Journal of Catalysis 332 (2015) 83–94

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Formation of β-Mo_2C below 600 °C using MoO_2 nanoparticles as precursor

Héctor J. Guzmán [a,*], Wenqian Xu [b], Dario Stacchiola [b], Gerardo Vitale [a], Carlos E. Scott [c], José A. Rodríguez [b], Pedro Pereira-Almao [c]

[a] *Chemistry Department, University of Calgary, Calgary, AB T2N 1N4, Canada*
[b] *Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA*
[c] *Schulich School of Engineering, University of Calgary, Calgary, AB T2N 1N4, Canada*

ARTICLE INFO

Article history:
Received 8 April 2015
Revised 19 September 2015
Accepted 23 September 2015
Available online 23 October 2015

Keywords:
Molybdenum carbide
Molybdenum dioxide
In-situ XRD
Carburization
Nanoparticles
Synchrotron
Methane
Ethylene glycol

ABSTRACT

In this work MoO_2 nanoparticles were prepared using ethylene glycol as a reducing agent and their transformation into the desired phase β-Mo_2C (hexagonal) was followed by *in-situ* X-ray diffraction with synchrotron radiation. CH_4/H_2 was employed as carburizing mixture and two different concentrations were tested, 10 and 20% v/v. TEM images obtained indicated that the particle size of the oxide precursor was about 4 nm while the XRD patterns showed that an amorphous phase precipitated along with the crystalline phase. This amorphous phase seemed to decrease the onset temperature of carburization and its transformation started before the crystalline MoO_2. On the other hand, an effect from the orientation of the (011), (−211) and (022) faces of the MoO_2 precursor toward a less energy demanding transformation might be occurring as well. The carburization process of the amorphous phase/MoO_2 nanoparticles started at about 560 °C, while in contrast for a commercial MoO_2 such process began at the temperature commonly reported in the literature (~670 °C). The hexagonal, thermodynamically stable phase of the Mo_2C was the main carburization product and no other intermediate phases were detected by XRD. The gas stream of the reaction was analyzed by mass spectrometry indicating the formation of CO and H_2O as by-products of the formation of the carbide.

1. Introduction

Noble metals such as platinum and palladium have been used as catalysts for reforming, isomerization and hydrogenation of crude oil feedstocks and hydrocarbons since the late 40s [1]; despite being the best suitable catalysts currently in use, the population growth and the expanding energy market have caused an increase on the demand of these precious metals up to a point where the market of palladium, for example, cannot close the gap [2]. In order to meet the upcoming energy requirements, efforts in research and development are pointing toward the design of new materials that can potentially substitute noble metals in many of the processes mentioned before. The scope is to use the most abundant elements present in Earth's crust instead of the less abundant and more expensive ones. Iron, silicon, aluminum, boron, etc., are being researched as new materials for a variety of catalysts [3]. On the other hand, molybdenum, which naturally occurs as molybdenite (MoS_2) and in association with copper ores, has been increasingly synthesized as carbide since the famous findings of Levy and Boudart regarding the platinum like behavior of WC [4].

Molybdenum carbide (Mo_2C) has a list of desired properties that makes it very attractive from an industrial standpoint: hydrogenation capabilities, nitrogen and sulfur [5,6] resistance, inexpensive synthesis precursors, nanoparticles formation, etc. The main drawbacks with this phase are the usual high temperatures of synthesis and the extremely complicated chemistry behind it, which makes it difficult to reproduce and control with the desired particle size and surface area.

The main objective of this work was to have a clear understanding of the carbide chemistry and under which conditions the temperature of synthesis can be decreased. In a previous work [7] it was determined that MoO_2 was the common intermediate phase that is transformed into Mo_2C, regardless of the starting material or carburizing mixture. Enough data have been consistently produced in the past years that suggest that Mo_2C can be formed at temperatures lower than 600 °C. In this work MoO_2 nanoparticles were carburized with a mixture of CH_4/H_2 and their crystallographic evolution was followed *in-situ* with synchrotron radiation. The results obtained indicate that a smaller particle size

---

[*] Corresponding author.
E-mail address: hguzman64@gmail.com (H.J. Guzmán).

http://dx.doi.org/10.1016/j.jcat.2015.09.013
0021-9517/

and amorphous nature of the precursor lead to a lower carburization temperature. The best results were found for MoO_2 nanoparticles of about 4 nm which carburized at 560 °C in comparison with the 670 °C required by commercial MoO_2.

2. Experimental methodology

Ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) (99.98%, STREM Chemicals), MoO_2 (99%, Sigma–Aldrich) and ethylene glycol (anhydrous, 99.8%, Sigma–Aldrich) were used as reagents without further purification.

For the synthesis of MoO_2 nanoparticles ethylene glycol (EG) [8] was used as reducing agent. On a typical preparation 0.36 g of AHM and 11.13 g of ethylene glycol were dissolved in 30 mL of water, transferred to an autoclave and maintained at 180 °C for 24 h. The resultant viscous black suspension was centrifuged and the precipitated solid was washed several times with water to remove the remaining organic material. For comparison purposes, commercial MoO_2 was also employed as metal precursor during the *in-situ* carburization experiments.

The *in-situ* time resolved X-ray diffraction (XRD) patterns were recorded at the beam line X7B in the National Synchrotron Light Source at Brookhaven National Laboratory (New York, USA). The wavelength of the radiation employed was 0.3196 Å.

The solids were analyzed in 3 different atmospheres: He and CH_4/H_2 (10 and 20% v/v) with a flow rate of 10 mL/min. The conditions used are listed below:

- He: 5 °C/min from 25 °C to 750 °C (ΔT between each XRD pattern = 14.6 °C).
- CH_4/H_2: 10 °C/min to 300 °C (ΔT between each XRD pattern = 14.6 °C); 5 °C/min to 750 °C (ΔT between each XRD pattern = 7.3 °C).

A temperature programmed experiment with isothermal stages using 10% v/v CH_4/H_2 was also performed with the following conditions:

- 10 °C/min from room temperature to 300 °C.
- 5 °C/min from 300 °C to 400 °C, isothermal for 4 h.
- 5 °C/min from 400 °C to 500 °C, isothermal for 4 h.

The setup employed for the experiments has been described elsewhere [7]. The gas stream was analyzed by mass spectrometry, using electron impact, with a residual gas analyzer model SRS RGA 200. The monitored molecules were CO, C_2H_4, CO_2, H_2, H_2O, CH_4, CH_2O, and CH_3OH and the (m/z) signals used taking into account interferences were the following: $N_2/CO/C_2H_4$ (28), CO_2 (44), H_2 (2), C_2H_3 (27), H_2O (18), CH_3 (15), CHO/C_2H_5 (29), and CH_3O (31). Calibration of the mass spectrometer was performed using standards of the gases of interest (CO, C_2H_4, CO_2, H_2, CH_4) diluted in He, with concentrations of 0, 1, 5 and 10% v/v.

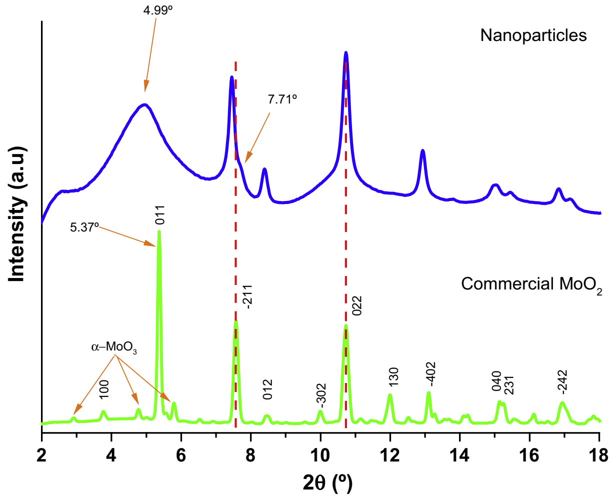

Fig. 1. XRD patterns for the MoO_2 obtained using EG as reducing agent and for the commercial MoO_2.

Crystalline domain sizes were calculated using Scherrer's equation using an instrumental broadening with FWHM = 0.084° and the MoO_2 PDF file #01-073-1249. The instrumental broadening was determined using the XRD pattern of LaB_6 as standard.

STEM images of the prepared samples were collected in a Hitachi HD2700C Scanning Transmission Electron Microscope with a High-Angle Annular Dark Field detector. The accelerating voltages employed were of 80–200 kV. The chamber pressure was around 10^{-7} Pa. Silicon nitride (Si_3N_4) was used to disperse the samples prior to analysis. EDX spectra were acquired with a Bruker SDD EDX detector.

3. Results and discussion

The synthesis of the MoO_2 using EG produced the desired material as can be seen in Fig. 1. The XRD pattern acquired for this solid showed that the most intense peak for the monoclinic MoO_2 phase (011) became extremely broad suggesting the presence of small crystalline domains and its maximum shifted toward lower angles by 0.38° (2θ). A similar result was found by Kim et al. when they used a mixture 1:1 water/ethanol to synthesize MoO_2 [9] and also by Chen et al. [8] when they used a mixture 1:1 water/ethylene glycol for a similar synthesis. On the other hand, it is possible that an amorphous phase was present along with the crystalline structure (as suggested by the peaks at 4.99° and 7.71°) and most probably was MoO_2 that did not crystallize well enough as to produce a diffraction pattern.

The rest of the peaks for the MoO_2 phase showed broadening as well. The XRD pattern for the commercial MoO_2 used in the *in-situ* experiments was plotted for comparison purposes. It can be appreciated that the peak at 7.57° was slightly shifted as well by 0.12°.

Fig. 2 shows STEM images acquired for the MoO_2 nanoparticles. It can be noticed in Fig. 2a and e that the nanoparticles were agglomerates of smaller spheres with sizes around 4 nm. The composition maps showed that these agglomerates were enriched in Mo and O, with no carbon present. Fig. 3 shows drawings of 4 and 10 nm nanoparticles of MoO_2 indicating the difference in surface topology.

3.1. In-situ experiments

3.1.1. Treatment under helium

The MoO_2 nanoparticles were treated under He and the *in-situ* XRD patterns were recorded as can be seen in Fig. 4. The results indicated that the nanoparticles were crystallized at about 582 °C into monoclinic MoO_2 and the peak that was originally at 4.99° in the nanoparticulated material was positioned at 5.33° after the thermal treatment, corresponding to the position usually reported for this phase (Fig. 5); moreover, the rest of the peaks with broad shapes became narrower and sharper after the treatment indicating further crystallization of the already existing material (inset in Fig. 5). It can be also said that if the initial sample was a mixture of MoO_2 + amorphous phase, the amorphous phase was converted into MoO_2. Interestingly enough the peak at 4.99° and the broad shoulder at 7.71° disappeared during this process indicating that they were possibly associated with the amorphous phase.

582 °C is below the so-called Tammann temperature [11] of the MoO_2 (627 °C) and probably the sintering and growth of the particles started earlier but since each XRD pattern was acquired with