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At Least Three Contiguous Atoms Are Necessary for CO Formation during Methanol Electrooxidation on Platinum

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It is well known that the oxidation of methanol on platinum electrodes follows two parallel paths:[1,2] a relatively fast one, usually known as the direct reaction pathway, and a very slow one, involving a strongly adsorbed intermediate acting as an electrocatalytic poison. The advent of in situ infrared reflectance spectroscopy at the beginning of the 1980s allowed the identification of CO as the poisoning intermediate,[3] but the identification of adsorbed formate as an intermediate in the non-CO pathway[4] has been possible only recently thanks to the high sensitivity of attenuated total reflectance−surface-enhanced infrared reflection absorption spectroscopy (ATR−SEIRAS). Investigation of structural effects in the oxidation of methanol on platinum electrodes was made possible by single-crystal electrochemistry with well-defined model surfaces.[5] The determination of the smallest number of surface atoms, and their geometric arrangement, necessary for a given reaction to proceed,[6] could help us to channel the methanol electrooxidation through the direct reaction pathway by fabricating a surface without sites suitable for the formation of adsorbed CO and with only those sites leading to the reactive intermediates.

Cyanide adsorbs on Pt(111) electrodes adopting a $(2\sqrt{3} \times 2\sqrt{3})$-$R30°$ structure, first detected using LEED by Stickney et al.,[7] and whose atomic, real space structure could be elucidated by in situ STM by Stuhlmann et al.[8] and later by Kim et al.[9] The structure consists of hexagonally packed arrays, each containing six CN groups adsorbed on top of a hexagon of Pt atoms surrounding a free Pt atom (see Figure 1). The cyanide coverage corresponding to the $(2\sqrt{3} \times 2\sqrt{3})R30°$ structure on Pt(111) is $\theta_{CN} = 0.5$. Cyanide adsorption on Pt(111) has been intensively studied by Huerta et al.[10] using cyclic voltammetry (CV) and spectroelectrochemical techniques. They have shown that the cyanide adlayer on Pt(111) is remarkably stable, no change being observed in the CVs of the cyanide-covered electrode upon repetitive cycling between 0.06 and 1.10 V versus RHE. Accordingly, as pointed out by Huerta et al.,[10a] the cyanide-covered Pt(111) electrode can be considered as a chemically modified electrode, with CN groups acting as a third body, blocking those Pt atoms onto which they are adsorbed, but leaving unaffected the CN-free Pt atoms onto which H, OH, or CO[10e,11] can adsorb. As we will show here, methanol molecules can also reach the free Pt atoms of a cyanide-modified Pt(111) electrode, which can therefore be used as a model surface to investigate the role of atomic ensembles in methanol electrooxidation.

The working electrodes were bead-type Pt single crystals (2 mm in diameter for CV, 4 mm in diameter for FT-IR experiments) prepared according to the method developed by Clavilier et al.,[12] oriented and polished parallel to the (111) plane (miscut < 0.05°). Before each experiment, the electrode was annealed in the flame of a Bunsen burner and cooled to room temperature in a $H_2 + N_2$ atmosphere. Cyanide-modified Pt(111) electrodes were prepared by immersion of a clean, well-ordered Pt(111) electrode in a 0.1 M KCN solution for approximately 3 min, after which the electrode was rinsed with ultrapure water and transferred to the (spectro)electrochemical cell containing cyanide-free 0.1 M $HClO_4$. A reversible hydrogen electrode (RHE), to which all the potentials in the text are referred, was used as reference.

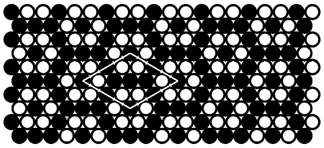

Figure 1. Ball model of the $(2\sqrt{3} \times 2\sqrt{3})R30°$ structure adopted by the cyanide adlayer on Pt(111) electrodes, according to ref 9. Black balls correspond to Pt atoms, and white balls to linearly chemisorbed CN groups.

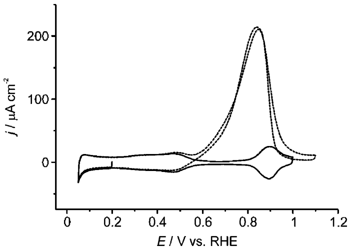

Figure 2. Cyclic voltammogram at 50 mV s^{-1} of a cyanide-modified Pt(111) electrode in 0.1 M $HClO_4$ + 0.2 M CH_3OH. The scan starts at 0.20 V in the negative direction. The solid line is the cyclic voltammogram of cyanide-modified Pt(111) in the blank electrolyte.

Figure 2 shows the CV of a cyanide-modified Pt(111) electrode in 0.1 M $HClO_4$ + 0.2 M CH_3OH. As can be seen, the hydrogen adsorption region remains unaffected, and contrary to what is observed in unmodified Pt(111) electrodes, there is nearly no hysteresis between the positive and the negative going sweeps. These two observations suggest that no poison intermediate (adsorbed CO) is being formed on the surface of the cyanide-modified Pt(111) electrode, as confirmed by the FT-IR spectra shown in Figure 3 (the band with frequencies increasing with potential from 2086 to 2135 cm^{-1} corresponds to CN adsorbed on top[8,9,10a,b,13,14]). The very small feature around 2060 cm^{-1} in the spectra between 0.50 and 0.70 V *could* be due to adsorbed CO, although this assignment is far from clear since it barely emerges from the noise, and, furthermore, it does not show the Stark shift which is a hallmark of adsorbed CO. The CV of cyanide-modified Pt(111) in 0.1 M $HClO_4$ + 0.2 M CH_3OH in Figure 2 also indicates that adsorbed hydrogen completely blocks the adsorption of CH_3OH, which occurs only at $E > 0.40$ V.

On the basis of the fact that, at $E < 0.45$ V, no CO_2 is detected on polycrystalline Pt in 0.1 M $HClO_4$ + 0.2 M CH_3OH using the very sensitive differential electrochemical mass spectrometry (DEMS) technique, Vielstich and Xia[15] have criticized the dual path mechanism and have suggested that methanol oxidation on Pt proceeds nearly exclusively via the adsorbed CO intermediate. However, Herrero et al.,[2] using also a 0.1 M $HClO_4$ + 0.2 M CH_3OH solution, showed that the charge density integrated from current transients, measured upon stepping the potential of Pt(111), Pt-

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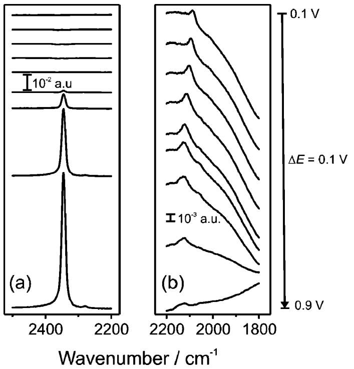

Figure 3. FT-IR spectra at increasing potentials of a cyanide-modified Pt(111) electrode in 0.1 M $HClO_4$ + 0.2 M CH_3OH. The spectra in the frequency region between 2500 and 2200 cm^{-1} (a) were calculated using the spectrum at 0.05 V as reference, while the spectra in the frequency regions between 2200 and 1800 cm^{-1} (b) were calculated using the spectrum at 1.30 V as reference.

(100), Pt(110), and Pt(poly) electrodes to several values above 0.45 V, can only be accounted for if some methanol reacts to CO_2 without formation of adsorbed CO. These results were confirmed later, also by current-transient measurements, by Jarvi et al.,[16] who showed that, on Pt(100), only CO forms from methanol at $E < 0.50$ V, in agreement with Vielstich and Xia,[15] but that, at $E \geq 0.50$ V, a path not involving adsorbed CO must contribute to the total CO_2 yield. The results reported here in Figures 2 and 3 are the ultimate proof that the dual path mechanism is indeed effective in the oxidation of methanol on Pt electrodes, and that CO_2 can be formed from methanol through a path which does not involve the formation of adsorbed CO since, on cyanide-modified Pt(111) electrodes, a considerable amount of CO_2 is formed upon methanol electrooxidation, although the formation of adsorbed CO has been completely inhibited. Even if the very small feature at ca. 2060 cm^{-1} in the spectra between 0.50 and 0.70 V does correspond to adsorbed CO, its band intensity is so small that our conclusion that methanol oxidation is channeled exclusively through the non-CO pathway must be correct (furthermore, on CN-modified Pt(111), oxidation of adsorbed CO does not occur below 0.90 V[10e,11]). According to Chen et al.,[4] the non-CO path must involve the formation of adsorbed formate.

There are four possible kinds of reactive sites on the surface of the cyanide-modified Pt(111) electrode (see Figure 1): (i) a single Pt atom, (ii) two adjacent Pt atoms, (iii) three Pt atoms arranged linearly, and (iv) three Pt atoms arranged forming a chevron with a 120° angle. This leads to the obvious conclusion that none of these reactive sites suffices for the dehydrogenation reaction of methanol to CO to occur, at least three contiguous Pt atoms being necessary. On the contrary and since simultaneous interaction of the methanol molecule with three Pt atoms on the cyanide-modified Pt(111) electrode seems unlikely, we suggest that the minimum atomic ensemble for the oxidation of methanol to CO_2 through the non-CO pathway consists of two adjacent platinum atoms. Chen et al.[4] have suggested that an adsorbed oxygenated species is necessary in order to form adsorbed formate from methanol. However, our observation of a significant methanol oxidation current in the CV of cyanide-modified Pt(111) (Figure 2) and of CO_2 formation in the corresponding FT-IR spectrum (Figure 3) already at 0.60 V, a potential well below the formation of adsorbed OH on cyanide-modified Pt(111) (see solid line in Figure 2), suggests that reaction of a methanol-derived adsorbate with bulk water (Eley−Rideal mechanism) to form adsorbed formate cannot be discarded, as already noted by Housmans et al.[17]

Cao et al.[18] have analyzed the possible paths for methanol dehydrogenation to CO on Pt(111) in the presence of water using DFT. It would be highly interesting to analyze, using DFT, how restricting the reactive sites to those present on the surface of the cyanide-modified Pt(111) affects each of the possible dehydrogenation pathways.

We have shown that CO formation is completely inhibited on cyanide-modified Pt(111) electrodes, indicating that two adjacent Pt atoms do not suffice for the dehydrogenation reaction, which requires at least three contiguous Pt atoms. Our results also suggest that, in the reactive pathway, reaction with bulk water of a methanol-derived adsorbate to form formate cannot be discarded. These results could help design an electrocatalyst able to oxidize methanol exclusively through the non-CO pathway because the formation of the adsorbed CO poison intermediate would be inhibited.

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Supporting Information Available: Experimental details regarding the FT-IR measurements. FT-IR spectra of methanol oxidation on an unmodified Pt(111) electrode under otherwise identical conditions as those corresponding to Figure 3. FT-IR spectra of cyanide-modified Pt(111), of a saturated CO adlayer on Pt(111), and of a saturated CO adlayer on cyanide-modified Pt(111), in CO-free 0.1 M $HClO_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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