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Metal-doped carbon xerogels for the electro-catalytic conversion of CO_2 to hydrocarbons

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ABSTRACT

Original carbon xerogels doped with transition metals Ni, Cu or Fe have been prepared as cathodes for the electro-catalytic reduction of CO_2 at atmospheric pressure. Commercial metallic and carbon materials have been also tested as cathodes for comparison, and the leaching of Ni based cathodes during reaction has been analyzed. Carbon xerogels doped with transition metals work very well as electro-catalysts in the transformation of CO_2 to gaseous hydrocarbons C_1–C_4. The product distribution strongly depends on the metal. In this reduction process not only the type of metal but also the textural and chemical properties of the carbon xerogel play an important role in the electro-catalytic performance. The use of xerogel-based electrodes considerably reduces the amount of transition metal required.

1. Introduction

CO_2 is a well-known greenhouse gas, and its increasing atmospheric concentration is thought to be one of the main causes of global climate change.[3] In particular, CO_2 emission from the use of fossil fuels contributes to the increasing concentration, because it constitutes a continuous net increase in the natural cycle of tropospheric carbon. Renewable energy sources thus receive a lot of attention, with complete journals dedicated to renewable energy research (Renewable Energy, Renewable and Sustainable Energy Reviews). However, many renewable energy sources such as solar, wind and tidal electricity do not produce the constant and tunable currents that fossil fuels provide. Storage of surplus electrical energy produced during peak production periods and its release during peak demand periods is thus crucial, especially as peak production and peak demand periods often do not coincide. A lot of research effort is directed towards storage in batteries [1]. However, the manufacture of batteries requires a lot of resources, reducing their contribution to controlling CO_2 emission. Moreover, battery life is as yet limited to about 1000 charging/discharging cycles, after which again resources are required to recycle their components into new batteries.

An alternative strategy to address the problem of storing temporary and local surpluses of renewable energy is the electro-catalytic reduction of CO_2 to hydrocarbons [2,3]. In a one-pot process, water is split to provide the required hydrogen atoms/ions which are reacted with CO_2 to form hydrocarbons that can be used directly in the existing infrastructure for transportation fuels. Next to storing the renewable energy, some CO_2 is removed from the atmosphere. O_2 is formed simultaneously, which can be used to burn the hydrocarbons to release the energy whenever required. For this process mainly sheet metal electrodes have been investigated [4–6].

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[3] Word Meteorological Organization 2012 http://www.wmo.int/.

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These materials have a very low specific metal surface areas, and so far the Faradaic efficiency of the electro-catalytic process is too low for commercial application. Thus new and improved electro-catalysts are still required for this attractive route to utilize CO_2 for storage of renewable energy in the form of hydrocarbons.

The direct electrochemical reduction of CO_2 in aqueous solution has been studied mainly on metal electrodes in the form of plates, both at atmospheric pressure and at higher pressures [5,7]. So far, copper electrodes have been shown to be quite unique in the activation of CO_2 to hydrocarbons, although the Faradaic efficiency is still low as a result of the dissociation of H_2O to H_2. Several studies have been concerned with elucidating the mechanism of electro-reduction of CO_2 to hydrocarbons, which seem to point to a Fischer–Tropsch mechanism of chain propagation [8,9].

The products obtained in the direct electrochemical reduction of CO_2 to hydrocarbons generally vary from one to six carbon atoms [9]. Oxygenates such as alcohols or carboxylic acids with chain lengths of the same order have also been obtained [10].

Some types of carbon materials, including carbon gels [11], have been successfully applied in electrochemical energy storage as supercapacitors, where the porous texture, surface area and surface chemistry of these materials play an important role. Alternatively, the application of carbon materials in electro-catalytic CO_2 reduction processes is a plausible option, which has been tested with platinum catalysts supported on carbon nanotubes, carbon cloth or carbon black [12,13], obtaining a wide distribution of products of up to nine carbon atoms. In these cases the platinum was deposited on the carbon substrate by impregnation.

Carbon gels, xerogels and aerogels are nanostructured materials obtained from the carbonization of organic gels, which are prepared by the sol–gel polycondensation of certain organic monomers, typically resorcinol (R) and formaldehyde (F) [14,15]. The textural characteristics of these materials strongly depend on a careful control of the reactant concentrations and the experimental conditions of the different synthesis steps: gelation, curing, drying and carbonization/activation [16,17]. For this reason, the surface area, pore volume, and pore size distribution are tuneable properties related to the synthesis and processing conditions, enabling the preparation of a wide spectrum of materials with unique properties, e.g., for adsorption and catalytic and electrochemical applications [18–23]. Moreover, carbon gels doped with transition metals show a high metal dispersion and a very good distribution of the metals throughout the carbon matrix [24–26]. The majority of metal cations will be embedded into the structure of the carbon gel, which minimizes the leaching of the metals in liquid phase applications. In this respect, these materials may have advantages over those catalysts or electro-catalysts prepared by impregnation of the corresponding metallic phase. Nevertheless, a percentage of the metal phase of the doped carbon gels will not be accessible to the reactants, although preparation techniques are available that minimize this aspect [27].

One important advantage of these materials as electro-catalysts compared to other carbon materials is that due to their method of preparation, they can be obtained directly as films or rods, the optimal and suitable shapes for the use as electrodes in a two-phase system. Alternatively, carbon gels can also be used for the manufacture of gas diffusion layers, to be used as electro-catalysts for the CO_2 reduction in three-phase catalytic systems: gas–liquid–solid.

In the present work we demonstrate the application of metal-doped carbon gels as promising electrodes and electro-catalysts in the electro-catalytic reduction of CO_2 to hydrocarbons.

2. Experimental

Ni, Cu and Fe doped carbon xerogels were prepared by dissolving resorcinol (R) and formaldehyde (F) in water and using the corresponding metal acetate as catalyst precursor (C). The stoichiometric R/F and R/C molar ratios were 0.20 and 13, respectively. The mixture was stirred to obtain homogeneous solutions that were cast into rectangular glass molds of 0.1 cm thickness, and cured for a certain period of time. The cure cycle included one day at room temperature, and five days at 80 °C to obtain the corresponding organic xerogel. Another xerogel, to be used as reference, was prepared in the same way but without adding any metal compounds. Finally, the organic xerogels were carbonized in a N_2 flow at a 900 °C during 5 h, and using a heating rate of 2 °C/min.

The total metal content of the sample was determined by burning off a portion of a xerogel at 800 °C in air and weighing the residue.

The characterization of the samples was carried out using gas adsorption, scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

The porous texture was analyzed by gas adsorption (N_2 and CO_2 at −196 and 0 °C, respectively). Prior to measuring the N_2 and CO_2 adsorption isotherms (Autosorb 1 Quantachrome), the samples were outgassed overnight at 110 °C under high vacuum (10^{-6} mbar). The BET equation was applied to the N_2 adsorption data from which the apparent surface area, S_{BET}, was obtained. The Dubinin–Radushkevich (DR) equation was applied to the CO_2 adsorption data in order to obtain the corresponding micropore volume (V_{mic}). Total pore volumes (V_{TOTAL}) are calculated from N_2 adsorption isotherms at −196 °C and at 0.995 relative pressure.

SEM was performed using a ZEISS DSM 950 (30 kV) scanning electron microscope, equipped with secondary electron detector, back-scatter electron detector, and using a Link Isis energy dispersive X-ray microanalysis system. All the samples were crushed before realizing this analysis.

HRTEM was carried out using a Phillips CM-20 electron microscope equipped with an EDAX microanalysis system. Magnification was up to 600,000×, with point resolution 0.27 nm and line resolution 0.14 nm.

XRD patterns were recorded with a Phillips PW1710 diffractometer using CuKα radiation. JCPDS files were searched to assign the different diffraction lines observed. Diffraction patterns were recorded between 10° and 70° (2θ) with a step of 0.02° and a time per step of 3 s. Only in the case of the Ni doped carbon xerogel the average crystal size could be determined using the Scherrer equation. For this calculation, the (200) line of Ni^0 has been used.