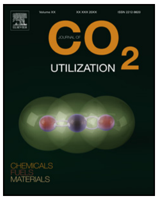
Journal of CO_2 Utilization 19 (2017) 137–145

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou



Selective CO_2 electroreduction to C_2H_4 on porous Cu films synthesized by sacrificial support method

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ARTICLE INFO

Article history:
Received 17 December 2016
Received in revised form 3 March 2017
Accepted 7 March 2017
Available online 28 March 2017

Keywords:
CO_2 electroreduction
Copper-based catalysts
Sacrificial support method
Selective electrocatalysis

ABSTRACT

A series of copper-based electrocatalysts were prepared by the Sacrificial Support Method (SSM) with variation of synthesis parameters. Thin films of the materials were evaluated for their electrocatalytic activities towards CO_2 electroreduction to short-chain (C_1-C_2) hydrocarbons by standard electrochemical methods. Gas-phase reaction products were quantified using an online gas chromatography system. At -0.98 V vs reversible hydrogen electrode (RHE), copper oxide-derived catalysts were found to have selectivity toward C_2H_4 approximately one order of magnitude higher than to CH_4. The highest selectivity towards C_2H_4 production at -0.98 V was demonstrated by the catalyst with cube morphology, synthesized with 20 wt% Cu: 80 wt% SiO_2 ratio in the precursor. Possible causes for this shift in selectivity are discussed in terms of the morphology and surface/core composition as determined by scanning electron microscopy (SEM), X-Ray diffraction (XRD), and X-Ray photoelectron spectroscopy (XPS).

1. Introduction

Carbon dioxide (CO_2) is generated in substantial quantities due to energy generating activities, accounting for 82% of the worldwide energy supply in 2014 [1]. The accumulation of atmospheric CO_2 can be attributed to its unregulated and continuous release, resulting in an increase in atmospheric concentration from 278 ppm to 400 ppm since the 1850s [2]. The current concentration of CO_2 strains the balance of the earth's natural carbon cycle, resulting in acidified oceans and drastic changes in global weather patterns and motivates developments of new technologies to reduce emission rates [1,3–5]. Existing methods of reducing CO_2 emissions include: increasing the percentage of energy generated from renewable or nuclear sources, utilizing CO_2 capture and storage (CCS) at point sources such as power plants [6,7,8], and CO_2 capture and conversion (CCC) into fuels or value added products. CCC would transform carbon emitting energy sources into carbon neutral processes by integration with intermittent renewable energy sources (e.g. solar or wind) to produce liquid or gas products, effectively reintroducing CO_2 into the energy cycle. This has been successfully demonstrated for the selective reduction of CO_2 to formic acid on Pb (94.1%) and Sn (70–80%) electrodes [9] and for syngas synthesis on alloys and Ag electrodes [10–14]. Methods of CO_2 conversion include reduction in solid oxide fuel cells, reduction by metal complexes, or electrochemical reduction on metal electrodes in aqueous solutions [8,10]. The main products of CO_2 reduction are small-chained carbon molecules (C_1-C_3) such as carbon monoxide (CO), formic acid (HCOOH), methane (CH_4), ethylene (C_2H_4), and alcohols ($C_nH_{2n+1}OH$) [15–29], depending on the catalyst used, applied voltage and operating conditions. Solid-state fuel cells are currently limited to producing CO because of their high operating temperatures [8,22,30,31]. Metal complexes that have been studied are not economically viable at their current efficiencies because they contain either Pt or Pd catalytic sites [8]. Metal electrodes in aqueous media can be incorporated into established fuel cell or electrolyzer technologies, replacing cathode catalysts typically employed for the hydrogen evolution reaction (HER) with catalysts designed for CO_2 electro-reduction (CER) while maintaining the oxygen evolution reaction (OER) at the anode

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http://dx.doi.org/10.1016/j.jcou.2017.03.006
2212-9820/

[8,10,11,32,33]. However, as discussed in a recent survey by Jhong et al. [34], the catalytic performance towards CER on metals in aqueous solutions is lacking, with very few available CER catalysts simultaneously exhibiting all the criteria for industrial application such as high current density, low applied voltage, durability, and selectivity towards a specific product.

Metal catalysts are categorized into four groups based on their main reduction products, as observed by Hori et al.: HCOOH (Pb, Tl, Hg, Sn, In, Cd), ii) CO (Au, Ag, Pd, Ga, Zn), iii) CH_4/C_2H_4 (Cu), and iv) H_2 (Pt, Ni, Fe, Ti) [26]. These product trends are supported by consistent, extensive observation of these categorical trends in many studies, suggesting dissimilar reaction mechanisms and/or different surface affinities for CO_2 reduction intermediates [15,16,19–24,26,35–37]. The catalytic activity of metals depends not only on their intrinsic atomic properties, but also on their surface characteristics such as roughness and surface area to volume ratios, both of which affect the plane edges exposed at the surface [32,38–40].

Among metal catalysts, Cu is unique in its ability to reduce CO_2 to small-chained hydrocarbons and alcohols at low temperatures and atmospheric pressures with surprisingly high conversion [25]. Since the 1980s, considerable effort has been made to elucidate the mechanism of CO_2 reduction on Cu with the purpose of engineering a catalyst that would promote hydrocarbon generation from CER in aqueous solutions [21–24,38,39,41–45]. Total faradaic efficiencies of CER on Cu range from 3 to 79%, with near equal ratios of CH_4 and C_2H_4 and varying amounts of H_2 [28,46–48].

Previous studies on single and poly-crystalline Cu have revealed that CER yields are very sensitive to surface structure. Hori et al. showed increased faradaic efficiencies towards C_2H_4 on Cu (100) and towards CH_4 on Cu (110), when compared with the products generated on Cu foil at the same potentials [38,39]. Increased faradaic efficiency towards C_2H_4 was also shown for the (111) surface at higher indexed facets, with Cu (711) having the highest ratio of 10:1 for selectivity of C_2H_4 to CH_4. Another example of the effect of surface morphology is posited by Baturina et al. [46], where preferential generation of C_2 species in product distribution are expected for CER on Cu nanoparticles because they are comprised of low-coordination sites and low-index facets, which are sites similar to Cu (311), Cu (511), and Cu (711) [46]. Impact of catalyst structure on selectivity is further supported by the observations of Tang et al. that Cu particles (50–100 nm) mainly yield C_2H_4 with minimal quantities of CH_4 (faradaic efficiencies of ca. 37% and 1%, respectively) [49]. Additional studies explore the properties of oxide-derived Cu catalysts, which correlate increased activity towards CER and selectivity towards C_2 products with the high $Cu_xO:Cu^{00}$ ratios formed during catalyst synthesis [50–53]. These improvements are primarily attributed to increased surface roughness and morphologies enhanced by cubed plane edges [100], which are formed during electrochemical reduction and subsequent reordering of the catalyst surface [51–53]. Further, in a study of cubic Cu nanoparticles, the suppression of CH_4 at low potentials (−0.6 V *vs.* RHE) was observed and the role of surface roughness was posited to alter localized pH [54]. These examples

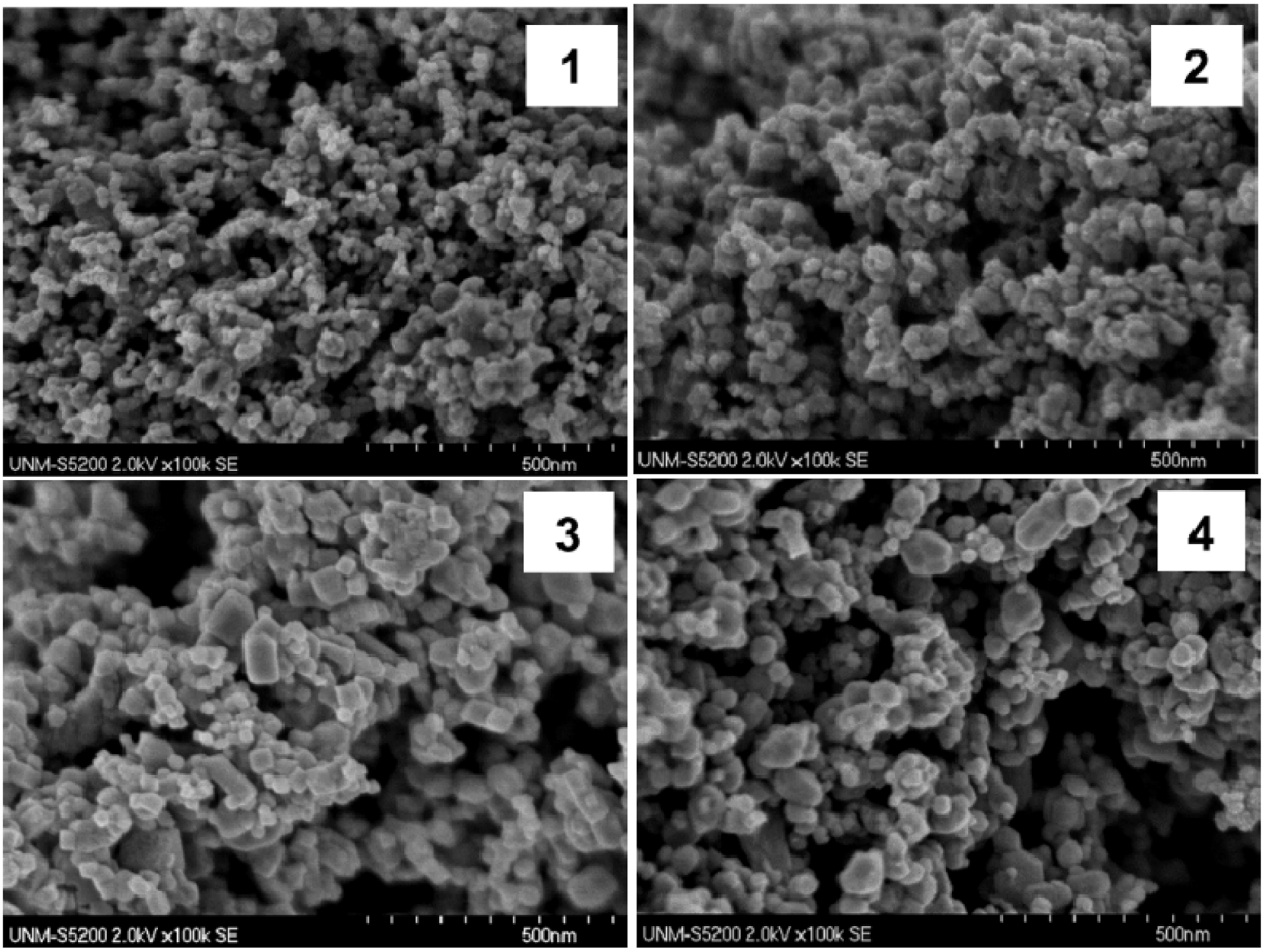

Fig. 1. SEM images of the sponge-like morphology Cu nanoparticles synthesized by SSM exhibit with varied precursor weight ratios of silica to copper: 1 – Cu_1 (5 wt% Cu: 95% silica), 2 – Cu_2 (10 wt% Cu: 90% silica), 3 – Cu_3 (20 wt% Cu: 80 wt% silica), and 4 – Cu_4 (30 wt% Cu: 70 wt% silica).