

Influence of adsorption processes on the CO₂ electroreduction: An electrochemical mass spectrometry study

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This paper is dedicated to Ronald W. Fawcett on the occasion of his 65th birthday and his long time contributions to Electrochemistry

Abstract

The reduction of CO₂ in sulfuric and perchloric acid electrolytes on a polycrystalline Cu surface has been investigated, using the online electrochemical mass spectrometry method (EC/MS). Gaseous products, such as CH₄, C₂H₄ and highly volatile products such as CH₃OH, HCHO, are formed at overpotentials of hydrogen evolution reaction. The EC/MS results suggest that the reduction products formed depend on the presence of preadsorbed sulfate on the surface. The adsorbed anion from the electrolyte plays a role at the potential where HCHO formation occurs on copper. A mechanism for this process, based on electrocatalytic hydrogenation, is proposed.

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Keywords: Carbon monoxide; Carbon dioxide; Copper; Online electrochemical mass spectrometry (EC/MS or DEMS); Anion adsorption

1. Introduction

The electrochemical reduction of CO₂ to generate hydrocarbon products at ambient temperatures has been seen as an attractive route for the conversion of this global warming effect gas into either potentially stored energy or as immediately available energy sources (e.g. CH₄, CH₃OH, HCOOH), in addition to providing useful precursor molecules for modern industrial chemistry applications [1]. Thus, transformation of carbon dioxide into more appealing molecules can be viewed as an environmentally friendly approach, in line with the Kyoto protocol, to at least reduce industrial CO₂ releases to atmosphere. Thus, electrochemical reduction methods could be more profitable for the industrial economy than simple storage of CO₂, in either solid forms e.g.

(Na₂CO₃) or as the compressed gas, injected into an exhausted/abandoned natural gas pocket [2].

The distribution of product types, arising from the CO₂ electroreduction reaction under consideration, depends strongly on the nature, the characteristics and the state/form of the electrocatalyst. Numerous heterogeneous catalysis or surface reactions on catalysts involve an initial reactant adsorption step or an adsorption of the intermediates in the process. This reactant adsorption step observed in catalytic hydrogenation and/or electrocatalytic hydrogenation, has been discussed previously in several publications [3–9]. These works have shown that adsorption of organic molecules on the catalyst is a critical step for realizing further reaction of the molecules. The process can be controlled through both the selectivity and the reactivity of the catalyst. Adsorption processes are known to be important in many electrochemical reactions that involve surfaces, such as in bulk metals electrodeposition, as well as in underpotential deposition (UPD) reactions [10–13], the

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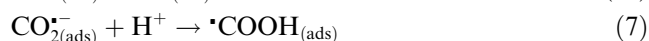
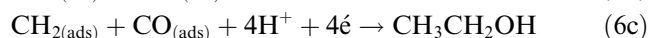
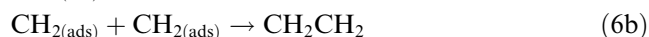
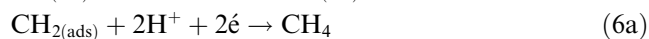
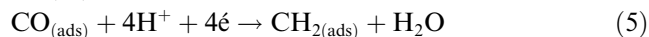
hydrogen evolution reaction (HER) and the oxygen reduction reaction (ORR) [14]. We have recently shown that, for the oxygen reduction reaction on copper single crystal surfaces [14], a compact layer of strongly adsorbed sulfate anions suppresses the initial adsorption of O₂ molecules on the surface, and the reaction pathway thus differs from the mechanism observed in the presence of perchlorate. The ORR occurs at a potential 200 mV more negative in the presence of SO₄²⁻ anions, than in the presence of ClO₄⁻, on a well defined Cu surface electrode. In the case of CO₂ reduction on Cu in neutral media, it has been observed that the adsorption of anions from electrolytes (KHCO₃, K₂HPO₄, K₂SO₄ or KClO₄) does have an influence on the products composition distribution [15]. On platinum polycrystalline, where the reactant is not strongly adsorbed on the surface, it has also been reported that the anion has a role in the CO₂ electroreduction process [16].

Numerous studies of CO₂ reduction on copper have also been made in various electrolytes [15], either of a basic or neutral character (KOH, KHCO₃, K₂HPO₄, K₂SO₄ and KClO₄) and also in methanol media. Further, a few experiments have been reported, where elevated pressures were utilized to increase the CO₂ solution concentration [17,18]. The majority of these reported works were undertaken utilising highly negative potentials, mainly on Ni and Cu surfaces in neutral or basic media. The reduction usually yielded HCOO⁻, CH₄, C₂H₄ and C₁–C₂–C₃ alcohols, Cu electrodes being the most active and yielding methane as the major product [19,20], followed by ethene. Hori and coworkers [21,22], using batch electrolysis and ex situ GC and LC/MS analysis, have worked extensively on CO and CO₂ reduction on copper, in both basic and neutral media. They found that in KHCO₃ media, CO₂ reduction produced higher level of methane and ethene than obtained from the reduction of a saturated CO solution, while the ethanol production remained at a low level. From CO reduction, ethene production was slightly more important than that of methane, and ethanol was also at a level comparable to methane formation. The authors also showed that the anion adsorption effect was present in both CO and CO₂ reductions conducted in HCO₃⁻ and H₂PO₄⁻ media. In KClO₄ and K₂SO₄ media (pH ≈ 5.8), there was little effect on the CO₂ reduction reaction leading to methane, ethane and ethanol production [15]. In the same paper, the authors reported that CO reduction gave high yields of C₂H₄, C₂H₅OH and *n*-C₃H₇OH at a Cu electrode immersed in high-pH solutions. From the CO₂ reduction, C₂H₄ and alcohols are preferentially formed in KCl, KClO₄, K₂SO₄ and in dilute KHCO₃ solutions, where non-equilibrium, localized high-pH regions favor the formation of ethene and alcohols. Hori et al. [23] have performed in situ IR analyses, in order to characterize the reaction intermediates for CO₂ electroreduction per-

formed on copper in carbonate media, in the potential region above that leading to the production of hydrogen. Their Infra-Red studies revealed the presence of both CO₂⁻ and CO species adsorbed on the copper surface during the CO₂ reduction.

At this time, only two papers on the products of CO₂ reduction on copper, as analyzed by mass spectrometry, have been located, one from Wasmus et al. [24] and the other from Friebe et al. [25]. Both sets of experiments were performed in KHCO₃ media and revealed the formation of methane and ethane under all conditions tested. Wasmus et al. reported a species of 31 mass units, which, while not formally identified, was neither methanol nor ethanol [24]. From both sets of reported experiments, the methane presence was more intense than that of ethene.

Studies in acidic media by means of an in situ analysis, performed at very negative potentials, have been less commonly reported. We have previously reported on the formation of methane, formaldehyde, formic acid and methanol, for the reduction of CO₂ and CO on polycrystalline platinum in HClO₄, using in situ electrochemical mass spectrometry (EC/MS or DEMS) [26]. The previously proposed mechanism is similar to the one reported by Hori and coworkers on copper in neutral media [15]. However Chaplin and Wragg [27] have suggested general reaction pathways, with reference to formate formation on numerous metal and electrolyte. An extensive review of CO₂ reduction, involving both homogeneous and heterogeneous catalysts, has been published by Sullivan [1]. The general mechanism is shown below,



In order to validate some adsorb intermediate step, some researcher have reported FTIR analysis. These in situ FTIR investigations, performed on polycrystalline Pt electrodes, have shown that species such as CO, CHO and COOH, seem to be formed in the H-UPD region [28], whereas on Cu electrodes, at -1 V vs. NHE in KHCO₃ media, Hori et al. [23] concluded that “the reduced CO₂” is identical to the band of adsorbed CO.

Our preliminary work [26] conducted on the CO and CO₂ reduction on a polycrystalline Pt electrode in acidic media, has shown some interesting results, such as the presence of methane and methanol. In this work, we

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