Photocatalytic Conversion of Bicarbonate into Formate by a CeO_2-SnO_2 Hybrid Synthesyzed via a Novel Greener Method

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Abstract

Emissions of CO_2 into the atmosphere due to fossil fuel burning are the main cause of global warming. Carbon dioxide emissions will have to be net-zero sometime between 2040 and 2060 in order to keep the global temperature rise in the 1.5-2.0°C range as stipulated by the Paris agreement of 2015. The development of technologies that assist in CO_2 capture and utilization (CCU) is therefore an important challenge in the current global scenario. In this work, we have synthesized and characterized a CeO_2-SnO_2 hybrid material via a novel, greener method, that showed photocatalytic activity in converting aqueous bicarbonate into formate. The catalyst was able to produce approximately 7, 14 and 16 mg of formate in 450 mL of a 0.1 M aqueous bicarbonate solution in respective UV-VIS irradiation times of 6, 24 and 48h. This corresponds to about 3, 6 and 7.5% conversion efficiency of inorganic carbon into organic carbon, respectively.

Keywords: CO_2 Reduction, Photocatalysis, Metal Oxide Hybrids

Introduction

The release of CO_2 into the atmosphere due to fossil fuel burning is the main cause of global warming (1). CO_2 emission will have to be net-zero sometime between 2040 and 2060 in order to keep the global temperature rise in the 1.5-2.0°C range as stipulated by the Paris agreement of 2015 (2). Thus, the development of technologies that assist in CO_2 capture and utilization (CCU) is an important challenge in the current global scenario.The use of aqueous alkaline sorbents (1)can convert CO_2 into HCO_3^- (Equation 1):

$$CO_{2(g)} + 2OH^-_{(aq)} \rightleftarrows HCO_3^-{}_{(aq)} + OH^-_{(aq)} \rightleftarrows CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \quad (1)$$

Carbon dioxide can be therefore reduced in the form of bicarbonate, an anion which is much more soluble in water than gaseous CO_2, in this way facilitating its reaction with heterogeneous catalysts suspended in aqueous solutions.In thiswork, we have synthesized (via a novel, greener method) and characterized a CeO_2-SnO_2 hybrid material that showed photocatalytic activity in converting aqueous bicarbonate into formate.

Experimental

Synthesis and Characterization of the Hybrid Catalyst

The catalyst was synthesized using $SnCl_2.2H_2O$ (99%, Synth, Brazil) and $Ce(NO_3)_3.6H_2O$ (99%, Dinâmica Química, Brazil) as metallic precursors. Precursors were weighed and mixed in a mortar with activated charcoal (Dinâmica Química, Brazil), then ground into a paste and subject to 30 min heating in a commercial microwave oven (Phillips, USA). The resulting solid was calcined in a muffle oven (Marconi, Brazil) at 650°C for 4h. The material was characterized via X-Ray Photoelectron Spectroscopy (XPS), X-ray diffraction (XRD), and UV-VIS diffuse reflectance spectroscopy (DRIFTS).

Photocatalysis Experiments

The irradiation experiments were carried out in a custom-made reactor with 450 mL of a 0.1 M bicarbonate:0.1%(m/m) catalyst solution/suspension. The exterior of the reactor is cooled in a thermostatized water bath (5°C). A commercial 400 W medium-pressure mercury vapor lamp, was employed as the radiation source. Radiation was filtered by a water filter kept at 2°C. Therefore, only UV and visible light could reach the catalytic system. Irradiation times of 6, 24 and 48 h were investigated. Blank and dark experiments were conducted as well in 6 and 48 h of reaction time. Formate was quantified by HPLC-UV under the following conditions: UV-VIS detector set at 250 nm, C18 column, isocratic elution (60:40 acetonitrile:water), column temperature = 30°C, 4 min runtime. Formate was quantified by the external standard method; standards were prepared in 0.1M sodium bicarbonate solution and 1mL of standard solution was neutralized with 0.5 mL of 15% HCl to eliminate bicarbonate interference prior to quantification. A calibration curve with and R-squared value of 0.99266 was obtained. Samples were subject to the same procedure prior to HPLC quantification of formate.

Results and Discussion

Characterization Results

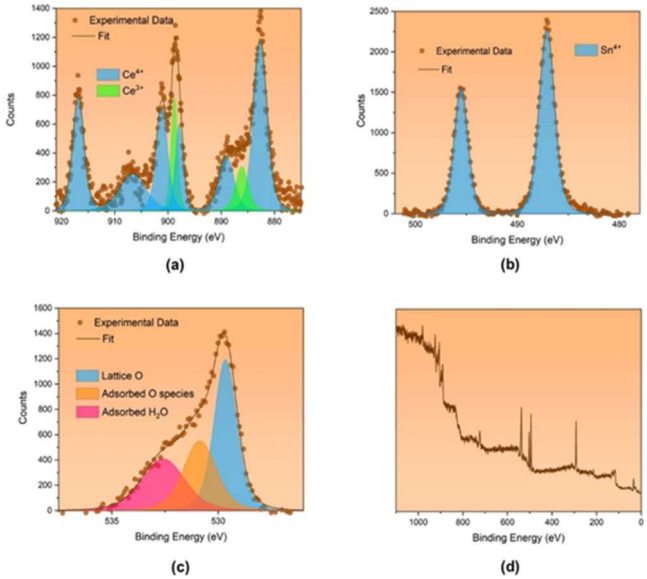

Figure 1.(a) Ce 3d XPS spectrum of the synthesized hybrid material; (b) Sn 3d XPS spectrum of the material; (c) O1s XPS spectrum of the material; (d) Survey XPS spectrum of the hybrid material.

The Ce 3d spectrum (Figure 1a) is qualitatively consistent with Ce (IV), showing also the presence of a few Ce(III) peaks. The presence of Sn is confirmed by its XPS spectrum (Figure 1b) with its characteristic spin-orbit splitting of 8.40 eV. Oxygen was detected as well in the XPS spectrum in the form of bound and adsorbed species. No other elements (except or adventitious C) were detected as the XPS survey spectrum shows (Figure 1d). The XRD diffractogram (not shown) confirms the presence of both CeO_2 and SnO_2 and suggests the successful formation of a SnO_2:CeO_2 hybrid (3). The Tauc plot of the DRFTS data shows the bandgap of the material to be 2.81 eV, which confirms it is a distinct material from its parent oxides whose bandgaps are 3.19 (CeO_2) and 3.60 eV (SnO_2).

Photocatalysis results

Table 1. Approximate absolute production of formate as a function of photocatalytic reaction time.

Reaction time (h)	**6**	**24**	**48**
$HCOO^-$ (mg)	7	14	16

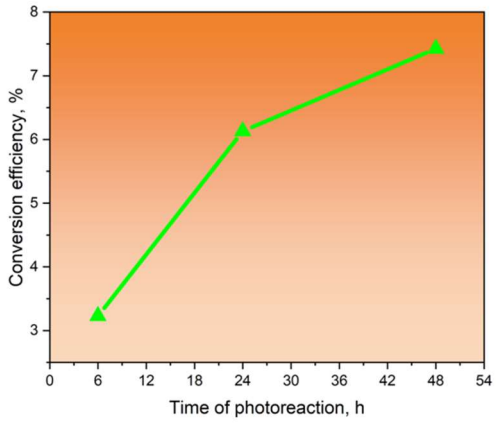

Figure 2. Bicarbonate conversion efficiency under UV-vis irradiation in the presence of the CeO_2-SnO_2 hybrid photocatalyst

Table 1 shows the approximate absolute production of formate as a function of photocatalytic reaction time. The catalyst was able to produce increasingly larger quantities of formate with increasing reaction times, showing that bicarbonate was indeed reduced into formate. Blank and dark experiments yielded no formate, which underscores the fact that photocatalytic activity can be attributed to the synthesized material. Conversion efficiency of inorganic into organic carbon was about 3% for 6h of irradiation time, increasing to about 6% in 24h of photoreaction and finally to about 7.5% in 48h of reaction. This suggests the optimal reaction time is 24h; further optimization experiments are needed, as well as further characterization of the catalyst.

Conclusions

A hybrid catalyst was synthesized via a novel greener route and characterized by a variety of methods. XPS and XRD confirm the identity of the material as a CeO_2-SnO_2 hybrid; DRIFTS confirms the material is distinct from its parent oxides. The material exhibited photocatalytic activity in converting aqueous HCO_3^- into formate, which shows it is a promising candidate for future CCU technologies. Further experimental optimization and characterization is needed, however, and is currently underway.

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References

1. V.-C. Nguyen, D. B. Nimbalkar, V. H. Huong, Y.-L. Lee, H. Teng. *J. Coll. Int. Sci.* 649 (2023) 918.
2. P. Gabrielli, M. Mazzani, M. Gazzotii.. *Ind. Eng. Chem. Res.* 59 (2020) 7033..
3. G. Manibalan, G. Murugadoss, R. Thangamuthu, M. R. Kumar, R. M. Kumar. *J. All. Compd.*, 792 (2019) 1150.