Effect of transition metals in the hydrogen evolution electrocatalytic activity of molybdenum carbide

Ana M. Gómez–Marín[*], Edson A. Ticianelli

Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780, Fisico Quimica, Av. Trabalhador Sao Carlense, São Carlos, CEP 13560-970, SP, Brazil

A B S T R A C T

In this work, the effect of transition metals (TMs), such as Fe, Co, Ni and Cu, on the activity toward the hydrogen evolution reaction (HER) of modified molybdenum carbide (TM-Mo_2C) catalysts has been evaluated. Catalysts were prepared by a temperature programmed reduction method in both an inert and a reductive atmosphere, and characterized by different physicochemical techniques. A high activity toward the HER is measured for all TM-Mo_2C catalysts, with onset potentials lower than -0.06 V, as detected by on-line differential electrochemical mass spectrometry, and mass activities between 29 and 50 mA mg^{-1}, which suggest them as promising non-precious electrocatalysts for this reaction. However, a decrease in the HER activity upon metal doping is measured, following an activity trend of α-Mo_2C > Fe-Mo_2C > Co-Mo_2C > Ni-Mo_2C > Cu-Mo_2C. *In situ* near-edge X-ray adsorption analysis reveals a positive charge of the TM in the materials in the electrochemical environment, at the origin of the deleterious effect of Fe, Co, Ni and Cu, in terms of an electronic effect that modifies the d-electron configuration of α-Mo_2C particles. Additionally, results also suggest that TM-Mo_2C is more stable (lower catalyst dissolution) in acid media than α-Mo_2C. Finally, because there is a catalyst deactivation toward the HER after the α-Mo_2C component of the catalysts is oxidized at $E > 0.7$ V, the oxidation process of α-Mo_2C is employed for estimating, as a first approximation, the number of surface active sites for the HER.

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1. Introduction

The global demand for a renewable energy source in a sustainable way has turned the attention toward the electrochemical, or photo-electrochemical, production of hydrogen from water splitting [1,2]. In these processes, the hydrogen evolution reaction (HER), in which aqueous protons in an acid media are reduced to hydrogen by electrons passed through a catalyst is the central reaction. Unfortunately, this reaction is not efficient enough unless a proper catalyst is employed. At present time, platinum (Pt) is the most effective electrocatalyst for the HER [3] but, because it is expensive and scarce, substitute materials have to be developed in order to assure a sustainable hydrogen production.

In the search for new and cheap catalytic materials, Molybdenum-based compounds, such as molybdenum sulfides, MoS_2, and molybdenum carbides, Mo_2C, have been recently demonstrated to be promising candidates as active electrocatalysts

for the HER [1,4–15]. However, the catalytic activity of these compounds is still lower than of Pt-based materials and hence, their catalytic activity should be improved in order to be considered as appropriate electrocatalysts for practical applications.

The modification of the electronic and chemical properties of a given material can be effectively reached by the introduction of another element into its lattice, well because of the formation of heteroatom bonds (ligand effect) or owing to the alteration of the average atom–atom bond length (strain effect) [3,16–23]. Inside this approach, transition metal doping of MoS_2 materials with Fe, Co and Ni has demonstrated to improve HER activity of these materials [5,6], while no enhancement has been found when the dopant metal, M^D, was Mn, Cu or Zn metals [6].

In the case of Mo_2C catalysts, the effect of transition metal doping has not been deeply studied. Recently, it has been reported that Fe-doped Mo_2C in acid media is more active towards the HER than pure Mo_2C, while Ni-doped Mo_2C is less active [13]. In contrast, Ni-doped Mo_2C has been found more active than pure Mo_2C in alkaline media [24]. However, comparing the catalytic activity between different materials, from different synthesis procedures, is not an easy task [15]. In this sense, materials prepared by different methods could give rise even to different phases of the same com-

pound [25,26], which may guide to contradictory conclusions. In this work, the influence of transition metal (Fe, Co, Ni and Cu) doping in the HER activity of molybdenum carbides is studied. For this, α-Mo$_2$C and Fe, Co and Ni doped α-Mo$_2$C materials were prepared by similar temperature programmed carburization procedures and their catalytic activity toward the HER was evaluated under similar conditions.

2. Experimental

2.1. Preparation of transition metal-modified molybdenum carbides

Transition metal-modified molybdenum carbide catalysts, TM-Mo$_2$C, (TM: Fe, Co, Ni or Cu) were prepared by a carbothermal carburization process consisting in the temperature programmed reduction (TPR) of the different metals on a carbon black substrate (Vulcan XC-72, Cabot Corp., USA) [27–32]. Table 1 resumes the chemical nature and composition of the different employed carbide precursors: MoO$_3$ (99.5%) and Co$_3$O$_4$ (99.5% < 50 nm), Fe$_2$O$_3$ ($\geq$99% < 5 μm) or NiO (99.8% < 50 nm); ammonium molybdate ((NH$_4$)$_6$Mo$_7$O$_{24}$ $\times$ 4H$_2$O) and Fe(CH$_3$COO)$_2$ (95%), Co(CH$_3$COO)$_2$ $\times$ 4H$_2$O (99%) and Ni(CH$_3$COO)$_2$ $\times$ 4H$_2$O (99%), all from Sigma Aldrich [27,28]. In the case of Cu-Mo$_2$C, only copper nitrate was used as a precursor.

The synthesis procedure consists of three steps: i) Preparation of precursor powders by deposition of metal precursors on the carbon substrate to produce 1 to 1 molar ratio of molybdenum and the corresponding transition metal [33]. ii) Carbothermal reduction of catalyst precursor powders to form the transition metal-modified-Mo$_2$C; and iii) Passivation of the catalyst surface. The first step was carried out in an ultrasonic bath to form well-dispersed slurries, using isopropanol as solvent. Then, the isopropanol was completely evaporated and solid precursors were dried at 80 °C overnight.

In the second step, the precursor powder, $\sim$200–700 mg, was loaded into a quartz tube, stuffed with quartz wool at the bottom to hold the powders, and its temperature was continuously raised at 1 °C min^{-1} from room temperature (RT) to the final carburization temperature, T_{carb}, and held there for a fixed time, t_h. Carburizations were performed either in an inert (Ar) or a reductive atmosphere (10% H$_2$/Ar) by employing a Micromeritics 2900 AutoChem II Chemisorption Analyzer Micrometrics, equipped with a thermal conductivity detector (TCD). The progress of carburization of metal oxide precursors was monitored by the TCD signal, interrupting the reaction at different temperatures and analyzing the samples by X-ray diffraction. Preparation conditions for all samples are summarized in Table 2.

In some cases, for comparing the effects both Ar and H$_2$/Ar-atmospheres, samples were also pre-heated from RT to 550 °C at a heating rate of 20 °C min^{-1} and held there for 30 min in Ar-atmosphere. Then, the temperature was raised at 1 °C min^{-1} to T_{carb}, samples Mo/Ar2 and NiMo/Ar-2, Table 2. The pre-heating step was necessary in order to assure that the carburization in each atmosphere takes place at similar temperatures. However, under these preparation conditions FeMo/Ar-2 and CoMo/Ar-2 gave rise to mixtures of TM-Mo$_2$C and bimetallic carbides [33]. Also, when T_{carb} in a H$_2$/Ar-atmosphere is 1000 °C, as the experiences in an Ar-atmosphere, Mo metal is also identified among the crystalline phases in the final products, as reported before [31]. Therefore, these experiences were not included in Table 2.

When the carburization process finalized, the TM-Mo$_2$C powders were cooled down by quenching at RT and passivated for 1 h in a stream of 2 vol% O$_2$/He mixture, to prevent further rapid bulk oxidation when samples are exposed to air. Additionally, in order to evaluate the stability of metal-modified α-Mo$_2$C catalysts in acid media and remove any free metallic species in the products, some samples were treated in boiling 1 M HCl for 2 h (acid treated TM-Mo$_2$C catalysts). This acid treatment can be also considered as an accelerated degradation test, chosen instead of common lengthy-stability tests, which usually consist in galvanostatic or potentiostatic electrolysis for several days, and that frequently are not enough to determine measurable differences in the catalytic activity when comparing two different materials.

2.2. Catalyst characterization

The diffraction patterns of TM-Mo$_2$C catalysts were measured by X-ray diffraction (XRD, RIGAKU model RU200B) in the 2θ range from 20 to 80° and using CuKα radiation. Peaks were identified on the basis of the Joint Committee on Power Diffraction Standards (JCPDS) files and references [4,10,13,31]. In this sense, α-Mo$_2$C corresponds to the hexagonal structure of Mo$_2$C. The crystallite size of products was established from XRD data using the Debye-Scherrer equation, $D_c = 0.9\lambda/(\beta \cos\theta)$, where λ is the wavelength of the X-ray radiation ($\lambda = 1.541$ Å), β is the width of the peak at half-maximum and θ is the Bragg angle. The 2–3 major peaks were used in calculations, which for α-Mo$_2$C phase (JCPDS 35-0787) correspond to the {101}, {002} and {100} planes, yielding similar values of D_c [29,30,32].

Scanning electron microscopy (SEM) images were performed on a LEO, 440 SEM-EDX system (Leica-Zeiss, DSM-960) and on a FEG JEOL JSM 7500F. Approximate chemical compositions of as prepared samples were estimated by energy dispersive X-ray spectroscopy (EDX, Isis System Series 300) with a microanalyzer (Link analytical QX 2000) and a Si (Li) detector, using a 20 keV incident electron beam., and reported data are the average of, at least five measurements taken from different region of the samples. Transmission electron microscopy (TEM) images were performed on a JOEL 2100 transmission electron microscope at 200 kV.

The X-ray absorption spectroscopy (XAS) measurements were undertaken at the SXS beam line at the National Synchrotron Light Laboratory (LNLS), Brazil, at the XAS beam line (D08 B XAFS2) [34].

Table 1
Composition of carbide precursors for different TM-α-Mo$_2$C samples.

Catalysts	Mo Precursor	wt.% Mo Precursor	TM Precursor	wt.% Metal Precursor	wt.% Vulcan Carbon black
Mo/H$_2$	MoO$_3$	77.2	–	–	22.8
CoMo/H$_2$	MoO$_3$	51.4	Co$_3$O$_4$	28.7	19.9
NiMo/H$_2$	MoO$_3$	53.3	NiO	27.5	19.2
FeMo/H$_2$	MoO$_3$	51.0	Fe$_2$O$_3$	28.5	20.5
Mo/Ar	(NH$_4$)$_6$Mo$_7$O$_{24}$ $\times$ 4H$_2$O	65.0	–	–	35.0
CoMo/Ar	(NH$_4$)$_6$Mo$_7$O$_{24}$ $\times$ 4H$_2$O	28.6	Co(CH$_3$COO)$_2$ $\times$ 4H$_2$O	40.2	31.2
FeMo/Ar	(NH$_4$)$_6$Mo$_7$O$_{24}$ $\times$ 4H$_2$O	32.5	Fe(CH$_3$COO)$_2$	32.1	35.4
NiMo/Ar	(NH$_4$)$_6$Mo$_7$O$_{24}$ $\times$ 4H$_2$O	28.6	Ni(CH$_3$COO)$_2$ $\times$ 4H$_2$O	40.2	31.2
CuMo/Ar	(NH$_4$)$_6$Mo$_7$O$_{24}$ $\times$ 4H$_2$O	30.3	Cu(NO$_3$)$_2$	38.3	31.4
Mo/Ar-2	MoO$_3$	77.3	–	–	22.7
NiMo/Ar-2	MoO$_3$	53.3	NiO	27.5	19.2