Synthesis of nanocrystalline molybdenum carbide materials and their characterization

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ABSTRACT

A convenient and practical method for the preparation of precursors to form molybdenum carbide materials using solutions of ammonium heptamolybdate and sucrose is presented. Depending on the temperature-programmed reaction protocol employed [i.e., low temperature and long times (523 K for 24 h, 598 K for 24 h and 673 K for 72 h) or high temperature and short times (1073 K for 30 min)], the C/Mo ratio of the precursors (i.e., 6.3, 3.6, 2.0, 1.0 and 0.6) and the presence or not of H$_2$, it is possible to produce nanocrystalline molybdenum carbide materials with the cubic or hexagonal phases. The two prepared phases of molybdenum carbide showed activity for the hydrogenation of toluene at 423 K to selectively produce methyl-cyclohexane. In the tested conditions, the hexagonal molybdenum carbide phase showed an initial higher activity but the deactivation of the catalyst was more pronounced than in the cubic molybdenum carbide catalyst.

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1. Introduction

As it has been pointed out by several authors [1–4], the sustainability and feasibility of many present and future technologies will depend on the ability to develop novel materials that can be produced with the most abundant chemical elements on earth. The replacement of the current scarce and/or rare elements by more abundant ones to design and produce materials that can fulfill the needs of the developed or developing technologies is a must. Noble metals like palladium or platinum are well known for their catalytic properties in many types of reactions. By using the current fuel-cell technology, an impractically large amount of platinum would be needed per vehicle, thus, even if using all the mined platinum for fuel-cell vehicles alone, it only would support the production of a couple of millions of vehicles per year which is around 5% of the global worldwide production of automobiles [3]. Attempts to develop Pt-like materials based on nitrogen-doped graphene have been carried out for their use in fuel cells [5–8], however, their practical commercial application is still far away.

Transition metal carbides are another important group of very interesting materials which have been studied for several years. Levy and Boudart [9] demonstrated in their work, published in 1973, that tungsten carbides behaved similar to platinum for some types of reactions, and thus, a new era of research in these types of materials began. Transition metal carbides in bulk or supported form, as well as promoted or not, have been tested and shown to be active for several types of reactions that are usually catalyzed by noble metals [9–40]. This has led to think those materials as promising substitutes for the noble metals; however, the possible commercial applications of these materials as catalysts have been restricted by the lack of a complete control and understanding of the relationship between the structure and its physical chemical properties, as well as a practical and cost-effective way of commercially producing them.

The typical way of synthesizing transition metal carbides is known as temperature-programmed reaction (TPR). Under the TPR route, a given amount of the oxide precursor (for instance, MoO$_3$ or WO$_3$) is heated while it is exposed to a mixture of hydrogen and hydrocarbon. During this thermal treatment, the oxide is progressively reduced to lower-valence oxide states further undergoing carburization to yield the desired carbide. Typical preparations of molybdenum carbides under the TPR route require temperature step ramps to obtain the final product at high temperature, which is normally the stable and well-known hexagonal molybdenum carbide phase.

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The depletion of light crude oil sources and the increase in oil prices have made commercially viable the extraction of heavy oils and bitumen sources. However, these types of feedstocks are of lower quality with large quantities of sulfur, nitrogen and metal component, and thus, requiring the development of novel catalysts and processes that can deal with them. Molybdenum carbide seems to be a promising candidate for developing commercial catalysts to replace the more expensive and, easier to poison, conventional noble metal catalysts used in the upgrading of crude oils.

Aiming to develop a most practical and cost-effective way of producing molybdenum carbide materials, we tested a combination of our previously developed TPR ramp route [14,15] with a modification of the carbide precursor, prepared by the solution route with ammonium heptamolybdate and sucrose [41], to produce low-temperature molybdenum carbide materials [16]. It was demonstrated in this work that it is possible to obtain nanocrystalline cubic molybdenum carbide materials at 673 K under the developed synthesis conditions and these solids showed hydrogenation activity in a model molecule like toluene. Also, our synchrotron X-ray diffraction (XRD) work carried out in situ with different precursors indicated that MoO_2 seems to be an important intermediate for the production of molybdenum carbides at high temperature [42].

The goal of this study is to go deeper into the understanding of the preparation of molybdenum carbides using the developed synthesis protocol mentioned above to produce a most viable cost-efficient catalyst. This work presents the methods of preparation, the characterization of these materials and their activity for the hydrogenation of toluene.

2. Experimental methods

2.1. Preparation of Mo_2C precursors

Ammonium heptamolybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot4H_2O$] (AHM), analytical reagent from BDH, and commercially available household sucrose $C_{12}H_{22}O_{11}$ were used as starting reagents without further purification or modification. The methodology of preparation is described in our previous work [16]. Briefly, a sucrose solution prepared with deionized water was added to the AHM solution, also prepared with deionized water, under magnetic stirring and homogenized for 15 min at room temperature, before the solution mixture was placed in an oven at 393 K for 24 h until it was completely dried. Five precursors with C/Mo molar ratios of 6.3, 3.6, 2.0, 1.0 and 0.6 were prepared this way and identified as P1, P2, P3, P4 and P5, respectively. The dried cakes were then crushed into an agate mortar to obtain fine powders of the precursors for further use.

2.2. Carburization of the precursors with the protocol 523 K (24 h), 598 K (24 h) and 673 K (72 h)

The production of the cubic molybdenum carbide at 673 K (low temperature and long-time protocol) requires a ramp-up protocol which was developed and explained in our previous works [14–16] and described as follows: approximately 1 g of each pulverized precursor was thermally treated in situ in a steel fixed-bed reactor to form Mo_2C under a H_2 flow of 50 scm³ min⁻¹ at atmospheric pressure and with the following conditions of low-temperature and long-time protocol: first temperature ramp from room temperature up to 523 K and held there for 24 h, second ramp from 523 to 598 K and held for 24 h and third ramp from 598 to 673 K and held there for 72 h. The heating rate to reach each temperature in the protocol was 10 K min⁻¹. After the treatments, the solids were allowed to cool to room temperature under nitrogen at atmospheric

pressure and with a N_2 flow of 180 scm³ min⁻¹. The solids produced in this way are covered with a thin carbon film that protects them from pyrophoric oxidation when exposed to the air, and thus, no passivation protocol with diluted oxygen is needed. The % yield was calculated as $Y = PR \times 100/IP$, where PR is the amount of product recovered after carburization and IP is the amount of the initial used precursor.

In order to get insights into the importance of the employed ramp protocol to produce the desired carbides, two additional studies were conducted. In the first one, the ramp protocol was carried out without reaching the last temperature of 673 K, i.e., each 24 h, ramps at 523 and 598 K were applied and the produced solid was cool down to room temperature under nitrogen. In the second study, a direct heating at 10 K min⁻¹ from room temperature to 673 K without passing for the 523 and 598 K temperature ramps was carried out, maintaining this temperature for 72 h. The solid was cooled down to room temperature under nitrogen atmosphere.

2.3. Carburization of the precursors with the protocol 1073 K (30 min)

Approximately 1.5 g of each pulverized precursor was thermally treated in situ in a quartz U-type reactor to form Mo_2C under a helium flow of 15 scm³ min⁻¹ at atmospheric pressure and increasing the temperature at 10 K min⁻¹ from room temperature up to 1073 K and maintaining this temperature for 30 min, which is going to be called the high-temperature and short-time protocol. Finally, the solids were allowed to cool down to room temperature under the helium flow. The solids produced in this way are also covered with a thin carbon film that protects them from pyrophoric oxidation when exposed to the air, and thus, no passivation protocol with diluted oxygen was needed in these cases. The % yield was calculated as $Y = PR \times 100/IP$, where PR is the amount of product recovered after carburization and IP is the amount of the initial used precursor.

2.4. Characterization of the prepared materials

2.4.1. X-ray powder diffraction

The X-ray analysis of the prepared materials was performed using a Rigaku ULTIMA III X-ray diffractometer with Cu Kα radiation as the X-ray source. The scan was done in the range of 10–90° 2θ degrees using a 0.02° step and a counting time of 0.8° per min to obtain the diffractogram for each prepared material. The domain crystal sizes were measured using the Scherrer equation, as implemented in the commercial software JADE [43] (provided with the diffractometer) by fitting the experimental profile to a pseudo-Voigt profile function, and then calculating the full-width at half-maximum (FWHM) of the peaks.

The simulated X-ray powder diffraction pattern of the MoO_2 structure was calculated with the program POWDER CELL v 2.4 [44] using the obtained experimental data for the MoO_2 material reported for the monoclinic structure [45] and by simulating the same conditions employed to obtain the experimental XRD patterns with an FWHM of 10° to account for very small crystalline domains of MoO_2 of about 1 nm.

2.4.2. Textural properties

The nitrogen adsorption–desorption measurements of the samples were performed at 77 K on a Micromeritics Tristar 3000 analyzer, utilizing Brunauer–Emmett–Teller (BET) calculations for surface area. 0.5 g of each sample was used for the analysis, and they were pretreated on a stream of helium at 423 K overnight before the measurements.