

Spectro-Electrochemical Examination of the Formation of Dimethyl Carbonate from CO and Methanol at Different Electrode Materials

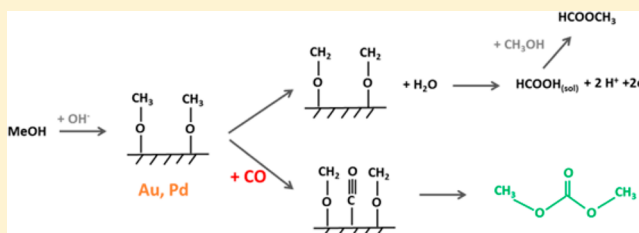
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Supporting Information

ABSTRACT: In this work, we report a fundamental mechanistic study of the electrochemical oxidative carbonylation of methanol with CO for the synthesis of dimethyl carbonate on metallic electrodes at low overpotentials. For the first time, the reaction was shown to take place on the metallic catalysts without need of oxidized metals or additives. Moreover, in-situ spectroelectrochemical techniques were applied to this electrosynthesis reaction in order to reveal the reaction intermediates and to shed light into the reaction mechanism. Fourier transformed infrared spectroscopy was used with different electrode materials (Au, Pd, Pt, and Ag) to assess the effect of the electrode material on the reaction and the dependence of products and intermediates on the applied potentials. It was observed that the dimethyl carbonate is only formed when the electrode is able to decompose/oxidize MeOH to form (adsorbed) methoxy groups that can further react with CO to dimethyl carbonate. Furthermore, the electrode needs to adsorb CO not too strongly; otherwise, further reaction will be inhibited because of surface poisoning by CO.



INTRODUCTION

Many industrial chemical processes involve a high-energy demand (often still derived from fossil fuels), toxic reactants, and the production of high amounts of waste. Therefore, the development of more efficient, less hazardous technologies, based on renewable energies, has become one of the most challenging topics for chemical synthesis. For achieving these goals, the combination of catalysis with electrochemical methods, that is, electrocatalysis, can play a very important role.¹ With electrochemical methods, toxic and dangerous chemicals can be replaced with clean electrons, the efficiency and selectivity of the reactions can be tuned by choosing the applied potential, and more importantly, the energy used can come from renewable sources like wind or solar.

Dimethyl carbonate (DMC) is an important chemical building block used in many industrial synthesis reactions because of its low ecotoxicity and bioaccumulation.² Moreover, it is also widely used as a fuel additive and as a polar solvent,³ increasing its needs of production. The industrial synthesis of DMC is based on oxidative carbonylation.² However, because of the high demand of this compound, the development of new sustainable methodologies (direct synthesis, less waste reagents, green energy) is much desired, especially in a moment that electrochemical production processes using gas diffusion electrodes are already established in chemical industry, as for example, the oxygen-depolarized cathodes in HCl electrolysis.⁴

Synthesis processes based on the carbonylation of methanol have been described in the literature.^{5–12} Most of these studies use heterogeneous catalysts to achieve the carbonylation of methanol with CO over solid catalysts such as CuY,^{6,7} Cu–

Pd,^{9,11} and activated Au.⁸ However, most processes still require high temperatures and pressures in order to achieve reactivity. Concerning electrochemical methodologies, the number of studies is more limited.^{13–15} MeOH carbonylation with CO was achieved with Pd¹⁴ and Au¹³ based electrodes. For Au/carbon electrodes, the application of high potentials > +1.3 V was required indicating that Au³⁺ was the active species for the formation of DMC. However, the activity gradually decreased at +1.5 V, and the authors suggested that DMC is produced by indirect electrochemical carbonylation mediated by the Au³⁺/Au⁺ redox reaction.¹³

Similar findings were described for Pd/C catalysts.¹⁴ In this case, the indirect electrochemical carbonylation of methanol and CO was promoted by the presence of an XBr mediator, with X = Li, Na, and tetrabutylammonium. It was suggested that the XBr promoter is electrochemically oxidized to Br₂ at the anode and that the latter works as an oxidant for the oxidative carbonylation. The main drawback of the existing studies comes from the lack of the direct identification of reaction intermediates, their interaction with the electrode materials, and their dependence on the applied potential.

In this work, we investigate the fundamental aspects of the mechanism of the electrocatalytic synthesis of DMC from MeOH and CO on precious metal electrodes (Au, Pd, Pt, and Ag). By means of in-situ Fourier transform infrared spectroscopy (FTIR), the solvent decomposition, reaction intermediates, and products were analyzed, and their dependence on the

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applied potential and electrode material was investigated. In contrast to previous studies,¹³ a low overpotential for the production of DMC was achieved (0.5 V), which reduces energy losses and increases the lifetime of the electrode. It was observed that the DMC is only formed when the electrode is able to decompose/oxidize MeOH to form (adsorbed) methoxy groups (having methyl formate as side product as a consequence) that can further react with CO to DMC. Furthermore, the electrode needs to adsorb CO not too strongly, otherwise further reaction will be inhibited because of surface poisoning by CO. These results give, for the first time, a detailed view on the reaction intermediates and their dependence on the electrode material and can contribute to the development of new and more effective processes for the synthesis of DMC.

RESULTS AND DISCUSSION

Electrochemical Formation of DMC on Au Electrodes.

Cyclic voltammograms (CV) in 0.1 M LiClO₄ in MeOH, with and without CO atmosphere, were obtained for the Au electrode to assess the electrochemical window and the presence of a possible faradaic process (Figure 1). The CV

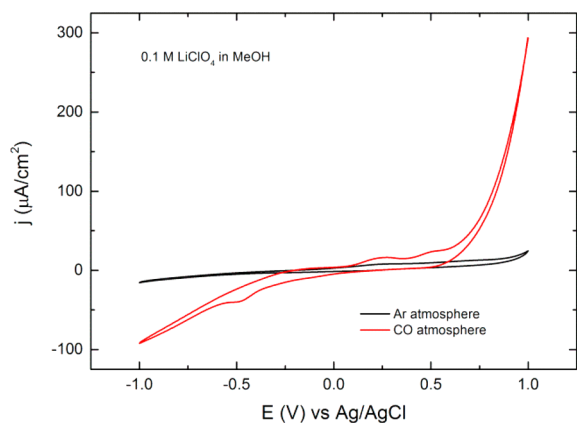


Figure 1. CVs obtained at the Au electrode in 0.1 M LiClO₄ in MeOH in Ar (black line) and CO (red line) atmosphere, scan rate of 100 mV/s.

shows that the Au electrode has a potential window of 2 V (from -1 to 1 V). The potential window is limited by residual water reduction at negative potentials and by MeOH decomposition at anodic potentials.

When CO is bubbled through the solution, the measured CV is significantly different. In the positive-going sweep, two oxidation waves are observed followed by a steep increase in current at potentials higher than 0.6 V. As these oxidation processes are not visible in the absence of CO, they are most likely related with CO oxidation or CO insertion into MeOH or with the formation of other products, as it will be clarified later with the FTIR results.

At negative potentials, reduction currents were obtained. We should bear in mind that the CVs were started at 0 V and that the potentials were scanned first positively up to 1 V and then back to negative potentials. As it is indicated by the FTIR spectra shown in the Supporting Information (Figure S1), the reduction processes correspond to the reduction of the products formed oxidatively. However, as the aim of this work is the oxidative carbonylation of MeOH with CO for the

spectroelectrochemical measurements, we concentrate on potentials from 0 to 1 V.

To look into the possible decomposition intermediates and products from MeOH at the Au electrode, FTIR spectra in Ar atmosphere were taken (Figure 2A).

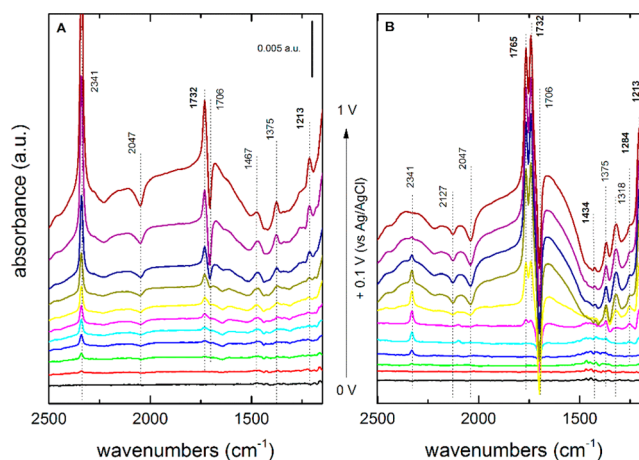


Figure 2. Spectra at different applied potentials (indicated in the figure) for the Au electrode in (A) Ar and (B) CO atmosphere in MeOH with 0.1 M LiClO₄ as supporting electrolyte.

The results in Figure 2A show that MeOH decomposition/oxidation starts at low potential, around 0.2 V. At this potential, a positive band appears at 2341 cm⁻¹ because of the presence of CO₂ in the thin layer from MeOH oxidation. At 0.4 V, another positive band at 1732 cm⁻¹ starts being observed. This band, together with a band of lower intensity at 1213 cm⁻¹, can be attributed to the formation of methyl formate (see Figure S3 for transmission spectra for product identification). Methyl formate is known as one of the products of direct oxidation of MeOH at platinum surfaces in aqueous media.¹⁶ In aqueous solution, MeOH dehydrogenation occurs to form a methoxy intermediate which is oxidized to formaldehyde. Formaldehyde is rapidly hydrated to methylene glycol that is then oxidized further to formic acid that reacts with MeOH to form methyl formate.¹⁶ As methyl formate is also a main product of methanol decomposition/oxidation in the present conditions, we can assume that a similar reaction mechanism is taking place at the Au electrode when MeOH is the solvent, especially because the solvent is not dry so that residual amounts of water allow the reaction to take place. Other bands present in the spectra (2047, 1706, 1467, 1375 cm⁻¹) are related with the solvent and supporting electrolyte or from the interference of both (see transmission spectra in Figure S2). The bands at 2047 and 1467 cm⁻¹ are due to the CH overtone and C–H bending from MeOH, respectively. Interestingly, the band at 1706 cm⁻¹ is observed for the spectra containing the supporting electrolyte, LiClO₄. This band is most likely due to the spontaneous formation of lithium methoxide when LiClO₄ is added to methanol.¹⁷ This intermediate is then consumed to form the product of MeOH decomposition/oxidation, that is, methyl formate.

When the solution is saturated with CO, the obtained spectra show a set of new bands (Figure 2B). Together with the bands described previously for methyl formate, three new bands are visible at 1761, 1434, and 1286 cm⁻¹. These bands are due to the formation of DMC as confirmed by the transmission spectra for DMC in MeOH (Figure S2). In fact, the formation

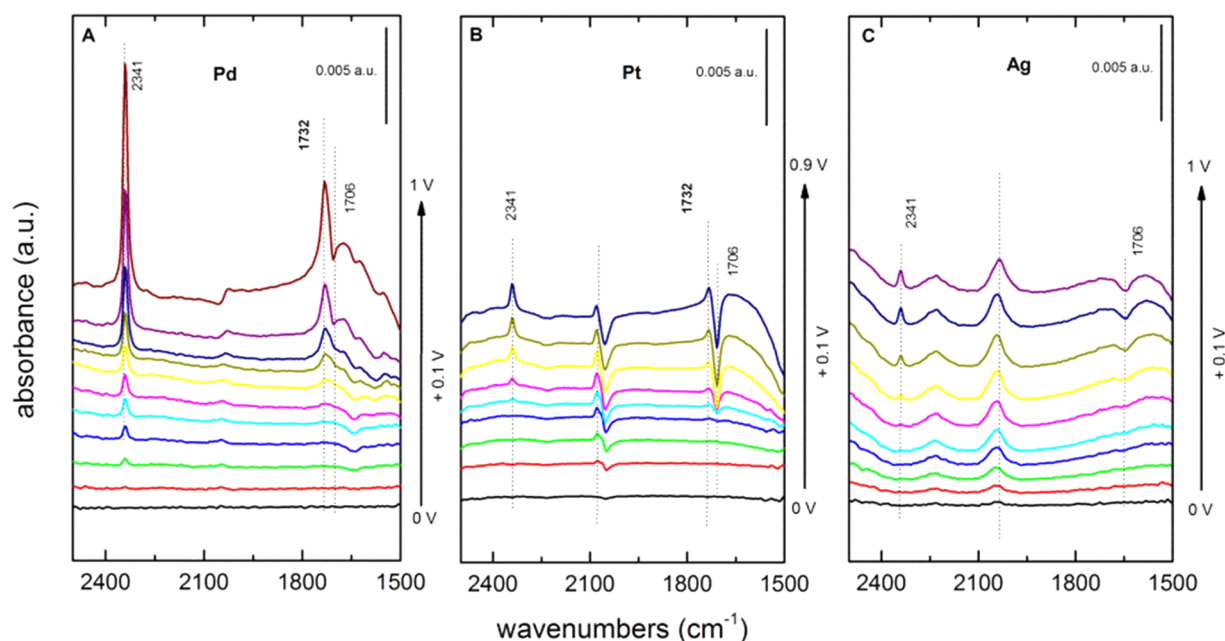


Figure 3. Spectra at different applied potentials (indicated in the figure) for the Pd, Pt, and Ag electrodes in Ar atmosphere in MeOH with 0.1 M LiClO_4 as supporting electrolyte.

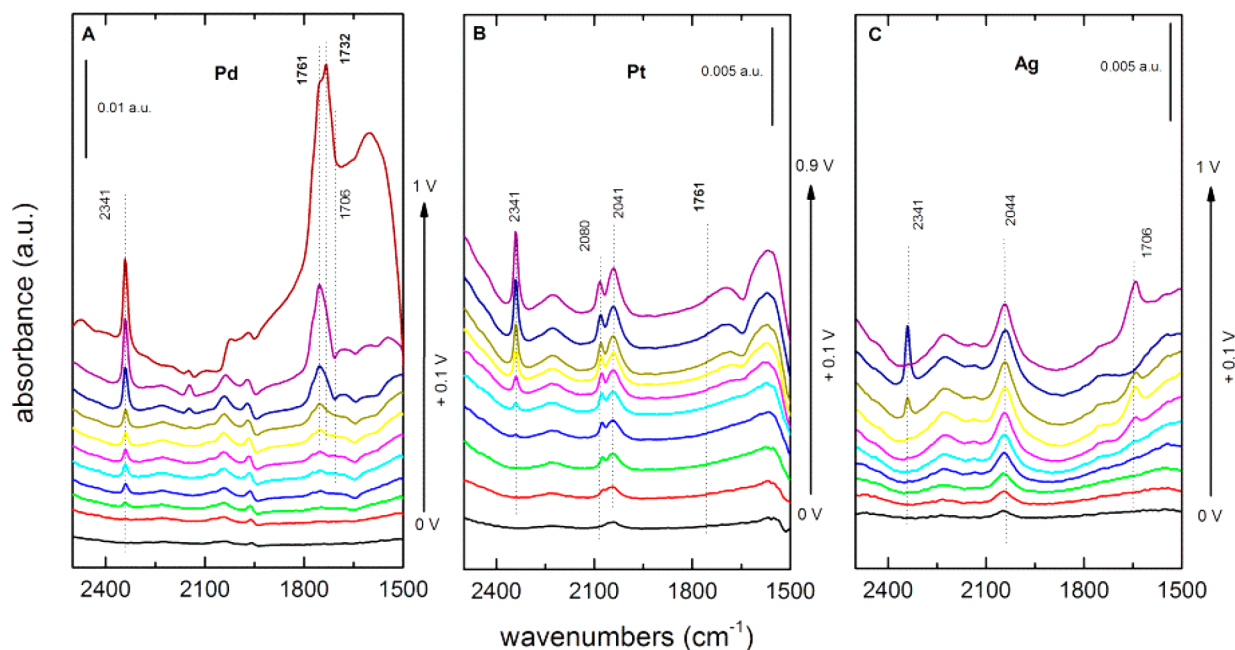


Figure 4. Spectra at different applied potentials (indicated in the figure) for the Pd, Pt, and Ag electrodes in CO saturated atmosphere in MeOH with 0.1 M LiClO_4 as supporting electrolyte.

of DMC from CO and methanol has already been described for Au electrodes.¹³ However, in that paper, a significantly higher applied potential was necessary for achieving conversion to DMC, and the presence of metal oxides was claimed to be required. In our experiment, the formation of DMC takes place at potentials as low as 0.4 V before the formation of Au oxides, which starts at potentials higher than 1 V (vs Ag/AgCl). The spectra also show a negative band at 2127 cm^{-1} revealing the consumption of CO at the interface. Interestingly, the band for CO_2 at 2341 cm^{-1} is much lower in intensity when CO is bubbled through the solution, although both CO and MeOH should also be oxidized to CO_2 . This suggests that MeOH

oxidation to CO_2 is inhibited in this case and that CO is preferentially taking part in the carbonylation reaction instead of being oxidized.

Effect of the Electrode Material. Aiming to understand the reaction mechanism for the formation of DMC from MeOH and CO and its dependence on the electrode material, experiments with Pd, Pt, and Ag electrodes were carried out. The spectra for these materials as a function of the applied potential for the blank solutions (0.1 M LiClO_4 in MeOH) and in CO atmosphere are presented in Figures 3 and 4.

The results in Figure 3 show some differences for MeOH decomposition/oxidation for the studied materials. For the Pd

electrode (Figure 3A), the obtained products are very similar to those described for Au (Figure 2A). The spectra show bands for CO₂ (2341 cm⁻¹) and methyl formate (1732 cm⁻¹). The band for CO₂ starts being observed at lower potential (around 0.2 V) than methyl formate, the formation of which begins at around 0.5 V. For Pt (Figure 3B), the same products are also observed at higher potential: 0.5 and 0.6 V, for CO₂ and methyl formate, respectively. Yet, another important band is observed, a bipolar band centered at 2041 cm⁻¹, characteristic of an adsorbed species on the electrode surface. According to the transmission spectra (Figure S1), this band can be attributed to MeOH (CH vibration overtones) as it is observed in the transmission spectra of the solvent itself, suggesting that MeOH is strongly adsorbed on the Pt electrode. For Ag (Figure 3C), no methyl formate is observed, and the band for CO₂ is very small and only visible at potentials higher than 0.7 V. However, Ag also shows a band for adsorbed MeOH at low potentials.

In the presence of CO (Figure 4), the three materials also show different characteristics toward the formation of DMC. The only material that shows the formation of DMC is Pd (Figure 4A), as observed by the presence of the band at 1761 cm⁻¹. For Pt and Ag (Figure 4 B and C), the band at 1761 cm⁻¹ is absent suggesting that DMC formation does not occur on these materials, at least not in the potential range used in this study. Not surprisingly, the results suggest that Pt is strongly blocked by the adsorption of CO as evidenced by the band at 2080 cm⁻¹¹⁸ and that the main reaction product is CO₂ from both CO and MeOH oxidation. In the case of Ag, the results for CO atmosphere are very similar to those in Ar atmosphere, and the main identified bands correspond to the adsorption of MeOH and CO₂ because of mild oxidation of MeOH at this surface.

On the basis of these results, we can suggest that there is a catalytic dependence on the electrode material for the synthesis of DMC from MeOH and CO. Materials like Pt, which bond CO too strongly, do not form DMC as the surface is blocked by the strong adsorbate, and the reaction cannot take place. On the other hand, Ag seems to be also blocked by strong adsorbates but in this case from MeOH inhibiting further reactions. Ag does not seem to adsorb CO under these conditions. Pd and Au have moderated adsorption energies for CO allowing it to be at the surface but not too strongly adsorbed, so that CO can further react and proceed with the carbonylation of MeOH. Another interesting observation is that both Pd and Au have methyl formate as product from MeOH decomposition/oxidation, suggesting that methyl formate is an important byproduct of the electrocatalytic synthesis of DMC.

Isotopically Labeled CO. Methyl formate has been described as a good carbonylation agent in homogeneous catalysts, including DMC synthesis.²⁰ However, in the conditions described in this work, if methyl formate was the carbonylation agent for the reaction, it would be expected that DMC would have been found also in the absence of CO. To shed some light on the carbonylation agent, experiments with isotopically labeled CO were performed to ensure its participation in the reaction. The Au electrode was chosen for these experiments as it shows the most intense bands for DMC. We should bear in mind that FTIR experiments in the thin-layer configuration are not quantitative, as the thin-layer thickness can be different from electrode to electrode. Nevertheless, the relative intensity of two bands should be proportional to the relative amount of the products. Comparing the bands of CO₂ and DMC in the spectra for Au and for Pd,

for Au the DMC bands are significantly more intense than the CO₂ bands, suggesting that Au is more active and selective for the electrosynthesis reaction than Pd.

The results for the Au electrode in 0.1 M LiClO₄ in MeOH with ¹³CO are presented in Figure 5. The spectra show bands at

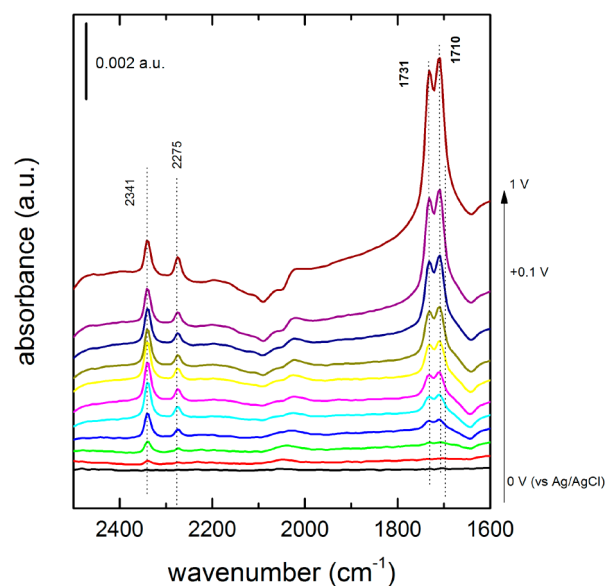


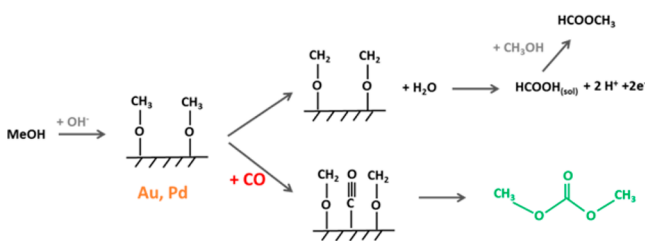
Figure 5. Spectra at different applied potentials (indicated in the figure) for the Au electrode in ¹³CO saturated atmosphere in MeOH with 0.1 M LiClO₄ as supporting electrolyte.

2341, 2275, 1731, and 1710 cm⁻¹ corresponding to ¹²CO₂, ¹³CO₂, methyl formate, and ¹²DMC, respectively. The band at 2341 cm⁻¹ increases in intensity from 0.2 V in accordance with Figure 2 and corresponds to the formation of ¹²CO₂ from the oxidation of MeOH. At slightly higher potentials (0.3 V), the band for ¹³CO₂ is also observed, corresponding to the oxidation of ¹³CO. Around 0.4 V, two additional bands can be observed, one at 1731 cm⁻¹, previously identified as methyl formate (Figure S1), and a second band at 1710 cm⁻¹. The latter is due to the formation of ¹³DMC as it presents a shift of about 50–60 cm⁻¹ in accordance with the expected shift for the replacement of ¹²C with ¹³C. No band at 1761 cm⁻¹ is observed in the spectra showing that all the formed DMC is coming from the reaction of ¹²CO with MeOH and not from methyl formate.

Reaction Scheme. The results presented earlier show that with the appropriate catalyst the formation of DMC from the electrocatalytic reaction of MeOH and CO can occur at low overpotentials. For this reaction to take place, the electrode should bind CO not too strongly in order to avoid surface poisoning and blockage (like for Pt), but it should still be able to oxidize/decompose methanol. The importance of MeOH decomposition on the surface is supported by the fact that, if methyl formate is not obtained as product from MeOH, DMC is also not observed as a product (such as for Ag, for example). The experiments with isotopically labeled CO clearly show that methyl formate does not take place in the formation of DMC, although DMC is only produced if the metal oxidizes MeOH to methyl formate. As mentioned earlier, it has been reported that in the direct oxidation of methanol on platinum electrodes¹⁶ the formation of methyl formate involves the formation of methoxy groups on the electrode surface. Methoxy groups have also been reported as important intermediates for the synthesis

of DMC from methanol gas phase catalysis.⁸ Therefore, we can relate the capability of the metal to form methyl formate with its ability to form methoxy groups, explaining the higher catalytic activity for DMC formation for metals that oxidize MeOH to methyl formate. Methyl formate is a side product from the reaction but also an indicator of the catalytic properties of the metal toward the formation of DMC in the presence of CO. On the basis of these findings, we suggest that the electrocatalytic reaction forming DMC takes place if both methoxy and CO are (not too strongly) adsorbed on the electrode surface, as illustrated in Scheme 1.

Scheme 1. Reaction Scheme for the Electrosynthesis of DMC from Methanol and CO on Au and Pd Electrodes



CONCLUSIONS

With this work, we show that the electrochemical synthesis of dimethyl carbonate from CO and methanol is very dependent on the electrode material properties toward the adsorption and stabilization of reaction intermediates such as methoxy groups. By investigating different electrode materials, it was observed that materials like Pt, which bond CO too strongly, do not form DMC as the surface is blocked by the strong adsorbate, and the reaction cannot take place. On the other hand, Ag seems to be also blocked by strong adsorbates but in this case from MeOH inhibiting further reactions. Ag does not seem to adsorb CO under these conditions. Both Pd and Au have moderated adsorption energies for CO allowing it to be at the surface but not too strongly adsorbed, so that CO can further react and proceed with the carbonylation of MeOH. The importance of MeOH decomposition on the surface is supported by the fact that, if methyl formate is not obtained as product from MeOH, DMC is also not observed as a product (such as for Ag, for example). On Au electrodes, the formation of DMC takes place at potentials as low as 0.4 V showing that oxidative carbonylation of MeOH does not require metal ions (oxidized metal) as catalyst and that the reaction can take place directly on the metal, which represents ideal conditions for industrial applications as the catalyst stability is improved. These results represent an important step further in the development of an electrochemical process for the synthesis of DMC and can help the development of more efficient and selective processes for electrocarbonylation reactions.

MATERIALS AND METHODS

The experiments were performed using a spectroelectrochemical cell with a three-electrode configuration as described elsewhere.^{19,20} The working electrodes (Au, Pd, Pt, and Ag) were discs mechanically polished with alumina suspension, rinsed with Milli-Q water (18.4 M Ω), and sonicated for 5 min before each experiment. A Pt coil was used as counter electrode and a Ag/AgCl electrode as reference. The electrode potential was controlled with a Potentiostat 466 System (Model ER466) from E-DAQ. All the experiments were performed at room temperature.

The electrolyte solution was prepared with 0.1 M LiClO₄ (Fluka, < 99%) in methanol (MeOH, 98% anhydrous from Sigma-Aldrich). Prior to the experiments, the solutions were purged with Ar (6.0 from Linde) to remove all the oxygen, and blank cyclic voltammograms were obtained. For the experiments with CO, the solutions were fluxed with CO (6.0 Linde) for 20 min after oxygen removal. During the electrochemical/spectroelectrochemical measurements, the gas flow was kept in the cell atmosphere. For the isotopically labeled experiments, CO with ¹³C > 99% from Cambridge Isotope laboratories was used.

In-situ Fourier transform infrared (FTIR) spectroscopy (Bruker Vertex 80 V IR spectrophotometer) was used to characterize the products and intermediates of the reaction. A CaF₂ prism bevelled at 60° was used, and the spectra correspond to an average of 100 interferograms with 8 cm⁻¹ resolution and p-polarized light. The experiments were performed in thin-layer configuration, where the working electrode was pressed onto the prismatic window at a controlled potential. After that, a reference spectrum was obtained and subtracted from the spectrum acquired at the sample potential. All the spectra in this work are presented as absorbance, according to $A = -\log(R/R_0)$, where R and R_0 are the reflectance corresponding to the single-beam spectra obtained at the sample and reference potentials, respectively. As a consequence, positive (negative) bands correspond to species present (absent) at the sample potential.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b08208.

Transmission spectra for species in solution
(PDF)

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Notes

The authors declare no competing financial interest.

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