Elucidation of the surface structure-selectivity relationship in ethanol electro-oxidation over platinum by density functional theory

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Citation: SHENG, T., LIN, W-F. and SUN, S-G., 2016. Elucidation of the surface structure-selectivity relationship in ethanol electro-oxidation over platinum by density functional theory. Physical Chemistry Chemical Physics, 18 (23), pp.15501-15504

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Metadata Record: https://dspace.lboro.ac.uk/2134/21371

Version: Published

Publisher: © Royal Society of Chemistry

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Showcasing research from the laboratory of Prof. Shi-Gang Sun at the Collaborative Innovation Centre of Chemistry for Energy Materials (iChEM), Xiamen University, China.

Title: Elucidation of the surface structure–selectivity relationship in ethanol electro-oxidation over platinum by density functional theory

This work successfully builds a general framework to comprehend the structure–selectivity relationship in ethanol electro-oxidation over platinum catalysts by density functional theory calculations. Based on the investigation of the reaction mechanisms on three basal planes and five stepped surfaces, it is identified that only (110) and n(111) × (110) sites can enhance CO₂ selectivity but other non-selective step sites are more beneficial to activity. This work gives insights into the catalytic process on practical catalysts with various surface sites, which is essential for the search of new highly active and selective catalysts.

As featured in:

Elucidation of the surface structure–selectivity relationship in ethanol electro-oxidation over platinum by density functional theory†

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Understanding the structure–selectivity relationship at atomic levels is one of the fundamental scientific challenges in surface science and catalysis, which is of great significance for rationally designing catalysts. For practical catalysts with a high complexity of surface structures, what sites may actually govern the product distribution is largely unresolved due to the current technological limitation in revealing the detailed selectivity at different surface sites. Surface structural effects on ethanol electrooxidation have been studied by using single-crystal planes or nanoparticles enclosed by unique facets, and the low-coordination sites on the surface have been identified to facilitate the reaction rate.8–16 However, in terms of selectivity, the low-coordination sites do not always promote CO2 selectivity. Experiments have shown that the formation of acetic acid was also enhanced by the presence of low-coordination sites.5,11 The formation of CO2 is sensitive to the surface structure, and surfaces with terraces of (111) symmetry separated by monoatomic (110) step sites were found to be very active for C–C bond breaking since the amounts of CO/CO2 produced increase with the step density.8–12,15,16

The Brønsted–Evans–Polanyi (BEP) relationship reveals that the thermodynamics of any catalytic reaction controls the kinetics in general.17–20 Since CO2 is considerably more stable than acetaldehyde and acetic acid as the major products in ethanol electrooxidation, the thermodynamically favored CO2 production is expected to be faster kinetically than acetic acid production, but in fact the CO2 selectivity is rather low. The underlying reason behind the low CO2 selectivity is believed to be the kinetics, which may significantly determine the reaction route. Therefore, a fundamental understanding of ethanol selective oxidation reactions is significant for elucidating the structure–selectivity relationship at the atomic level, also shedding light on the selectivity concerned in many other electrocatalytic systems.

To date, a general framework for describing the structure–selectivity relationship in ethanol electrooxidation is still lacking, and many puzzles regarding the catalytic selectivity of different sites have not been rationalized yet. In particular, the following questions remain to be solved: What is the key factor determining the complete oxidative (to form CO2) or partial oxidative...
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Fig. 1  Unit stereographic triangle of platinum single-crystal surfaces and the models of surface atomic arrangements.


Fig. 2 Reaction mechanism for ethanol selective dehydrogenation via the α-dehydrogenation pathway (blue) or the β-dehydrogenation pathway (red). The key intermediate structures on Pt(111) are displayed.
pathway (the blue columns). The smallest overall barrier difference between the two pathways is obtained on Pt(111), i.e., 0.87 eV via the β-dehydrogenation pathway and 0.89 eV via the α-dehydrogenation pathway, indicating that the reaction rates for the formation of CH₂CO* via the two pathways are rather close. But on the other surfaces, the advantage of the β-dehydrogenation pathway in kinetics is considerable owing to a lower barrier of 0.16–0.35 eV, which would result in increasing the rate at about two to four orders of magnitude compared with that via the α-dehydrogenation pathway at room temperature. It is therefore suggested that the β-dehydrogenation pathway is more favoured kinetically for C–C bond breaking.

Whether CH₂CO* or CHCO* is a reasonable precursor for C–C bond splitting is found to be dependent on the surface structure. We have thus examined the two possible pathways: (i) CH₂CO* → CHCO* → CH* + CO* and (ii) CH₂CO* → CH₂* + CO*, respectively. If the dehydrogenation barrier is lower than the C–C bond breaking barrier, it would suggest the dehydrogenation to CHCO* could occur first. The comparison barriers between paths (i) and (ii) are displayed in Fig. S4 (ESI†). From our results, on Pt(111), Pt(100) and Pt(310), the mechanism follows path (i), while on other five surfaces, the C–C bond breaking in CH₂CO* may occur directly without involving the formation of CHCO*. According to the favoured pathways, the C–C bond breaking barriers on different surfaces are presented in Fig. S5 (ESI†). It can be seen that all the barriers are 0.48–0.77 eV, indicating that the C–C bond breaking rate is reasonable kinetically. Once CH₂* is produced from CH₂CO*, it would be further decomposed into CH* which is stable on the surface since the further C* formation is prohibited by thermodynamics or kinetics. As a result of C–C bond breaking, one would expect the final C1 products to be CH* and CO* on major surfaces.

From the above kinetic analyses, it is shown that the selectivity towards CO* formation versus that towards CH₂CO* formation on platinum is determined by the competition between the elementary step of CH₃CHOH* → CH₂COH* and the step of CH₃CHOH* → CH₂CHOH*. The barriers in C–C bond breaking steps being presented are reasonably low, such that the origin of low CO₂ selectivity should date back to the selective dehydrogenation in CH₃CHOH*. Only when the β-dehydrogenation pathway is preferred kinetically than the α-dehydrogenation pathway in CH₃CHOH*, ethanol C–C bond breaking can occur. We thus defined the selectivity as the difference between the barrier of α-dehydrogenation ($E_{α,α-CH}$) and that of β-dehydrogenation ($E_{β,β-CH}$) as follows:

$$ΔE_a = E_{α,α-CH} - E_{β,β-CH}$$

Quantitatively, the higher $ΔE_a$ indicates the more favoured β-dehydrogenation and the higher possibility of forming C1 products. The comparison of the selectivities obtained on a series of Pt surfaces is shown in Fig. 4, based on the above definition. It is found that the stepped Pt(110) surface possesses the highest selectivity with $ΔE_a$ being 0.13 eV, indicating that the predominant products (>99%, estimated by the Boltzmann distribution) on the surface would be CH* and CO* at low potentials. Upon increasing the width of the (111) terrace, (110) step sites could still hold the selectivity. On Pt(331), the selectivity is reduced to 82%, lower than that on Pt(110). Although having the same local structure of (110) sites, the presence of (111) terrace lowers the selectivity, indicating that the width of the terrace may affect the intrinsic properties of the step sites.

In the [011] zone, $ΔE_a$ is −0.22 eV on Pt(111) and −0.19 eV on Pt(100), respectively, suggesting that hardly any C1 product can form on the surface. The monoatomic (100) step on the (111) terrace, as the most common defect on surfaces, presents a moderate ability to break the C–C bond, although it is not comparable with the selectivities on Pt(110) and Pt(331); about 32% ethanol on the Pt(211) step would decompose into CH* and CO* finally. However, the monoatomic (111) step on the (100) terrace cannot promote CO₂ selectivity. The selectivity obtained on Pt(511) is almost the same as that on Pt(100). Herein, in the [011] zone, only upon increasing the density of n(111) × (100) step sites, the selectivity can be enhanced. In the [001] zone, despite the selectivities on Pt(320) and Pt(310) being better than that on Pt(100), the former two surfaces still cannot provide any C1 product, indicating that the increase of step sites in this zone is not beneficial to CO₂ production.

The overall barriers in their kinetically favoured pathways can depict appropriately the activity in ethanol dehydrogenation on different surfaces. It can be seen from Table 1 that Pt(111) is the least active for ethanol dehydrogenation with the highest barrier Fig. 4 Comparison of the selectivity ($ΔE_a$, in eV) on a series of Pt surfaces.
of 0.78 eV and Pt(100) is more active with a lower barrier of 0.64 eV. Pt(211), Pt(511), Pt(310) and Pt(320) steps are the most active where the barriers are between 0.51 and 0.54 eV. The activities on Pt(110) and Pt(331) are similar with the overall barriers being 0.68 and 0.70 eV, which are determined by the C–C bond breaking barriers. The activities are in the following order:

\[(111) < (110) \approx (331) < (100) < (310) \approx (211) \approx (320) \approx (511)\]

From these results, it is understood that the presence of (110) or \(n(111) \times (110)\) step sites may give rise to a high CO2 selectivity on practical catalysts, successfully explaining the experimental observations.8–12,15,16 However, the activities of such sites are less than other typical step sites, on which the partial oxidation to acetic acid is preferred. The reactive selectivity is strongly dependent on the local structure of the step sites and the low-coordination sites are not always active for C–C bond breaking. These findings highlight the need for control of the surface structure that will allow facile C–C bond breaking but hardly provide a high activity at the same time. It is reasonable to infer that how to balance the selectivity and activity will be more crucial for making platinum catalysts more efficient. It is hardly possible that pure platinum catalysts are sufficiently active for complete ethanol electrooxidation to CO2 without acetic acid as the partial oxidation product in DEFCs.

In summary, we have successfully built a general framework to comprehend the surface structure–selectivity relationship in ethanol electrooxidation on platinum catalysts. The reasonable formation mechanisms for the C1 products are pointed out via the β-dehydrogenation pathway from CH3CHOH*. The selectivity is defined as the barrier difference based on the kinetic analyses. It is found that only (110) and \(n(111) \times (110)\) step sites may enhance CO2 selectivity but other non-selective step sites are more beneficial to the activity towards partial oxidation. This work could help gain more insights into the catalytic processes on practical catalysts with various surface sites, which is essential for the search for new highly active and selective catalysts.

This work was supported by the NSFC (21361140374, 21321062 and 21573183) and the EPSRC (EP/I013229/1).

### Notes and references