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Analysis of the electrocatalytic activity of α-molybdenum carbide thin porous electrodes toward the hydrogen evolution reaction

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ABSTRACT

In the last years, transition metal carbides have appeared as novel materials with promising catalytic properties toward important practical reactions. In this work, the use of the thin porous electrodes for evaluating the hydrogen evolution reaction (HER) of hexagonal molybdenum carbides (α-Mo_2C)-based materials is analyzed and the effect of catalyst's load, L_{cat}, and catalyst's dispersion are discussed in terms of kinetic parameters calculated by employing the electrode geometric area. Catalysts were characterized by X-ray diffraction, energy dispersive X-ray analysis, X-ray photoelectron spectroscopy, cyclic voltammetry and differential electrochemical mass spectrometry. Results have shown that, even for the same catalyst, mass activities and specific activities depend on L_{cat}. and catalyst's dispersion. In contrast, intrinsic kinetic parameters, calculated from double layer capacitance normalizations, can be considered rather constant. XPS analysis of samples under different electrochemical treatments reveals a surface enrichment of carbon terminated planes after the HER, suggesting a higher HER activity on these planes. An investigation of the electrochemical oxidation of α-$Mo_2C$and the catalyst's HER activity show a direct correlation between active sites for HER and active sites for catalyst oxidation. Therefore, this oxidation is also used to estimate HER intrinsic parameters. Finally, the activity of a composite sample, in which α-Mo_2C is the only active component, is also evaluated.

1. Introduction

The worldwide necessity of a renewable energy source in a sustainable way has prompted the research toward the electrochemical, or photo-electrochemical, production of hydrogen [1,2]. In this process, hydrogen is produced as a final product of the electrolysis of water, which takes place onto a proper catalyst. Unfortunately, after decades of research on new materials, platinum (Pt) continues being the most effective electrocatalyst for this reaction at present time [3,4], and, because Pt is expensive and scarce, other catalytic materials must be developed before this technology can be suitable for commercial applications.

In this sense, several works have recently proposed molybdenum-based compounds, such as molybdenum sulfides, MoS_2, and molybdenum carbides, Mo_2C, as promising candidates to be active catalysts for the hydrogen evolution reaction (HER) in both acid and alkaline media [1,5–16].

However, the catalytic HER activity of molybdenum-based compounds is still not enough for substituting Pt-based materials and hence it should be improved. The most popular strategies for this goal involve either the fabrication of different nanostructures that may display a high density of the most active sites [14], or increasing the catalyst's surface area by dispersion of nanoparticles of the active material into electronic conductors, such as carbon-derived compounds [1,8,13,15,17,18]. Though, in this latter case, improvements on the HER catalytic activity have been also explained as a consequence of the better electron transport in carbon supported materials [1,8,13,15,17,18]. These approaches do not alter the electronic properties of the catalysts, but physically increase the number of active sites accessible for catalyzing per geometric area of the electrode and thus, enhance the apparent HER current density.

The modification of the electronic and chemical properties of any material can be effectively reached either 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) [4,19]. For example, it has been reported that transition metal doping of MoS_2 materials with Fe, Co and Ni may significantly improve HER activity of these

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materials, but not with Mn, Cu and Zn metals, specially under neutral conditions [4,10]. For Mo_2C catalysts, the effect of metal doping is not that clear. Xiong et al. have found Ni-doped Mo_2C more active than non-doped Mo_2C for the HER activity in alkaline media [20], although in acid media, recent results suggest that it is less active [11].

In any case, in the search of new and better catalytic materials, determining the intrinsic activity of different materials is a crucial step for establishing a clear path toward the improvement of the catalyst's performance. Only then, the effect on the catalytic activity of the different factors mentioned above, such as the structure, dispersion, and composition of the catalyst, can be unambiguously examined. However, one of the main drawbacks when comparing the catalytic activity of diverse materials, from different synthesis procedures, is to find accurate descriptors of their real catalytic activity. This is especially true for Mo_2C-based compounds, for which no experimental approach has been established to assess their intrinsic catalytic activity toward the HER. In contrast, for MoS_2-based compounds, their electrochemical oxidation at high potentials has been proposed for determining the surface concentration of MoS_2 atoms, allowing the calculation of the intrinsic catalytic activity of these materials [5,21].

For evaluating the HER activity, thin porous electrodes are commonly employed, in which catalysts are deposited onto a glassy carbon electrode and tested in an ordinary electrochemical cell [1,5,7–9,13–17,22–25], sometimes including significant ohmic drops. Then, from these polarization curves, catalytic activities are usually extracted in terms of Tafel slopes, current densities at a reference potential (E_r), $j_{E=Er}$, and exchange current densities, j_0, calculated by employing the electrode geometric area, or mass activities at E_r, $MA_{E=Er}$, for catalysts in which the amount of active material is not even reported. Under this approach, different values for the HER activity of Mo_2C-based materials have been reported, under diverse set of experimental parameters [1,5,7–9,13–17,22–24], but no intrinsic activities have been determined so far, which forbids to set any guidelines for the design of new, more active Mo_2C-based materials.

In this work, the HER activity of several α-Mo_2C-based materials is evaluated by using thin porous electrodes and the experimental methodology is carefully analyzed, in order to determine the effect of catalyst's dispersion and catalyst's load on kinetic parameters calculated by employing the electrode geometric area. Additionally, the electrochemical oxidation of α-Mo_2C at high potentials is also studied and later employed for estimating intrinsic kinetic parameters for the HER, which are compared to similar parameters computed from double layer capacitance measurements. Finally, intrinsic kinetic parameters for the HER activity of a composite sample, in which α-Mo_2C is the only active component, are also assessed. Here, it is important to note that, considering the different possible phases for molybdenum carbides [24,25] and the lack of an unique definition in the literature, α-Mo_2C corresponds to the hexagonal structure of Mo_2C, following the notation convention defined by the Joint Committee on Power Diffraction Standards (JCPDS) files and references [9,12,16,25,26].

2. Experimental

2.1. Preparation of Catalysts

All samples were prepared by a carbothermal carburization process of the metal oxide precursor, MoO_3 (Sigma Aldrich, 99.5%), by using a temperature programmed reduction (TPR) method [26–31]. The preparation conditions for all samples, including the starting materials, are summarized in Table 1. Briefly, the process consists of three steps. First, wet impregnation of MoO_3 on carbon black (Vulcan XC-72, Cabot Corp., USA) was carried out in an ultrasonic bath to form a well-dispersed slurry, using isopropanol as solvent. Then, the isopropanol was completely evaporated and the solid precursor was dried at 80 °C overnight.

Second, the catalyst precursor powder, ~200–700 mg, was pre-heated, in an inert atmosphere (Ar), from room temperature (RT) to 550 °C, at 20 °C min^{-1}, and held there for 30 min. Subsequently, the temperature of the sample was continuously raised at 1 °C min^{-1} until to the final carburization temperature, T_{carb}, and held there for a fixed time, t_h, Table 1. For the sample named F, the last heating rate was 3 °C min^{-1}, while the samples named B and G were not pre-heated, and the heating was from RT to T_{carb} at a heating rate of 1 °C min^{-1} in an 10% H_2/Ar atmosphere. TPR experiments were performed using a Micromeritics 2900 AutoChem II Chemisorption Analyzer Micrometrics equipped with a thermal conductivity detector (TCD). Finally, once the carburization process is finished, resulting catalysts were cooled down to RT and passivated for 90 min in a stream of 2 vol% O_2/He mixture.

2.2. Catalyst characterization

The diffraction patterns of all samples were measured by X-ray diffraction (XRD, RIGAKU model RU200B) in the 2θ range from 20 to 80° and using CuKα radiation. The crystallite size (Table 1) 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 (λ = 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_2C phase (JCPDS 35-0787) correspond to the {101}, {002} and {100} planes and for MoO_2 phase (JCPDS 32-0671) correspond to the {-111} and {-211} planes. In all cases, the major peaks yielded similar values of D_c [24–29].

Approximate chemical compositions of all samples, were estimated by energy dispersive X-ray spectroscopy (EDX, Isis System Series 300) in a scanning electron microscope LEO, 440 SEM-EDX system (Leica-Zeiss, DSM-960) with a microanalyzer (Link analytical QX 2000) and a Si (Li) detector, using a 20 keV incident electron beam.

Table 1
Composition of precursors, carburization conditions and main Mo-crystalline phases, identified by XRD, for different α-Mo_2C samples.

Catalysts	*wt.% MoO_3*	*wt.% Carbon black*	*Carburization gas*	*T_{carb} (°C)*	*Holding time, t_h (min)*	*Mo-Crystalline phases*	*Crystallite size (nm)* *
A	77.3	22.7	Ar	750	20	α-Mo_2C	35
B	77.2	22.8	10% H_2-Ar	725	30	α-Mo_2C	29
C	81.3	18.7	Ar	800	45	α-Mo_2C	40
D	81.3	18.7	Ar	900	30	α-Mo_2C	42
E	81.3	18.7	Ar	700	720	α-Mo_2C	41
F	81.3	18.7	Ar	700	0	MoO_2 and α-Mo_2C	42/35
G	77.2	22.8	10% H_2-Ar	625	30	MoO_2	39

* Calculated from XRD data.