

Electrocatalytic Reduction of CO₂ on Co/Ni Nanoparticles (P-13H)

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1. Introduction

Currently, the electrochemical reduction of CO₂ is considered as an attractive way for obtaining fuels. The method could produce different compounds to be used directly as fuels such as methane (CH₄) and methanol (CH₃OH), or as raw materials for industrial uses such as formic acid (HCOOH) and formaldehyde (CH₂O) [1]. Great efforts have been devoted to the development of homogeneous and heterogeneous catalysts for this purpose. The main challenge so far is the design of catalysts with high selectivity, stability and efficiency at low potential. While, at the same time they are composed of cheap and abundant materials making the process economically feasible [2]. The electrocatalysts are typically composed of transition metals. For example, Cu and Cu based compounds produce hydrocarbon products, mainly methane, ethylene and ethanol, with economically useful efficiencies [3]. Co based compounds such as cobalt oxides and porphyrins have been seen to promote a selective electroreduction of CO₂ to CO with a faradaic efficiency of 75% [4]. Additionally, studies of Ni as a catalyst showed high efficiency to generate CO from CO₂, reaching a maximum efficiency of 97% [5]. In this work, we report the use of Co/Ni nanoparticles supported on mesoporous carbon (CM Co/Ni) and carbon nanotubes (NTC Co/Ni), as catalysts for the reduction of CO₂ in aqueous medium and the respective identification and quantification of the possible products.

2. Experimental

2.1 Nanoparticles Synthesis

Co/Ni nanoparticles were synthesized on mesoporous carbon and carbon nanotubes.

Co/Ni nanoparticles supported on carbon nanotubes were synthesized by using sodium dodecyl sulfate (SDS) as a stabilizer. NiCl₂ · 6H₂O and CoCl₂ · 6H₂O were used as precursor salts. The metal to carbon mass ratio was 20 % w/w while the Ni:Co:SDS ratio was 1:1:0.05 molar, respectively. The synthesis was carried out in basic medium, using hydrazine as reducing agent at 80°C. Finally, the product was washed and dried for 24 hours at 80°C.

Co/Ni nanoparticles supported on mesoporous carbon were obtained using NaBH₄ as reducing agent without ad-

justing the media pH. NaBH₄ was added in a molar ratio of 5:1 (NaBH₄ to metal salt) to a suspension of the carbon support containing NiSO₄ · 6H₂O and Co(NO₃)₂ · 6H₂O precursors at 0 °C. The reaction flask was stirred while the temperature was maintained at 0 °C for 6 hours. The powder obtained was washed with milli-Q water in a Soxhlet apparatus and dried in a vacuum oven at 80 °C for 24 h. The metal to mesoporous carbon ratio was also 20%.

The supported catalysts were characterized by powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDS). To determine the distribution and size of the nanoparticles.

2.2 Electrochemical characterization

Electrochemical measurements were performed using a 60-mL glass cell and a rotating disc-ring electrode. The electrode consisted on a carbon disk with an area of 0.196 cm² and a platinum ring of 0.110 cm². The reference electrode was Ag/AgCl (KCl sat.), while the counter electrode was a platinum wire 10 cm in length and 1 mm of diameter. A catalyst ink was prepared by weighing 5 mg of the catalyst, 15 mg of 5% PVDF dissolved in N-methylpyrrolidone (NMP) as adhesive and 30 mg NMP as solvent, uniformly mixed for 15 minutes in an ultrasonic bath. Subsequently, a 10 µL drop was deposited on the carbon disc and dried at 80 °C. The electrochemical characterization of the catalyst was carried out at 25 °C. Linear voltammetry was carried out between 0.4 to -1.3 V vs SHE with a sweep rate of 10 mV/s in 0.1 M KHCO₃ as electrolyte saturated with N₂ and CO₂. In order to determine and quantify the possible products of CO₂ reduction, ion chromatography (IC) was performed for liquid products, while the gaseous products were determined by RRDE.

Chronoamperometry was carried out for 900 seconds at discrete potentials between -0.8 to -1.3 V vs SHE with intervals of 0.1 V in a previously saturated solution with CO₂. Liquid samples were obtained for IC analysis. More volatile products were determined by RRDE experiments in the same set up with the electrode rotating at 900 rpm. The products generated on the disk can be detected by applying the corresponding oxidation potential in the ring electrode. While the disk was subjected to fixed potentials between -0.8 and 1.3 V vs SHE, cyclic voltammetries were carried out in the ring electrode between 0.0 and 1.0 V vs

SHE at 10 mV/s. After identification of the products, quantification was performed by a linear voltammetry between 0.2 and -1.3 V vs SHE at 10 mV/s on the disk while the ring was fixed at 0.6 V vs SHE at a rotation of 900 rpm. The relation of currents between the disk and the ring allows to obtain the faradaic conversion efficiency.

3. Results

Figure 1 shows the linear voltammetry obtained for Co/Ni nanoparticles supported on mesoporous carbon (fig 1a) and carbon nanotubes (fig 1b). The linear voltammetry in the presence of CO₂ shows a shift to higher potentials, indicative of a facile reduction process for both catalysts. Figure 2 presents the cyclic voltametries carried out on the ring at different disk potentials.

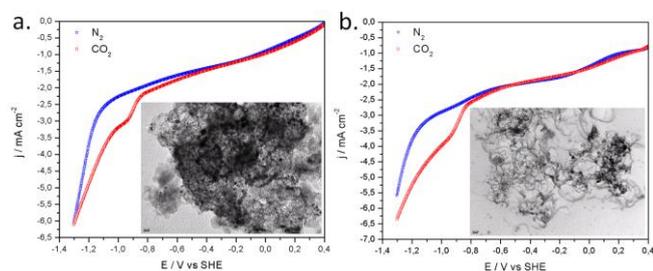


Fig. 1. Linear sweep voltammetry in 0.1 M KHCO₃ saturated with N₂ and CO₂ at a sweep rate of 10 mV/s. a) CM Co/Ni, b) NTC Co/Ni. Inset: TEM images of the corresponding material.

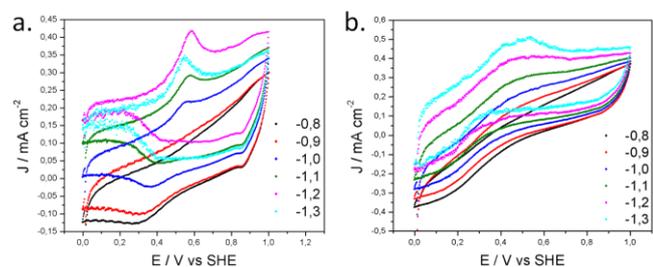


Fig. 2. Cyclic voltammety of the ring electrode between 0.0 V and 1.0 V vs SHE at 900 rpm and a sweeping rate of 10 mV/s at different disk electrode potentials. a) CM Co/Ni, b) NTC Co/Ni.

Figure 3 shows the disk and ring currents as a function of the disk sweep potential while the ring potential is fixed at 0.6 V vs SHE. The current ratio allows to calculate the faradaic conversion efficiency

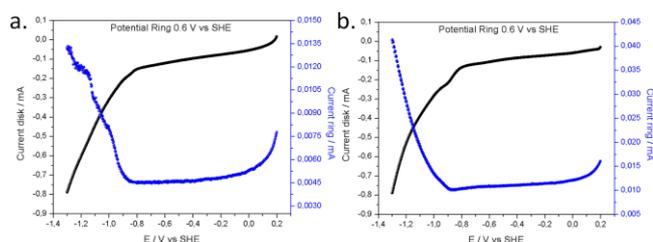


Fig. 3. RRDE LSV carried out at the disk electrode at 10 mV/s and 900 rpm between -0.2 V to -1.3 V vs SHE with the potential ring applied at 0.6 V vs SHE. a) CM Co/Ni, b) NTC Co/Ni.

4. Discussion

The TEM images inserted in figure 1 show the distribution and size of the nanoparticles. In the CM Co/Ni system can be see a homogeneous distribution of the nanoparticles on the support, with an average size of 4.4 nm and a circular morphology. In NTC Co/Ni carbon tubes of various thicknesses are observed, with particles of an average size of 10.7 nm, with elongated and circular shapes.

The curves in figure 1 show an increase in current density at potentials close to -0.9 V in both systems. Being 3.0 mA/cm² for CM Co/Ni and 3.5 mA/cm² for NTC Co/Ni when the solution is saturated with CO₂. This indicates the existence of additional reduction processes that do not occur in a solution rich in N₂, where the current density is 2.0 mA/cm² in CM Co/Ni and 2.7 mA/cm² in NTC Co/Ni. These is indicative on the ability of the catalysts to electrochemically reduce CO₂. To identify the products obtained at each potential, cyclic voltammetry on the ring electrode was performed while the disk potential remained fixed. The results are presented in Figure 2. For potentials of -0.8 V and -0.9 V vs SHE, no definite characteristics are observed in the voltammogram in neither of the two systems. As we increase the potential on the disk, we observe the appearance of a peak around 0.55 V vs SHE with an increasing peak current as the potential becomes more negative. The peak in both systems corresponds to the oxidation of CO, as reported in the literature [6]. This CO is the product of the CO₂ reduction process occurring on the disk.

After identifying the product resulting from the reduction of CO₂, we proceed to quantify and determine the faradaic conversion efficiency (*f*) by applying equation 1 [7].

$$f = \frac{i_R}{|i_D|N} \times 100 \quad (1)$$

Where *i_R* is the ring current, *i_D* the disk current and *N* is the collection efficiency of the rotating electrode. *N* depends on each system and was calculated independently for each catalyst. An *N*= 0.14 was obtained for CM Co/ Ni and *N*= 0.16 for NTC Co/Ni. Using equation 1, we found a maximum conversion efficiency to CO of 19% at -1.0 V vs SHE in the CM Co/Ni system and 34.5% at -1.25 V vs SHE in the NTC Co/Ni system. In addition, with the measurements made by IC, a maximum HCOOH percentage of 33% at -0.9 V vs SHE in CM Co/Ni and 39% at -1.1 V vs SHE in NTC Co/Ni was determined.

5. Conclusions

Electrochemical studies of catalysts based on Co/Ni nanoparticles supported on CM and NTC show catalytic activity towards the CO₂ reduction reaction. CO and HCOOH were generated in considerable amounts. The quantification of the soluble products by IC and the RRDE experiments indicate a maximum conversion efficiency to HCOOH of 33% and to CO of 19% in the CM Co/Ni catalyst, and in NTC Co/Ni 39% to HCOOH and 34.5% to CO.

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