the ν(C=O)$_{acyl}$ stretch mode at ca.1565–1575 cm^{-1} [29,30]. The acyl intermediate species corresponds to the coordination to the metal through the carbon of the carbonyl group. McManus *et al.* [21] observed a similar behavior when glyceraldehyde thermally decomposed on a Pt(111) surface, with a ν(C=O)$_{acyl}$ stretch mode

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centered at 1595 cm^{-1}. Thus, we attribute the 1585 cm^{-1} band to the origin of the strong electrode deactivation as a result of acyl intermediate species that are stable within the range of the studied potential. Gomes *et al.* [20] using the SFG technique proposed the formation of acetyl as one of the intermediates of ethanol electrooxidation on Pt in acidic media, featured by the ν(C=O)$_{acyl}$ stretch mode at 1546 cm^{-1}. Additionally, we should take into account that the glycerol molecule has multiple reactive centers to interact with metal sites and in the case of adsorption through the carbonylic group without C–C bond cleavage, the resulting adsorbed acyl can still interact with the surface by means of the oxygen lone pair of the hydroxyl group from the C2 carbon, named as glyceroyl by Schnaidt *et al.* [31] and correlated with the presence of a band centered at 1640 cm^{-1}. Despite the differences, we tentatively assign the frequency mode observed at 1585 cm^{-1} to the C=O stretch mode of adsorbed acyl species.

Other features of the spectra consist of bands at 1722 cm^{-1}, indicating the presence of the C=O stretching of carbonyl groups from non-adsorbed carboxylic acids and aldehydes namely: glyceraldehyde, dihydroxyacetone, glyceric acid, among others [9,12].

In summary, a general mechanism can be proposed for the electrocatalytic oxidation of glycerol on Pt(111) in alkali media: considering the high pH adsorption of glycerol, the interaction of the molecule with the electrode surface seems to occur, initially, through an alkoxyde molecule [8,11,32] by dehydrogenation of a primary hydroxyl group to yield an aldose adsorbate which undergoes dehydrogenation of the C–H bond to form an acyl intermediate that keeps adsorbed regardless the applied potential. The strong surface interaction of acyl species with the electrode surface and its stability over a wide potential window suggests the GEOR on Pt(111) in alkaline media occurs mainly through surface intermediates that weakly coordinate to the surface, for instance by the oxygen lone pair (from alkoxides, aldehydes or carboxylates) which can be further oxidized within the studied potential window. Thus, the low hysteresis observed in alkaline media suggests that the acyl species are stable within the studied potential with minor contribution to the overall reaction rate.

4. Conclusions

The electrochemical studies of GEOR in alkaline media show that the Pt(111) electrode suffers strong deactivation once the surface attains potentials higher than 0.8 V. *In situ* FTIR shows evidence that carboxylates and acyl are the main intermediates formed during the GEOR. Moreover, the acyl species represents the main intermediate that remains stable on the surface, even at potentials where the surface oxide formation is highly favored, while the carboxylates are the reactive intermediates.

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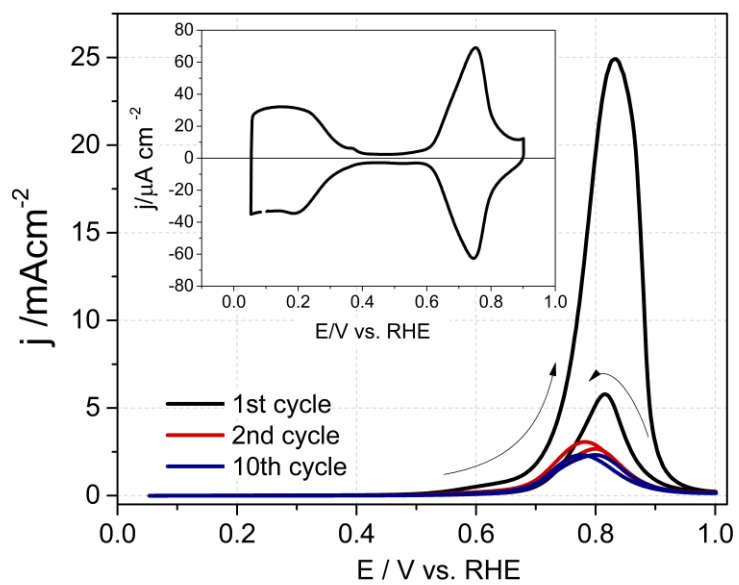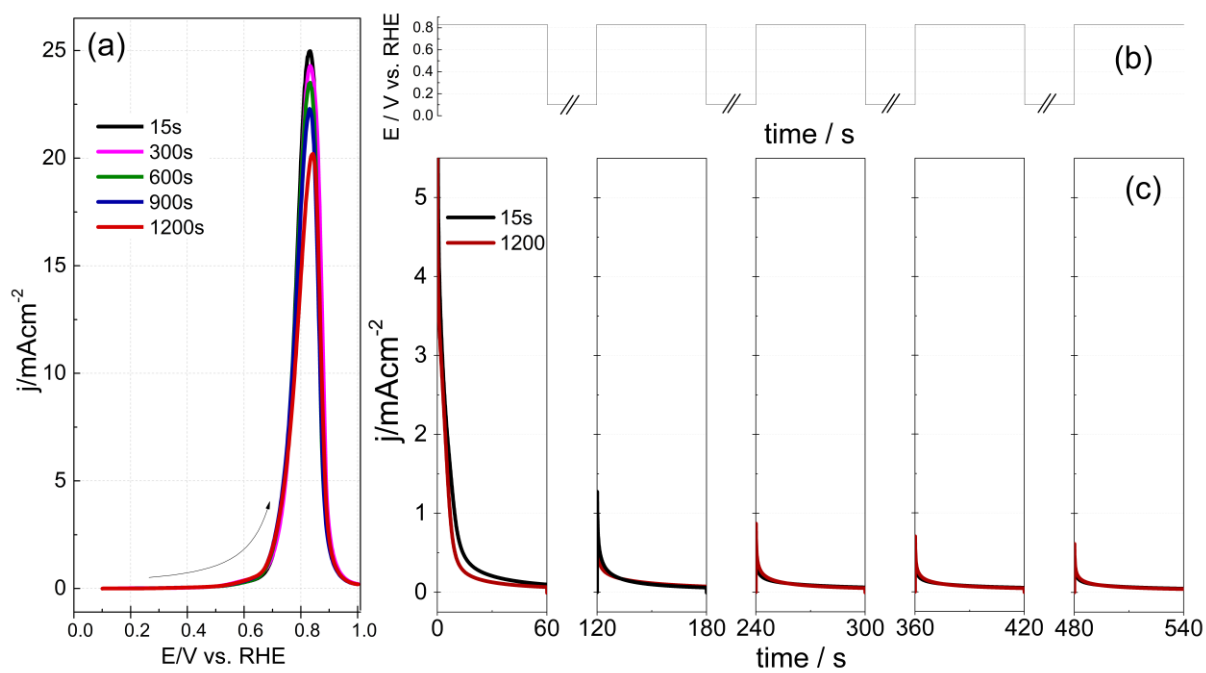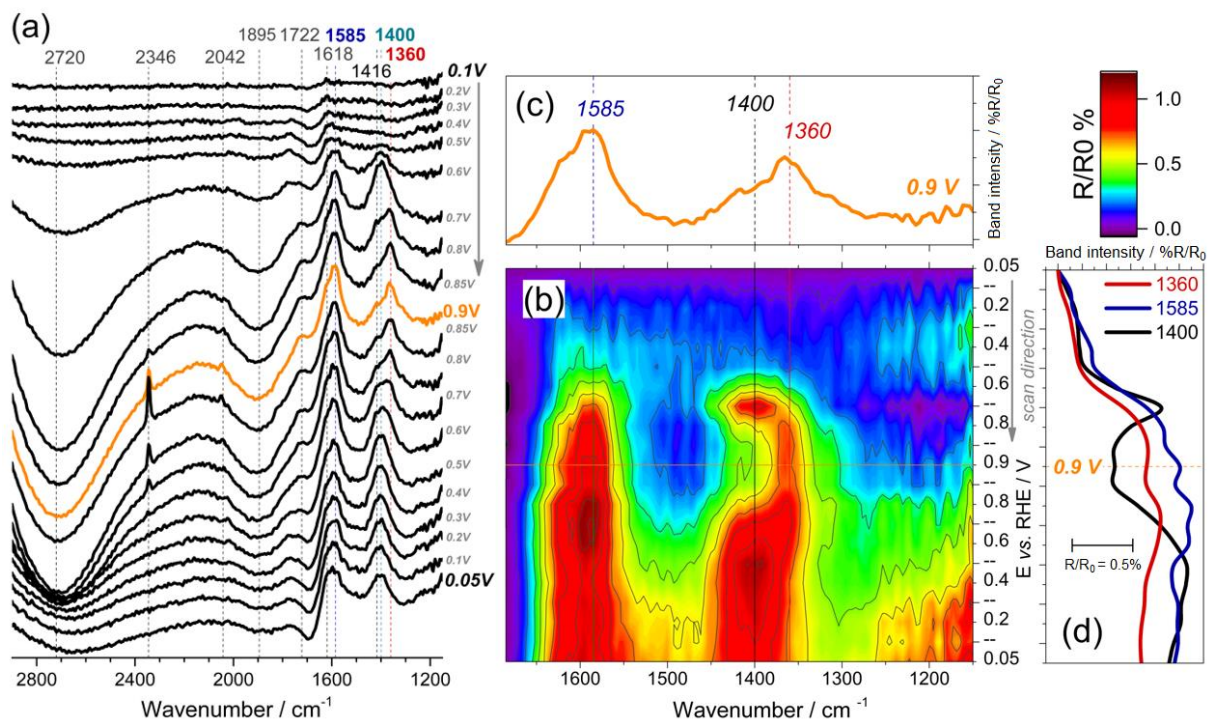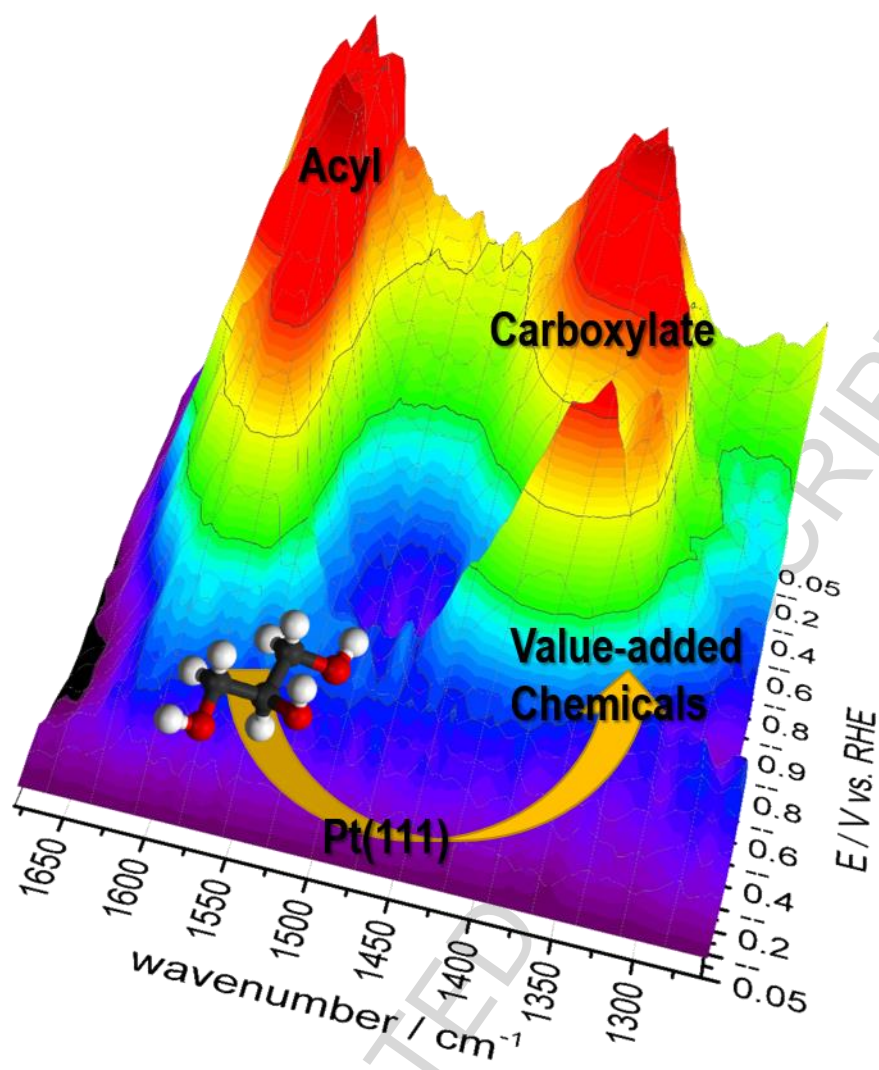
Figure 1

Figure 2

Figure 3

Graphical abstract

Highlights

- Pt(111) surface is strongly deactivated during glycerol electrooxidation in alkaline media;
- *In situ* FTIR results show evidence of a stable adsorbate;
- At low potentials glycerol does not adsorb on Pt(111) surface through strong adsorbates.