Carbon Support Effects and Mechanistic Details of the Electrocatalytic Activity of Polyoxometalates Investigated via Square Wave Voltacoulometry

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ABSTRACT: The catalytic activity of surface-confined molecular species, as affected by the nature of the support, has been investigated by square wave voltacoulometry (SWVC). This technique has proven to be very powerful and advantageous for the study of electroactive and electrocatalytic monolayers. Here, the value of SWVC for the elucidation of the catalytic species and routes when the catalyst can undergo multiple electron transfers is assessed. The redox behavior in acidic water solution of the immobilized Keggin type polyoxomolybdate [PMo12O40]3− and its catalytic performance toward the reduction of bromate have been studied experimentally. Three different supports are considered: boron-doped diamond (BDD), bare glassy carbon, and graphene oxide modified glassy carbon. For all of them, the SWVC response enables the accurate identification and analysis of the catalytic pathways and species. Mechanistic details are easily obtained on the basis of the additivity of the contributions associated with the electron transfer and with the catalytic process to the SWVC response. The results obtained reveal the significant influence of the support on the redox properties and on the catalytic activity of the polyoxomolybdate. Among the supports tested, glassy-carbon supports show the highest catalytic performance with apparent rate constants that are up to 1 order of magnitude faster than those on BDD.

KEYWORDS: polyoxometalates, surface-confined electrocatalysts, square wave voltacoulometry, support effects, bromate reduction

1. INTRODUCTION

Polyoxometalates (POMs),1−4 in particular those of Keggin type, are very attractive compounds in electrocatalysis (toward bromate reduction,5,6 water oxidation,7,8 hydrogen evolution reaction,9 nitrite reduction10 and oxidation,11 etc.) for their appropriate and tunable redox properties that feature multiple oxidation states and fast stepwise electron transfers. In their use appropriate and tunable redox properties that feature multiple oxidation states and fast stepwise electron transfers. In their use, cyclic voltammetry (CV) is currently the reference technique in these types of studies, since it enables the simple and rapid qualitative analysis of the system.17 Nevertheless, experimental CV curves of surface-bound species can be considerably affected by different drawbacks, including the complex influence of non-Faradaic contributions18 and deviations from the theoretical response due to the staircase like (instead of linear) perturbation applied by digital instruments.19 Alternatively, potential pulse techniques such as staircase and square wave voltammetry20−25 offer notable advantages: better resolution and higher sensitivity, among others. Moreover, the pulsed nature of the potential perturbation allows for the kinetic discrimination between the different components of the corresponding kinetic and thermodynamic magnitudes. In this context, electrochemical techniques are very valuable tools, since they provide direct access to the above from the analysis of the electrocatalyst’s electrochemical response. Among the techniques available, cyclic voltammetry (CV) is currently the reference technique in these types of studies, since it enables the simple and rapid qualitative analysis of the system.17 Nevertheless, experimental CV curves of surface-bound species can be considerably affected by different drawbacks, including the complex influence of non-Faradaic contributions18 and deviations from the theoretical response due to the staircase like (instead of linear) perturbation applied by digital instruments.19 Alternatively, potential pulse techniques such as staircase and square wave voltammetry20−25 offer notable advantages: better resolution and higher sensitivity, among others. Moreover, the pulsed nature of the potential perturbation allows for the kinetic discrimination between the different components of the reaction.
response on the basis of their intrinsically different temporal dependences, a fact that is of great value in the analysis of electrocatalytic processes.

In this work, the above questions are investigated by examining the electrochemistry of surface-confined \([\text{PMo}_{12}\text{O}_{40}]^{3−}\) (POM-Mo) in acidic water solution and, more importantly, its electrocatalytic activity toward the reduction of bromate after immobilization on three different supports: boron-doped diamond (BDD), bare glassy carbon (GC), and graphene oxide modified glassy carbon (GC-Gox). Other immobilization methods involving coadsorbates, organic–inorganic hybrids, and support functionalization have been avoided to focus on support-only effects.

For the experimental studies carried out here, the electrochemical techniques square wave voltacoulometry (SWVC) and square wave voltammetry (SWV) are employed. The SWVC method was designed in our research group, and it is very powerful in the investigation of electroactive monolayers. Specifically, in the case of redox monolayers with fast electron transfer kinetics (as desired for ideal electrocatalysts) the Faradaic charge response can be measured without any problem, unlike the case for the current response; also, on the basis of the additivity of the different components in the overall SWVC response, the Faradaic contribution can be decoupled from the non-Faradaic and catalytic ones. Moreover, the occurrence of the catalytic process is easily detected from the appearance of a peculiar charge-potential sigmoidal response of opposite sign that is highly sensitive to the catalytic rate constant. Finally, the subtractive nature of SWVC leads to responses that are better defined and less distorted by background signals in comparison to CV, which allows for more accurate and simpler quantitative analyses.

Making use of the SWVC method and of the corresponding analytical theory developed by our research group for multiple electron transfers of immobilized redox molecules, we have determined the first six apparent formal potentials of the surface confined POM-Mo in the aforementioned three supports, finding an excellent agreement between theoretical and experimental results in all cases. Next, the electrocatalytic performance of POM-Mo toward the reduction of bromate (\(\text{BrO}_3^−\)) is evaluated. Bromate is considered to be potentially carcinogenic and nephrotoxic, and it has been classified as a category I, group B2 carcinogen, with the maximum level in drinking water being set by the European Union and the U.S. Environmental Protection Agency at 10 μg L−1.3

In our study, the catalytic mechanism for the electro-reduction of bromate is not postulated a priori but inferred from the fitting of theoretical and experimental data; this is not an easy task, considering that multiple catalytic routes can be envisaged. Thus, an analysis of the experimental SWVC response is tackled assuming a support-dependent catalytic activity and three different catalytic states: H\(_2\)PMo\(_{12}\)O\(_{40}\)\(^{3−}\), H\(_4\)PMo\(_{12}\)O\(_{40}\)\(^{3−}\), and H\(_6\)PMo\(_{12}\)O\(_{40}\)\(^{3−}\). The results offer a general view of the overall mechanism of the electrocatalytic reduction of bromate together with accurate values of the corresponding catalytic rate constants at each support. The latter reveals the degree of suitability of the different conducting supports to maximize the catalytic efficiency.

2. EXPERIMENTAL SECTION

2.1. Reagents and Instrumentation. Na\(_3\)PMo\(_{12}\)O\(_{40}\) (Merck), KBrO\(_3\), graphene oxide (Gox), and HClO\(_4\) (Sigma-Aldrich) were reagent grade and were used as received. The modification of the different electrodes by \([\text{PMo}_{12}\text{O}_{40}]^{3−}\) was performed by direct immobilization of the complex from an aqueous 0.1 mM POM-Mo solution, 1.0 M in HClO\(_4\) via cyclic voltammetry in the range +1.0 to −0.20 V (vs SCE) at 0.5 V s\(^{−1}\) for 20 min. Next, the electrode was thoroughly rinsed with water and transferred to the electrolyte solution. The response of the monolayer thus obtained is
stable for several days with no significant loss of signal for all of the supports tested.

A three-electrode setup was employed in the experiments with BDD (Windsor Scientific, doping level ca. 0.1%), bare GC (CH Instruments), and modified GC disk electrodes of 0.3 cm diameter acting as the working electrodes. The counter electrode was a Pt foil, and the reference electrode was a saturated calomel electrode (SCE, CH Instruments). Solutions were prepared with distilled deionized water (Milli-Q filtering system). Nitrogen gas was passed through solutions for deaeration for 20 min prior to measurements, with a nitrogen atmosphere maintained over the solution during all of the experiments.

2.2. Electrode Preparation. The BDD and GC electrodes were mechanically polished on alumina slurry (1.0 and 0.05 μm, Buehler), washed, and cleaned electrochemically by anodic polarization at 1.8 V (vs SCE) for 5 min followed by cathodic polarization at −1.0 V for 1 min in 1.0 M HClO4 solution. Next, the potential was cycled between +1.5 and −0.3 V in the same medium until a stable voltammogram was obtained. Then, the electrode was rinsed with ethanol and water. The modification of the GC electrode with graphene oxide was performed by drop-casting a suspension of Gox (8 μL) at the electrode surface followed by slow evaporation of the solvent.

2.3. Electrochemical Measurements and Data Analysis. SWVC, SWV, and CV were performed using a homemade computer-driven potentiostat—galvanostat. The charge record is implemented in the instrument by simply integrating the current obtained during the application of each potential pulse. The net SWVC and SWV response corresponds to the difference in charge or current signals obtained between two successive half-cycles (see below).

In both SWVC and SWV, the following potential sequence is applied34,35 (see Figure 1):

\[
E_m = E_{\text{initial}} - \left[ \frac{\text{Int}(m + \frac{1}{2})}{N} \right] \Delta E_{\text{st}} - (-1)^{m+1} E_{SW}
\]

where \( m = 1, 2, ..., N \)

\[
E_m = E_{\text{initial}} - \frac{\text{Int}(m + \frac{1}{2})}{N} \Delta E_{\text{st}} - (-1)^{m+1} E_{SW}
\]

(1)

where \( N \) is the total number of potential pulses applied, \( \Delta E_{\text{st}} \) is the potential step of the staircase, and \( E_{SW} \) is the square wave amplitude. Accordingly, three input parameters are necessary to be specified in SWVC(C) measurements: \( \Delta E_{\text{st}}, E_{SW} \) and the frequency \( f \) or the pulse length \( \tau \) (see Figure 1).

The charge (SWVC) or current (SWV) responses are sampled at the end of each potential pulse, and the net response \( (Q_{SW} \text{ or } I_{SW}) \) is given by the subtraction of the charge or the current corresponding to a pulse with odd index (forward charge or current) and the signal of the following pulse with even index (reverse charge or current):

\[
Q_{SW,c} = Q_{2c-1} - Q_{2c} = Q_{f} - Q_{r}
\]

\[
I_{SW,c} = I_{2c-1} - I_{2c} = I_{f} - I_{r}
\]

(2)

where \( c \) refers to the \( c \)th pair of pulses or cycle and subscripts \( f \) and \( r \) to the forward \((2c - 1)\) and reverse \((2c)\) components of each cycle. The SW charge or current is plotted versus the arithmetic average of the potentials applied:

\[
E_{\text{index,c}} = E_{\text{initial}} - (c - 1) \Delta E_{\text{st}}
\]

In order to enhance the contribution of the catalytic response to the signal, low frequencies were employed in the SWVC experiments: \( f = 5 \) Hz \((\tau = 100 \text{ ms})\). In addition, constant stirring of the solution was maintained during the experiments in order to keep pseudo-first-order conditions for the catalysis.

The baseline correction of the experimental SWVC curves was performed by fitting of the charge values obtained outside the Faradaic region to a polynomial of third degree followed by subtraction by means of the “Transforms” routines of SigmaPlot 10.0 for Windows.

3. RESULTS AND DISCUSSION

In this paper, the square wave potential waveform will be applied to examine the electrochemistry of POM-Mo confined at three different conducting supports (BDD, GC, and GC-GOx) as well as its electrocatalytic activity toward the reduction of bromate. The study will be based on the quantitative analysis of the corresponding charge-potential \((Q_{SW}/E)\) and current—potential \((I_{SW}/E)\) curves.

3.1. POM-Mo Response. At the potential interval of the study \((0.0–1.0 V \text{ vs SCE})\) in strongly acidic solutions where proton transfers are assumed to not be rate limiting, the surface-confined POM-Mo moieties undergo a six-electron—six-proton transfer process, in agreement with Scheme 1,13,36,37

| Scheme 1. Six-Electron—Six-Proton Electroreduction of Polyoxomolybdate \([\text{PMo}_{12}\text{O}_{40}]^{3−}\) in Acidic Aqueous Media |
|---------------------------------|--------------------------------------------------|
| \(\text{PMo}_{12}\text{O}_{40}^{3−} + e^- + H^+ \rightleftharpoons \text{HPMo}_{12}\text{O}_{40}^{2−}\) | Sub-Process 1 |
| \(\text{HPMo}_{12}\text{O}_{40}^{2−} + e^- + H^+ \rightleftharpoons \text{H}_{2}\text{PMo}_{12}\text{O}_{40}^{−}\) | Overall Process |
| \(\text{H}_{2}\text{PMo}_{12}\text{O}_{40}^{−} + e^- + H^+ \rightleftharpoons 2\text{PMo}_{12}\text{O}_{40}^{2−}\) | Sub-Process 2 |
| \(2\text{PMo}_{12}\text{O}_{40}^{2−} + e^- + H^+ \rightleftharpoons 3\text{PMo}_{12}\text{O}_{40}^{−}\) | Sub-Process 3 |

In previous papers,28 it has been reported that the SWVC charge—potential response of the overall process in Scheme 1 when the POM-Mo monolayers are formed at BDD electrodes can be modeled as three independent reversible bielectronic reduction processes coupled with biprotonations, which will be called subprocesses 1—3. This approach is completely valid at BDD, since the \(Q_{SW}/E\) responses (Figure 2) show three well-separated peaks (see ref 28).

For either bare or modified GC supports, the above approach is not strictly valid, since there is a partial overlapping of the charge—potential response of subprocesses 1 and 2 (see Figure 2). Nevertheless, when the average apparent formal potentials of the bielectronic transfers \((E_0' = (E_0'_{1} + E_0'_{2})/2\) with \( s = 1 – 3\)) differ by more than ca. 100 mV and \(E_{SW}' = E_{SW} - E_{SW}^0 \geq -90 \text{ mV}\), the \(Q_{SW}/E\) curves corresponding to a six-electron—transfer process are equivalent to that of three independent two-step processes with maximum differences of 7% under the conditions considered here (i.e., \(E_{SW} = 30 \text{ mV}\) and \( f = 5 \text{ Hz}\)) (see Figure S1 in the Supporting Information). This behavior is directly related to the subtractive nature of the SWVC technique (see eq 2). However, it is worth noting that the individual excesses (or coverages) must be calculated on the basis of a six-electron transfer mechanism (see sections S11 and S12 in the Supporting Information) because the assumption of three independent two-electron transfers (three independent EE mechanisms) does not reflect correctly their evolution with the applied potential.

According to the above, for the sake of simplicity the analysis of the charge—potential curves of the POM-Mo monolayers at the three supports under study will consider the three independent bielectronic subprocesses given in Scheme 2, where the two electrons are not necessarily transferred simultaneously but according to the corresponding \(\Delta E_{SW}' = E_{SW}'_{c} - E_{SW}'_{f}\) value (see below). The above approach will also be followed for the analysis of the current—potential curves, such
that the expressions for the responses of the overall process in Scheme 1 can be written as

\[
Q = Q_1^{EE} + Q_2^{EE} + Q_3^{EE}
\]

\[
I = I_1^{EE} + I_2^{EE} + I_3^{EE}
\]

(4)

with \(Q_{s}^{EE}\) and \(I_{s}^{EE}\) being the charge-potential and current-potential responses of the individual bielectronic transfer subprocess \(s\) given by Scheme 2, which in SWVC \((Q_{SW}^{EE} vs E)\) and SWV \((I_{SW}^{EE} vs E)\) are given by 28, 29

\[
Q_{SW,s}^{EE} = Q_{SW,s}^{EE,f} - Q_{SW,s}^{EE,r} = Q_{f}((1 - 2f_{O,s}^{EE,f} - f_{O,s}^{EE,r})
\]

\[
- (1 - 2f_{O,s}^{EE,f} - f_{O,s}^{EE,r})
\]

\[
I_{SW,s}^{EE,f} - I_{SW,s}^{EE,r} = Q_{f}\left[\frac{df_{O,s}^{EE,f}}{dt} + \frac{df_{O,s}^{EE,r}}{dt}\right]
\]

\[
- \left(\frac{df_{O,s}^{EE,f}}{dt} + \frac{df_{O,s}^{EE,r}}{dt}\right)
\]

(5)

where \(Q_{f} = FA\Gamma_{T}\) (with \(\Gamma_{T}\) being the total excess) and the expressions of the normalized surface excesses (or surface coverages) \(f_{O,s}^{EE,f}\) and \(f_{O,s}^{EE,r}\) (\(s = 1-3\); “f” and “r” stand for the forward and reverse pulses of each SW cycle) are defined as \(f_{O,s}^{EE,s} = \Gamma_{O,s}^{EE}/\Gamma_{T}\) and \(f_{O,s}^{EE,r} = \Gamma_{O,s}^{EE}/\Gamma_{T}\) and their expressions are given in sections SI1 and SI3 in the Supporting Information. Considering EE mechanisms instead of simultaneous two-electron transfers (single two-electron processes) in Scheme 2 is crucial to describe and understand the electrochemical responses obtained experimentally. Note that there are relevant differences in the potential locations, peak heights, and half-peak widths between the responses of the two situations mentioned above, as discussed in ref 38.

Figure 2 shows the experimental and theoretical \(Q_{SW}/E\) curves obtained for POM-Mo confined at BDD (Figure 2a), GC (Figure 2b), and GC-Gox (Figure 2c) in 1 M HClO4 solutions. The responses corresponding to the three hypothetical bielectronic transfers \(Q_{SW,s}^{EE}\) are also included (dashed blue lines). The experimental \(Q_{SW}/E\) curves were analyzed with the theoretical equations deduced (eq S12 in the Supporting Information). As can be seen, an excellent agreement between theoretical and experimental curves is achieved for the three supports considered with the values of the six apparent formal potentials indicated in Table 1.

At BDD (Figure 2a), three separated peaks related to subprocesses 1–3 in Scheme 1 can be clearly observed. Thus, the value of the peak potential coincides with the corresponding average apparent formal potential \(\bar{E}_{s}^{w}\) (dashed vertical lines)

\[
\bar{E}_{s}^{w} = \frac{E_{s,2}^{0} + E_{s,1}^{0}}{2}
\]

and the half-peak width enables the determination of \(\Delta E_{s}^{w} = E_{s,2}^{0} - E_{s,1}^{0}\) as discussed in ref 28. The total charge \(Q_{f}\) \((=FA\Gamma_{T})\) is obtained from the peak heights. Another interesting parameter

Figure 2. Best-fit theoretical (solid black lines, eqs 4 and 5) and experimental (red points) square wave voltammetric curves in 1 M HClO4 corresponding to the electroreduction of POM-Mo immobilized on the different supports considered (indicated on the graphs). The responses of the three hypothetical individual bielectronic transfers have also been included (dashed blue lines) as well as the corresponding average apparent formal potential (dashed black lines). \(\Delta E_{s} = 5\) mV, \(E_{SW} = 30\) mV, and \(r = 100\) ms \((f = 5\) Hz).
can be analyzed as indicated above to determine the peak at most negative potentials corresponding to subprocess \( \Delta E_0^R = E_0^R - E_{10}^F \) and Individual Apparent Formal Potentials \( (E_0^F) \) Corresponding to the Direct Response of \( \text{POM-Mo} \) Monolayers at BDD, GC, and GC-Gox Electrodes in 1 M HClO\(_4\) Shown in Figures 2–4.

Table 1. Total Charge (Q\(_F\)), Average Apparent Formal Potentials \( (E_0^F) \), Differences between Apparent Formal Potentials \( (\Delta E_0^F) \), and Individual Apparent Formal Potentials \( (E_0^F) \) Corresponding to the Direct Response of \( \text{POM-Mo} \) Monolayers at BDD, GC, and GC-Gox Electrodes in 1 M HClO\(_4\) Shown in Figures 2–4

<table>
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<th>process</th>
<th>process</th>
<th>Q(_F)/μC</th>
<th>E(0^F)/mV</th>
<th>ΔE(0^F)/mV</th>
<th>E(0^F)(_{\text{ave}})/mV</th>
<th>n(_{\text{eff}})</th>
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<td>101</td>
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</table>

\( \Delta E_{\text{ave}} = 5 \text{ mV}, E_{\text{30V}} = 30 \text{ mV}, \) and \( \tau = 100 \text{ ms.} \) All potentials are referred to SCE.

Table 1. Total Charge (Q\(_F\)), Average Apparent Formal Potentials \( (E_0^F) \), Differences between Apparent Formal Potentials \( (\Delta E_0^F) \), and Individual Apparent Formal Potentials \( (E_0^F) \) Corresponding to the Direct Response of \( \text{POM-Mo} \) Monolayers at BDD, GC, and GC-Gox Electrodes in 1 M HClO\(_4\) Shown in Figures 2–4. For each EE process is the “effective electron number”, \( n_{\text{eff}} \) defined as

\[
n_{\text{eff}} = 1 + \frac{(\% \text{ character } E_{2e}^-)}{100} = 1 + \frac{2e^{-\Delta E_0^F/RT}}{1 + 2e^{-\Delta E_0^F/RT}}
\]

with \((\% \text{ character } E_{2e}^-)/100\) being the probability of the second electron to be transferred in an apparently simultaneous way with the first electron at \( E = E_0^0 \). The values of all the above magnitudes are included in Table 1 for the three electrodes.

In the case of the GC and GC-Gox electrodes (Figure 2b,c), the peak at most negative potentials corresponding to subprocess 3 can be analyzed as indicated above to determine \( E_0^F \) (from the peak potential), \( \Delta E_0^F \) (from the half-peak width), and \( Q_0 \) (from the peak height). On the other hand, the \( Q_{\text{30V}}/E \) responses of subprocesses 1 and 2 are partially overlapped, giving rise to a broad peak with a hump at around 0.45–0.5 V. Hence, the fitting of the whole peak was performed with four adjustable parameters \( (E_1^0, E_2^0, \Delta E_1^0, \) and \( \Delta E_2^0) \) according to two independent EE mechanisms (see also section S12 in the Supporting Information). The values of the apparent formal potentials corresponding to the best fit of the experimental curves are given in Table 1. Note that in this case the \( E_1^0 \) and \( E_2^0 \) values do not coincide with any particular feature of the experimental \( Q_{\text{30V}}/E \) curve.

Among the data in Table 1 it is worth highlighting that the converted charge values obtained for GC and GC-Gox are quite similar \( (Q_0 = 1.09 \text{ and } 0.90 \mu \text{C for GC and GC-Gox, respectively, corresponding to a full monolayer coverage with a total excess of } \Gamma_T \approx 10^{-10} \text{ mol cm}^{-2}) \), and are 3 times larger than that obtained at BDD \( (Q_0 \approx 0.3 \mu \text{C}, i.e., \text{a submonolayer with } \Gamma_T \approx 10^{-11} \text{ mol cm}^{-2}) \). Since the geometric areas of the BDD and GC electrodes are identical, the experimental \( Q_0 \) values indicate that GC surfaces show higher roughness and/or that POM-Mo has higher affinity for GC (either naked or modified). Moreover, \( \Delta E_0^F \) decreases in the order BDD > GC ≈ GC-Gox, especially in the case of process 2, where \( \Delta E_0^F \) varies by more than \(-130 \text{ mV} \) (from +101 mV at BDD to \(-30 \text{ mV} \) at GC-Gox). The lower \( \Delta E_0^F \) values for GC and GC-Gox may be related to differences in the structure, adsorption, and "microenvironment" of the POM-Mo moiety. These factors affect distinctly the redox properties and the chemical reactivity of the immobilized POM-Mo depending on the nature of the support, as reported with graphene supports.

To get further insight into the above question, the evolution of the individual apparent formal potentials of the successive reduction processes \( (E_0^F) \) are plotted in Figure 3. The value of \( E_0^F \) is (statistically) the same in all the supports considered. Then, a quasi-linear decrease of ca. \(-55 \text{ mV per reduction step} \) is observed at both GC and GC-Gox. Clear deviations from this trend are observed in the second and fourth electroreductions on BDD with "inversions" of the ordering of the apparent formal potentials: \( E_1^0 \approx E_2^0 > E_0^0 \). This behavior indicates a particularly strong stabilization of the corresponding reduced states (i.e., \( \text{H}_2\text{POMo}_{12}\text{O}_{40} \) and \( \text{H}_4\text{POMo}_{12}\text{O}_{40} \)). If the protonation energy varied linearly with the charge of the POM molecule as predicted for solution-phase POMs by DFT calculations, its effect would not break the linear trend of the apparent formal potentials of a given POM isomer. Hence, the deviations observed at BDD may point to the occurrence of reversible POM isomerization and/or reorientation processes. Regarding the former, POM isomers are known to show different LUMO energies and redox properties, with \( \beta \) isomers being more easily reduced than \( \alpha \) isomers and becoming more stable after a few reduction steps. Also, studies of POM on silver surfaces have revealed the reorientation of the surface-bound molecules as...
scarcely a factor in the SWV responses of POM-Mo immobilized on the different supports considered (indicated on the graphs). The responses of the three hypothetical individual bielectronic transfers have also been included (dashed black lines) as well as the corresponding average apparent formal potential (dashed blue lines).

Figure 4 shows the experimental and theoretical \( I_{SW}/E \) curves corresponding to POM-Mo monolayers at BDD (Figure 4a), GC (Figure 4b), and GC-Gox (Figure 4c) in 1 M HClO₄ solutions. The responses corresponding to the three hypothetical individual bielectronic transfers \( I_{SW}^{EE} \) are also plotted (dashed blue lines).

Since fully reversible electron transfer processes are not expected to give any measurable current response in potential pulse or step techniques,²⁴,²⁵ then the fact that \( I_{SW}/E \) curves were registered indicates a certain degree of nonreversibility. This seems to contrast with the excellent fittings obtained in Figure 2 under the assumption of reversible electron transfers. In order to shed light on this, Figure 5 shows the variation of the normalized \( I_{SW}/E \) peak current and potential (Figure 5a,b) and \( Q_{SW}/E \) peak charge and potential (Figure 5c,d) of an EE mechanism with log \( k_0 \) (with \( k_0 = k' \tau \) or \( k_0 = k^0/(2f) \)) for \( \Delta E' \) values in the range of those obtained experimentally (Table 1). By comparing the curves in Figure 5a,c, it can be concluded that the peak charge of the \( Q_{SW}/E \) curves only deviates significantly (>8%) from the fully reversible behavior for log \( k_0 < 0.18 \), whereas the \( I_{SW}/E \) curves show clear deviations from the reversible limit (i.e., from \( I_{SW}^{rev} \approx 0 \) by more than 5% of the maximum value of the peak current) at larger \( k_0 \) values: log \( k_0 < 0.41 \). Therefore, for log \( k_0 > 0.18 \) the \( Q_{SW}/E \) curves can be treated as "reversible" (eq S10 in the Supporting Information), while a measurable \( I_{SW}/E \) response will be obtained if log \( k_0 < 0.41 \). It is worth noting that, according to Figure 5b, the peak potential is less sensitive than the peak current to the electron transfer kinetics. Thus, \( E'_{peak} \) retains "reversible features" for log \( k_0 \geq -0.5 \) such that its value coincides with the average apparent formal potential \( E_{app}^{0} \) (with a maximum difference of 2 mV).

According to the above discussion, the experimental \( I_{SW}/E \) response can be used to study the electron transfer kinetics of the surface-confined POM-Mo. The \( I_{SW}/E \) curves were analyzed with the theoretical solutions corresponding to three independent quasi-reversible two-electron transfers (see eqs S17 and S18 in the Supporting Information) using the values of the apparent formal potentials in Table 1, \( \alpha_q = \alpha_n = 0.5 \), and the standard heterogeneous rate constants \( (k_0^1 \text{ and } k_0^2) \) as fitting parameters. The \( k_0^1 \) values corresponding to the best agreement between theoretical and experimental \( I_{SW}/E \) curves (Figure 4) are given in Table 2. They lie within the range 3.8–18.2 s⁻¹ (−0.4 < log \( k_0^0 < 0.26 \) ), being of the same order of magnitude for all of the supports and slightly slower at GC and GC-Gox than at BDD.

In the case of quasi-reversible charge transfer reactions, under the working conditions employed here the assumption of additivity in the current response (eq 4) is justified for the values of the rate constants found for POM-Mo monolayers at BDD, since the \( I_{SW}/E \) curves are sufficiently separated (see Figure 4a). In the case of GC and GC-Gox, the above does not strictly hold for subprocesses 1 and 2 due to the partial overlapping of the SWV peaks. Therefore, the corresponding values of the rate constants obtained from eq 4 and eqs S17 and S18 in the Supporting Information should only be taken as estimates.

As discussed above, the SWVC curves of POM-Mo are scarcely affected by the electrode kinetics in such a way that the additivity assumption is fully valid under all the conditions examined here. Therefore, for the following studies only the SWVC responses of POM-Mo will be analyzed.

3.2. Electrocatalysis of the Bromate Reduction. The electrocatalytic reduction of bromate by POM-Mo confined at the three electrodes considered has been investigated using
Previous studies in the literature considered the electrochemical activity of POM-Mo attached directly to glassy-carbon electrodes\textsuperscript{5,6} as well as in other contexts including their use as dopants of conducting polymers, combined with nanoparticles and subject to different functionalization procedures.\textsuperscript{6,12,44−49} Regarding the electrocatalytic reduction by POM-Mo of bromate and similar species (iodate, chlorate, and oxygen, among others), different reaction mechanisms have been proposed. Most of them assume that H\textsubscript{4}PMo\textsubscript{12}O\textsubscript{40}\textsuperscript{3−} is the only active catalytic species, with very few exceptions where the possibility of two (or even three) catalytic routes driven by H\textsubscript{2}PMo\textsubscript{12}O\textsubscript{40}\textsuperscript{3−}, H\textsubscript{4}PMo\textsubscript{12}O\textsubscript{40}\textsuperscript{3−}, and H\textsubscript{6}PMo\textsubscript{12}O\textsubscript{40}\textsuperscript{3−} were explicitly considered or at least mentioned.\textsuperscript{44−46,49} Here, we propose that bromate can be reduced by the two-, four- and six-electron-reduced species (i.e., subprocesses 1−3 in Scheme 1), giving rise to the possible catalytic pathways given in Scheme 3. Each catalytic subprocess in Scheme 3 can be modeled as shown in Scheme 4, where $k_{c,s}$ is the apparent rate constant of the catalytic step for subprocess $s$ ($s = 1−3$), also denoted as the “turnover frequency” (TOF).\textsuperscript{17} According to Schemes 3 and 4, the occurrence of a “direct” catalytic process is assumed a priori for all of the subprocesses. Note that this scheme includes more simple situations where only one or two subprocesses are active, the apparent rate constants of the other routes being negligible or null. Moreover, in the following it will be considered that no concentration gradients of bromate arise due to the constant stirring of the solution. Hence, the heterogeneous chemical step in each process between the surface-confined POM-Mo and the
glassy-carbon electrodes\textsuperscript{5,6} as well as in other contexts including their use as dopants of conducting polymers, combined with nanoparticles and subject to different functionalization procedures.\textsuperscript{6,12,44−49} Regarding the electrocatalytic reduction by POM-Mo of bromate and similar species (iodate, chlorate, and oxygen, among others), different reaction mechanisms have been proposed. Most of them assume that H\textsubscript{4}PMo\textsubscript{12}O\textsubscript{40}\textsuperscript{3−} is the only active catalytic species, with very few exceptions where the possibility of two (or even three) catalytic routes driven by H\textsubscript{2}PMo\textsubscript{12}O\textsubscript{40}\textsuperscript{3−}, H\textsubscript{4}PMo\textsubscript{12}O\textsubscript{40}\textsuperscript{3−}, and H\textsubscript{6}PMo\textsubscript{12}O\textsubscript{40}\textsuperscript{3−} were explicitly considered or at least mentioned.\textsuperscript{44−46,49} Here, we propose that bromate can be reduced by the two-, four- and six-electron-reduced species (i.e., subprocesses 1−3 in Scheme 1), giving rise to the possible catalytic pathways given in Scheme 3. Each catalytic subprocess in Scheme 3 can be modeled as shown in Scheme 4, where $k_{c,s}$ is the apparent rate constant of the catalytic step for subprocess $s$ ($s = 1−3$), also denoted as the “turnover frequency” (TOF).\textsuperscript{17} According to Schemes 3 and 4, the occurrence of a “direct” catalytic process is assumed a priori for all of the subprocesses. Note that this scheme includes more simple situations where only one or two subprocesses are active, the apparent rate constants of the other routes being negligible or null. Moreover, in the following it will be considered that no concentration gradients of bromate arise due to the constant stirring of the solution. Hence, the heterogeneous chemical step in each process between the surface-confined POM-Mo and the
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solution-phase bromate follows a pseudo-first-order kinetics (see below).

Provided that the electron transfers behave as reversible, the surface excesses are constant over each potential pulse and are identical with those calculated in the absence of the catalytic reaction, since eqs S5 and S6 in the Supporting Information are valid. The charge contributions associated with the electron transfers and to the catalysis are additive such that for the SW potential waveform it can be written that

$$Q_{SW} = Q(SW,1) + Q(SW,2) + Q(SW,3)$$

with $Q_{SW,s}$ being given by eq 5 and $k_{c,s}^{app}$ the dimensionless apparent catalytic rate constant

$$k_{c,s}^{app} = \frac{k_{c,s}}{\tau_{BrO_3^-}} s = 1 - 3$$

and $O_{3s}$, $O_{5s}$ and $O_{7s}$ being the species $H_3PMo_{12}O_{40}^{3-}$, $H_3PMo_{12}O_{40}^{3-}$ and $H_3PMo_{12}O_{40}^{3-}$, respectively. Since the $Q_{SW}/E$ curves depend on the individual values of the surface excesses of the catalyst states $f_{O_{3s}}$ as indicated in Scheme 4, they must be calculated considering a six-electron-transfer mechanism (eqs S5 and S6 in the Supporting Information) with the applied potential corresponding to the reverse pulse of the corresponding SW cycle because the assumption of three independent two electron transfers does not provide appropriate results.

In order to quantify the catalytic rate constants for the different routes, SWVC experiments were run in the presence of different concentrations of bromate in the range 0.9–5.0 mM in 1 M HClO$_4$ solutions. As shown in Figure 6, the occurrence of the catalytic process affects very apparently the $Q_{SW}/E$ curves, mainly at the most cathodic potentials, where the sign of the charge changes and a negative charge plateau appears. These negative charges arise as a consequence of the catalytic contributions to the overall response, as can be deduced from eq 7. Eventually, this can lead to the disappearance of the third peak at large bromate concentrations (see Figures 6b,c). At the three electrodes, negative charge values are only observed in the peaks corresponding to subprocesses 2 and 3 in Scheme 3, whereas the peak of process 1 remains unaffected. The scarce effect on the response related to subprocess 1 indicates that under these conditions $k_{c,1}^{app}$ is very small.

The experimental $Q_{SW}/E$ responses were fitted with eqs 7 and 8 and eqs S11 and S12 in the Supporting Information, by using the values of the apparent formal potentials given in Table 1 and the dimensionless catalytic rate constants of subprocesses 1 and 2, $k_{c,s}^{app} (=k_{c,s}^{cataly} \cdot \tau_{BrO_3^-}$ with $s = 1, 2$), as fitting parameters. The $k_{c,s}^{app}$ value was directly determined from the charge value of the plateau ($Q_{SW}^{plateau}$) observed at the most negative potentials as follows:
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$$F_{c,3}^{\text{app}} = \frac{Q_{\text{SW}}^{\text{plateau}}}{Q_{F}}$$ (9)

since in this region the applied potentials are very negative with respect to all the formal potentials such that $f_{O_{5}^+} = 0$, $f_{O_{3}^+} = 0$, and $f_{O_{2}} = 1$ (see eq S11 in the Supporting Information), $Q_{\text{SW}}^{\text{EE},1} = Q_{\text{SW}}^{\text{EE},2} = Q_{\text{SW}}^{\text{EE},3} = 0$ (see eq 5 and eq S11), and eq 9 is immediately deduced from eq 7.

The results are shown in Figure 6 (symbols), where an excellent agreement between the best-fit theoretical and experimental $Q_{\text{SW}}/E$ curves is observed for all of the bromate concentrations and electrodes tested.

Further mechanistic details of the catalysis can be gained by examining the hypothetical individual contributions of subprocesses 1–3 ($Q_{\text{SW}}^s$) to the catalysis (red, blue, and green lines, respectively). The theoretical (eq 7) and experimental curves are shown for a given concentration of bromate (4.3 mM, points) in Figure 7 at BDD (Figure 7a), GC (Figure 7b), and GC-Gox (Figure 7c). In line with the above assumptions, each subprocess has a potential interval of stability where the two-, four- and six-electron-reduced species are active. In the case of the species H$_4$PMo$_{12}$O$_{40}^{$+}, no effect is observed upon the addition of bromate, whereas species H$_4$PMo$_{12}$O$_{40}^{$−} and H$_3$PMo$_{12}$O$_{40}^{$−}$ give rise to different catalytic contributions to the total response, with the most reduced species being the most active one (see green lines in Figure 7). Note that species H$_4$PMo$_{12}$O$_{40}^{$−}$ is not stable at potentials below 0.15 V such that its contribution to the response becomes null at the most negative potentials scanned (see blue lines in Figure 7).

By comparison of the catalytic activities of the three electrodes, it can be inferred that POM-Mo monolayers exhibit higher catalytic activity at GC, and specially at GC-Gox, than at BDD. Thus, a 1 mM-increase of the BrO$_3^−$ concentration gives rise to an increase in the plateau charge (relative to the total charge, $Q_{F}$) by 0.105 $\mu$C at BDD, by 0.578 $\mu$C at GC, and by 0.958 $\mu$C at GC-Gox.

The values obtained for $k_{c,3}^{\text{app}}$ for the three electrodes have been plotted versus the BrO$_3^−$ concentration in Figure 8 for the determination of the true apparent catalytic constants $k_{c,3}^{\text{app}}$ (Table 3). From the values obtained it can be concluded that the catalytic route 1 in Scheme 3 is negligible at the three supports and, therefore, POM-Mo must reach the oxidation state H$_4$PMo$_{12}$O$_{40}^{$+}$ to show some catalytic activity, in line with the results reported at GC electrodes. Hence, routes 2 and 3 are responsible for the catalysis observed. Route 3 shows higher catalytic efficiency in all cases ($k_{c,3}^{\text{app}} > k_{c,2}^{\text{app}}$), and $k_{c,2}^{\text{app}}$ and $k_{c,3}^{\text{app}}$ are 1 order of magnitude higher at GC-Gox than at BDD. These details are very clearly illustrated by the experimental SWVC curves in Figure 7, where the first peak is unaffected by the presence of bromate whereas the second and third peaks decrease with the concentration of BrO$_3^−$, this effect being more apparent at GC-Gox.

The combined catalytic activity of species H$_4$PMo$_{12}$O$_{40}^{$+}$ and H$_3$PMo$_{12}$O$_{40}^{$−}$ at GC electrodes makes them adequate supports for the electrocatalytic reduction of bromate, modification with graphene oxide improving the catalysis. Note that the poor catalytic performance on BDD can be associated in part with the particular thermodynamic stabilizations of certain POM-Mo reduced states discussed in Figure 2, which can lead to lower electrocatalytic activity toward reduction reactions.

4. CONCLUSIONS

The results reported in this work contribute to a more complete mechanistic picture of the electrocatalytic activity of surface-confined polyoxometalates, also pointing out how this can be significantly affected by the nature of the support. Thus, the quantitative electrochemical study of the polyoxomolybdate [PMo$_{12}$O$_{40}^{$3−}$] (POM-Mo) immobilized on different carbon...
With regard to the former, a quasi-linear dependence of the apparent formal potentials of surface-bound POM-Mo with the reduction state is observed on bare and modified GC electrodes. On the other hand, the reduction potential of POM-Mo adsorbed on BDD shows significant deviations from this trend, with the particular thermodynamic stabilization of certain reduced states.

The electrocatalytic activity of POM-Mo toward bromate reduction when it is confined on BDD also shows considerable differences with respect to GC and GC-Gox, the catalytic rate constants differing by an order of magnitude between them. The analysis of all the experimental SWVC curves in the presence of bromate is consistent with the existence of two different catalytic species: H₄PMo₁₂O₄₀⁴⁻ and H₆PMo₁₂O₄₀⁴⁻. Both feature the fastest catalysis when POM-Mo is attached to graphene oxide modified GC surfaces and the slowest catalysis with POM-Mo immobilized on BDD. The differences may point out the key role played by the support-dependent stabilization of the different reduced states of POM-Mo in the performance of the electrocatalysis. Quantum chemical calculations as well as infrared spectroscopy can provide further insight into the physicochemical origin of such stabilization.

The electrochemical study here performed also demonstrates that square wave voltacoulometry (SWVC), designed by our research group, is a powerful technique for the elucidation of the electrocatalytic mechanism and performance of surface-bound redox catalysts. Important advantages of SWVC versus CV for the study of these systems have been demonstrated theoretically and pointed out experimentally. Mainly, the charge-potential response of reversible single- and multiple-electron transfers in the presence of a coupled catalytic process can be split into the contributions of the “intrinsic” electrochemical response of the surface-confined catalyst and that of the catalytic process. Moreover, the occurrence of the catalysis can be easily verified by the appearance of a charge-potential sigmoid of opposite sign, the plateau of which is directly related to the value of the corresponding catalytic rate constant. It is also worth highlighting that the SWVC response of electrochemically quasi-reversible catalysts is less affected by the electrode kinetics than by the signal in square wave voltammetry. All these advantages make the elucidation of the electrocatalytic mechanism and its quantitative analysis more accurate and simple.

## ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b03392.

Mathematical derivation of the analytical solution for the SWVC response of reversible multistep electrode processes, comparison among six-electron transfers, two independent four-electron and two-electron transfers, and three independent two-electron transfers, and mathematical derivation of the analytical solution for the SWV response of nonreversible two-electron electrode processes (PDF)

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Figure 8. Linear regression analysis of the dimensionless catalytic rate constant $\bar{k}_{c,i}$ on the different supports considered (indicated on the graphs).

Table 3. Catalytic Rate Constants for the Three Catalytic Routes in Scheme 3 for the Three Electrodes under Study

<table>
<thead>
<tr>
<th>electrode</th>
<th>$k_{c,1}^{TP}$ (M⁻¹ s⁻¹)</th>
<th>$k_{c,2}^{TP}$ (M⁻¹ s⁻¹)</th>
<th>$k_{c,3}^{TP}$ (M⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDD</td>
<td>0</td>
<td>784</td>
<td>948</td>
</tr>
<tr>
<td>GC</td>
<td>0</td>
<td>603</td>
<td>4903</td>
</tr>
<tr>
<td>GC-Gox</td>
<td>0</td>
<td>6525</td>
<td>7435</td>
</tr>
</tbody>
</table>

These data have been obtained from the linear plots shown in Figure 8. $\Delta E_{st} = 5$ mV, $E_{SW} = 30$ mV, and $\tau = 100$ ms.
The authors declare no competing financial interest.

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