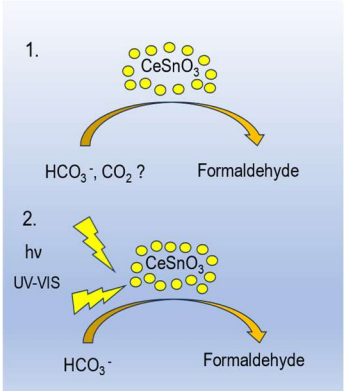
Catalytic and Photocatalytic Conversion of HCO_3^- Into Formaldehyde Intermediated by a Novel Catalyst of Empirical Formula $CeSnO_3$

POSTER
Ph.D. Student: Y
Journal: CEJ

L. Hansen[1], *M.A.R. Siqueira*[2], *D. Weibel*[1] *. (1) Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, Porto Alegre , Brazil, hansen.lcs@gmail.com (2) Universidade Feevale, RS-239 2755, Novo Hamburgo, Brazil.*



We herein describe the performance of a novel catalyst of empirical formula $CeSnO_3$ in converting aqueous bicarbonate into formaldehyde (HCHO). Two dark catalysis experiments were conducted at room temperature for six hours, where the catalyst was continously suspended in 0,1 M solution of $NaHCO_3^-$. Two photocatalytic experiments were then conducted for six hours in a custom made reactor in a bath kept at 5°C, and the reactor's water filter kept at 2°C (thus only UV and visible light could reach the catalyst). A blank experiment, where the catalyst was suspended for six hours in deionized water with no irradiation was lastly conducted Formaldehyde was quatified via HPLC-UV. In the dark catalysis experiments, an average of 15.5 mg of formaldehyde were produced after 6 hours of reaction. Photocatalytic production of HCHO averaged 4.5 mg, whereas in the blank experiment, 0.5 mg of HCHO were produced. More experiments are under way.

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 One technology that would be an ideal alternative to direct gaseous carbon dioxide capture, with all of its shortcomings, would be the use of aqueous alkaline sorbents [1], which would 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 containing captured CO_2 in the form of bicarbonate. In this sense, we describe the catalytic and photocatalytic production of formaldehyde (HCHO) from HCO_3^- by a novel catalyst of empirical formula $CeSnO_3$, whose characterization is presented in a previous work by the authors [3].

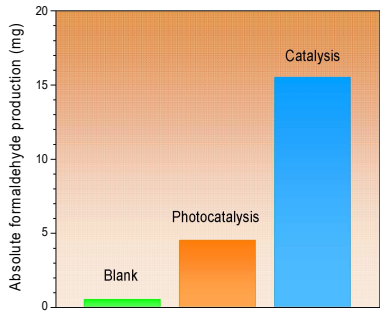
Materials and Methods

The catalytic and photocalytic HCHO production experiments were performed with a solution/suspension of 0.1 M $NaHCO_3^-$ (Êxodo Química)/0,1% $CeSnO_3$. The photocatalytic experiments were carried out in a custom made reactor. The reator is cooled in a thermostatized water bath (5°C). A commercial 400 W medium-pressure mercury vapor lamp, without its external bulb is used as a source of radiation. The radiation supplied by the lamp was filtered by a water filter, being the water supplied by an ultrathermostatized bath (Marconi, Brazil) kept at 2°C.Thus, only UV and visible light reached the photocatalyst. Agitation was provided by a magnetic stir bar placed inside the reactor. Four hundred-fifty mL of solution were loaded into the reactor for each experiment. The solution was irradiated for 6h after a 1h equilibration step. Two dark catalysis experiments were conducted at room temperature in 500 mL Erlenmeyer flasks under agitation for 6h. A blank experiment was also carried out with 500 mL of a 0.1% suspension of the catalyst. Formaldehyde was quantified in a Shimadzu LC-20 liquid chromatograph (Shimadzu Corp., Japan) using the external standard method (concentrations of 21.6, 43.2, 86.4, 260.4, and 868 mg L^{-1}). Standards were all prepared in 0.1M bicarbonate solutions. Samples and standards were subject to the same derivatization procedure, described as follows: ten milliliters of the sample were volumetrically transferred to a 25 mL volumetric flask. Ten milliliters of HPLC-grade acetonitrile (Sigma) were then added, followed by 1mL of a 1:4 H_3PO_4 (Sigma) solution. Two-hundred microliters of a 6 g/L DNPH (Inlab) solution were added for derivatizing HCHO. The remainder of the volume was completed by acetonitrile up to the 25 mL mark in each volumetric flask. Samples from the experiments were spiked with 2.17 mg of HCHO, as matrix effects were perceived to be hindering the analyte signal. Volumes smaller than 10 mL of stock solution were used in the preparation of standards. In this case, the

difference in volume was completed with 0.1 M sodium bicarbonate solution.Chromatographic conditions were the following: flow rate = 1.500 mL/min, column temperature = 30.0 °C, UV-VIS detector set at 360 nm, isocratic elution (60:40 acetonitrile:water).

Results and Discussion

Figure 1 shows the absolute production of formaldehyde (average of 2 experiments for the catalytic and photocatalytic productions) in mg in each of the experiments:



As shown in figure 1, the highest production of formaldehyde was in the dark catalysis experiments. Production of formaldehyde in the photocatalytic experiments was less than one-third of the production of HCHO in the catalytic experiments (4.5 versus 15.5 mg, repectively). The apparently smaller production of HCHO in the phototocatalytic experiments may be actually due to the photolysis of formaldehyde [4] as it is produced in the experiment under UV/visible irradiation. Experiments employing only visible light sources, such as LEDs, could help ascertain whether the photocatalytic production of formaldehyde is due to visible light, and its degradation due to UV light. Figure 1 also shows that the catalyst was able to produce a small amount of HCHO in the blank experiment. The production is probably due to the reduction of dissolved carbon dioxide in the deionized water. Further experiments, made under low temperature conditions and in the presence of pressurized CO_2, will be carried out in the future in order to check if HCHO production from CO_2 could be higher than the one observed here or not.

Table 1 shows the yield of the experiments regarding the conversion of aqueous bicarbonate into formaldehyde. Yield was calculated as a percentage of the amount in mg of carbon that was converted to formaldehye to the amount of carbon present in solution from aqueous bicarbonate:

Table 1. Yield of HCHO production experiments

Experiment	Yield%
Catalysis	1.03
Photocatalysis	0.30

Table 1 puts into perspective the absolute amounts of formaldehyde produced in each modality of experiment. One can notice that yields were very small (the quantity of bicarbonate in solution in each experiment was about 600 mg). This points to the need of additional optimization experiments, which will also be conducted in the future.

CIPOA 6TH BRAZIL
Iberoamerican Conference on Advanced Oxidation Technologies
October 07 to 11, 2024
OCEANIA CONVENTION CENTER - Florianópolis/SC

Figure captions

Figure 1. Production of HCHO (mg) in each experiment

Conclusions

A catalyst of empirical formula $CeSnO_3$ has shown catalytic and photocatlytic activity in converting aqueous bicarbonate into aqueous formaldehyde,as well possibly in converting dissolved carbon dioxide to HCHO. Further photocatalytic and optmization experiments are under way.

References

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