Formation of β -Mo₂C below 600 °C using MoO₂ nanoparticles as precursor

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Abstract

In this work MoO₂ nanoparticles were prepared using ethylene glycol as a reducing agent and their transformation into the desired phase β -Mo₂C (hexagonal) was followed by *in-situ* X-ray Diffraction with synchrotron radiation. CH₄/H₂ 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 MoO₂. On the other hand, an effect from the orientation of the (011), (-211) and (022) faces of the MoO₂ precursor toward a less energy demanding transformation might be occurring as well. The carburization process of the amorphous phase/MoO₂ nanoparticles started at about 560 °C, while in contrast for a commercial MoO₂ such process began at the temperature commonly reported in the literature (~670 °C). The hexagonal, thermodynamically stable phase of the Mo₂C 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 H₂O as by-products of the formation of the carbide.

1.- Introduction

Noble metals like platinum and palladium have been used as catalysts for reforming, isomerization and hydrogenation of crude oil feedstocks and hydrocarbons since the late 40's¹; although, despite being the best suitable catalysts currently in use, the population growth and the expanding energy market has caused an increase on the demand of these precious metals up to a point where the market of palladium, for example, cannot close the gap². 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 catalysts³. 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 behaviour 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 is to have a clear understanding of the carbide chemistry and under which conditions the temperature of synthesis can be decreased. In a previous work⁷ 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 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 to the 670 °C required by commercial MoO_2 .

2.- Experimental methodology

Ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) (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 patterns (XRDs) 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 CH₄/H₂ (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).
- CH₄/H₂: 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 CH₄/H₂ 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 elsewhere⁷. 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, C₂H₄, CO₂, H₂, H₂O, CH₄, CH₂O, CH₃OH and the (m/z) signals used taking into account interferences were the following: N₂/CO/C₂H₄ (28), CO₂ (44), H₂ (2), C₂H₃ (27), H₂O (18), CH₃ (15), CHO/C₂H₅ (29), CH₃O (31). Calibration of the mass spectrometer was performed using standards of the gases of interest (CO, C₂H₄, CO₂, H₂, CH₄) diluted in He, with concentrations of 0, 1, 5 and 10 % v/v.

Crystalline domain sizes were calculated using Scherrer's equation using an instrumental broadening with FWHM = 0.084° and the MoO₂ PDF file #01-073-1249. The instrumental broadening was determined using the XRD pattern of LaB₆ 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 (Si₃N₄) 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 MoO₂ 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 MoO₂ phase (011) became extremely broad suggesting the presence of small crystalline domains and its maximum shifted toward lower angles by 0.38° (2 θ). A similar result was found by Kim et al. when they used a mixture 1:1 water ethanol to synthesize MoO₂⁹ 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. 1: XRD patterns for the MoO_2 obtained using EG as reducing agent and for the commercial MoO_2 .

Fig. 2 shows STEM images acquired for the MoO_2 nanoparticles. It can be noticed in Figs. **2a** and **2e** 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.

Fig. 2: STEM images of the MoO_2 nanoparticles. (a) Agglomerate of particles; (b), (c) and (d) Composition maps of (a); (e) agglomerate of particles.

Fig. 3: CPK representation of spherical nanoparticles of MoO₂: (a) 4 nm nanoparticle and (b) 10 nm nanoparticle. Red atoms represent oxygen type O(1), yellow atoms represent oxygen type O(2) (according to the nomenclature of reference 13) and blue atoms represent molybdenum. Drawings carried out with Materials Studio V7.0¹⁰

3.1- in-situ experiments

3.1.1 Treatment under Helium

The MoO₂ 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 crystallized at about 582 °C into monoclinic MoO₂ 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 crystallization of the already existing material (inset in Fig. 5). It can be also said that if the initial sample was a mixture of MoO₂ + amorphous phase, the amorphous phase was converted into MoO₂. 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 of the so called Tamman temperature¹¹ of the MoO₂ (627 °C) and probably the sintering and growth of the particles started earlier but since each XRD pattern was acquired with 14.6 °C of difference the exact temperature cannot be determined. It has been assumed that the driving force for sintering is the greater mobility of the surface atoms (surface free energy) present in the material¹². In this case the behaviour observed goes in agreement with the principle that the surface energy of nanoparticles is higher than in bulk materials; therefore a lower temperature for the mobility of surface atoms is required, which can be extrapolated to a higher reactivity and the explanation for the reduction in the carburization temperature seen in this work.

Fig. 4: XRD patterns acquired during the thermal treatment of the MoO₂ nanoparticles in He ($\Delta T = 14.6$ °C).

Fig. 5: XRD patterns of MoO₂ nanoparticles before, during and after thermal treatment in He.

3.1.2.- Treatment under 10 % CH₄/H₂

When the MoO₂ nanoparticles were treated with the carburizing mixture, the carbide began to appear at about 557 °C (+/- 7.3 °C). As can be noticed in Fig. 6, at that temperature, broadening in 2 areas of the MoO₂ pattern indicated the growth of the new phase, which eventually crystallized completely at 615 °C. From 615 °C and until the finalization of the thermal treatment, the β-Mo₂C just became slightly more crystalline since the width of the peaks was still noticeable, suggesting the presence of extremely small domains.

Fig. 6: XRD patterns of MoO₂ nanoparticles carburized under 10 % CH₄/H₂.

On the other hand, when the same treatment was performed with commercial MoO₂ (Fig. 7) the β -Mo₂C began to appear at around 674 °C, which coincided with the results obtained in a previous work⁷. In this case, the α -MoO₃ present as an impurity disappeared at about 483 °C, while the MoO₂ was completely transformed into the carbide at 750 °C.

Fig. 7: XRD patterns of commercial MoO_2 carburized under 10 % CH_4/H_2 .

STEM images for the solid obtained after thermal treatment of the MoO_2 nanoparticles were acquired and are shown in Fig. 8. It can be observed that the sample was composed of agglomerates of around $2\text{ }\mu\text{m}$ in size (Fig. 8b) with smaller particles below the 10 nm range (Figs. 8a). EDX in the area shown in Fig. 8d gave as a result that the particles had a certain amount of carbon, as opposed to the results obtained for the original solid (Fig. 2). The presence of oxygen came from exposure of the solid to air during sample manipulation.

Fig. 8: STEM images of the MoO_2 nanoparticles after thermal treatment in 10 % CH_4/H_2 . (a) and (b) agglomerates of particles; (c) magnification of the area marked in (b) with the respective composition maps (d, e, f).

3.1.3.- Temperature programmed experiment (TPR) with isothermal stages

The results for the temperature programmed experiment with isothermal stages are shown in Fig. 9.

Fig. 9: XRD patterns of the isothermal experiment in every stage compared to the ramp up experiment.

These results indicate that no detectable carburization occurred below 400 °C; only crystallization of the MoO₂ phase happened during this stage. After reaching 500 °C and 4 h of reaction a slight broadening in the MoO₂ pattern could be recorded indicating the modification of the MoO₂ by detectable small crystalline domains of Mo₂C (black circles in Fig. 9). The pattern of the ramp up experiment at 571 °C (Fig. 6) was plotted for comparison purposes. It is clear that broadening was occurring for the solid after 4 h of reaction, suggesting that the carbide was beginning to crystallize, requiring only a longer period of time for reaction completion. On the other hand, it is interesting to point out the fact that the peak for the plane (011) (5.33°) never grew as it did during the thermal treatment with He, probably because the amorphous phase was the one initially being carburized.

3.1.4.- Treatment under 20 % CH₄/H₂

In this case, when the MoO₂ nanoparticles were submitted to thermal treatment under 20 % CH₄/H₂ a carburization temperature similar to that of a commercial MoO₂ was obtained. Fig. 10 shows the *in-situ* XRD patterns for this experiment. The first appearance of the Mo₂C phase was detected at 644 °C while the MoO₂ was completely transformed at 703 °C. The final phase is plotted along with the PDF file of the Mo₂C indicating that only nano-domains of the hexagonal phase crystallized under these conditions (Fig. 11).

Fig. 10: XRD patterns of MoO₂ nanoparticles carburized under 20 % CH₄/H₂.

Fig. 11: XRD pattern of the phase obtained during the carburization of MoO₂ nanoparticles under 20 % CH₄/H₂.

The fact that the carburization did not occur at low temperatures, as previously seen, seems to be caused by a difference in the planes (011), (-211) and (022) of the nano-MoO₂. Fig. 12 shows the side and top views of the atoms exposed in the planes (011), (-211) and (022) of the MoO₂ material. As can be seen, those planes contain oxygen atoms that need to be removed and replaced by carbon in order to form the carbide material. In a previous work¹³, it was found that by comparison of total energies of the systems (when only one oxygen atom is replaced by carbon in the crystal structure of MoO₂) the structures with one O(1)-type oxygen center substituted by carbon are the most stable. Substitution of any of the O(2)-type centers by carbon requires an additional 47 kJ mol⁻¹. According to that result, it seems that O(1)-type oxygen atoms are more favored for the carbon replacement, and thus, if the original O(2)-type atoms are the ones exposed they would require more energy for the transformation to take place or they may be ending up as part of the produced carbide (oxycarbide).

Fig. 12: Ball and stick representation of the atoms exposed on the selected surfaces of MoO_2 : (a) side and top view of plane (011), (b) side and top view of plane (-211), and (c) side and top view of plane (022). Red atoms represent oxygen type O(1), yellow atoms represent oxygen type O(2) (according to the nomenclature of reference 13) and blue atoms represent molybdenum. Drawings carried out with Materials Studio V7.0¹⁰

In Fig. 13 all the initial XRD patterns of the MoO_2 nanoparticles acquired for each experiment performed were plotted along with a record of the days after synthesis. Two main observations can be made; the first one indicates that all the signals are the same except the ones obtained at day 12; the second one, if assuming the presence of an amorphous phase, indicates that less of this phase was present for the last experiment and it probably was converted into MoO_2 since all the signals at higher angles were sharper; which is a direct indication of a larger crystalline domain.

According to the XRD patterns of Fig. 13, the planes (011), (-211) and (022) were the ones that changed the most. From the drawings showed in Fig. 3, if more of these planes are presented in the bulk and not at the surface the carburization might not occur as easy as expected, probably because the diffusion of the carbon atoms into the deeper layers of the structure is hindered once the carburization of the surface layers have been completed or because of the removal of the

oxygen atoms becomes more energy demanding as previously discussed. This observation suggests that those particular planes have an enormous influence during the carburization.

The intensity ratio of the peaks corresponding to the planes -211 (7.45°) and 022 (10.73°) was determined to illustrate the fact that the initial phase of the MoO_2 was always the same for each experiment excepting the MoO_2 that had a ratio -211/022 of 1.10 as can be noticed in Fig.13.

Fig. 13: Initial XRD patterns of the MoO_2 nanoparticles for each one of the experiments performed.

Interestingly enough, the crystalline domains sizes calculated for these samples using Scherrer's equation showed not significant variations among them (Table 1), suggesting that the presence of an amorphous phase might be also responsible for the transformation to Mo_2C at low temperature.

Table 1: Scherrer's calculations

Sample	Diffraction line (2 θ) (-211)	Crystalline domain size (nm) +/- 2
He	7.459	17
10 % CH ₄ /H ₂	7.454	14
10 % CH ₄ /H ₂ (isothermal stages)	7.474	15
20 % CH ₄ /H ₂	7.527	14

In order to explain the influence of those particular faces in the carburization temperature 4 assumptions can be made:

- It is well known that oxygen mobility is possible in MoO₂ as described by the Mars-van Krevelen mechanism for hydrocarbon reforming^{14,15}; therefore, since oxygen has to be replaced by carbon, oxygen mobility is compromised in these particular stacked planes (as previously discussed).
- It is not the oxygen mobility that is compromised but the ability for H₂ to be absorbed/dissociated on those planes and carry out the reduction of the metal oxide.
- Neither the oxygen mobility nor the H₂ adsorption has been undermined but the CH₄ adsorption or C-H bond activation in order to carburize the structure.
- The dissociation of CH₄ might not be the problem but the diffusion of the carbon atoms into the deeper layers of the structure might be hindered, difficulting the overall process.

For the third assumption, it has been reported that the use of hydrocarbons such as propane, butane, acetylene, which are easier to activate, yield MoC_{1-x} and Mo₂C at a lower temperatures than that of CH₄. As an example, Xiao et al.¹⁶ obtained MoC_{1-x} at 550 °C with a mixture 5 % C₄H₁₀/H₂ after 1 h of reaction, but in their case they used commercial MoO₃; which might explain why 1 h was required for the carbide formation.

3.2.- Mass spectrometry

3.2.1.- Treatment under 10 % CH₄/H₂ (MoO₂ nanoparticles)

The mass spectrometry results for the thermal treatment of the MoO₂ nanoparticles in He did not show any appreciable formation of gases during the crystallization of the solid, as expected. On

the other hand, when the carburization was carried out with 10 % CH_4/H_2 , CO_2 began evolving from the solid at around 190 °C and until the temperature was around 430 °C (Fig. 13). The maximum was around 320 °C, which probably indicates that a reduction was taking place since the surface was most likely oxidized ($\alpha\text{-MoO}_3$) as it has been reported elsewhere^{7,17}; although in this case the reduction occurred at much lower temperature. The CO_2 evolution could have been attributed to a small percentage of the ethylene glycol that was still on the sample and decomposed upon heating, although since no CO_2 was detected under the treatment under He it can be concluded that the CO_2 is a product of the reduction of the MoO_3 by CH_4 . This observation highlights the fact that the C-H bond of CH_4 might be activated at low temperature under the presence of nanoparticles.

Fig.13: Mass spectrometry results of MoO_2 nanoparticles carburized under 10 % CH_4/H_2 .

The fact that CO_2 began to be produced at around 190 °C leads us to think that C-H activation might be feasible at low temperature over the surface of nanoparticles and in principle, carburization might occur on the top atomic layers at these temperature ranges; although this is

just a hypothesis that has not yet been published anywhere else and has to be corroborated. Nonetheless, it is known that the particle size can have an influence in the activation required for certain reactions to occur; for example, Pushkarev et al.²⁴ reported that there is an influence of the particle size of the Pt on the activation energy for the hydrogenation of toluene. These authors found that the activation energy decreases from 39 KJ/mol for 1.5 nm particles to 32 KJ/mol for 5.2 nm particles, attributing this phenomenon to a change in the energy of adsorption of the reactants over the surface of the particles. A similar behavior might be occurring in the case of the MoO₂/MoO₃ nanoparticles and CH₄, although as pointed out before this observation might be plausible but it has to be confirmed.

It has been reported in the literature that when MoO₃ is heated in the presence of H₂ the gas molecules are incorporated into the metal oxide structure forming the so called molybdenum bronzes¹⁸⁻²⁰. On the other hand, computational studies have shown that the removal of oxygen from this type of structure create sites that are able to bind either H₂ or methyl groups over the metallic center²¹.

It is well known that the rate determining step in CH₄ activation is the breaking of the first C-H bond (435 KJ/mol)²², when this occurs the methyl group becomes extremely reactive. For example, Pak et al. demonstrated that MoO₃ is capable of oxidizing methyl radicals (coming from the decomposition of azomethane) into CH₃OH at 300 °C²³.

Taking the previous studies into consideration it is plausible to think that the MoO₃ present on top of the MoO₂ nanoparticles catalyzed the activation of CH₄ and subsequent oxidation to form CO₂ as the molybdenum oxide was being reduced during the process, probably following a Mars-van Krevelen type of mechanism, where the oxygen used to oxidize the hydrocarbon is lattice oxygen. As stated before, the higher surface free energy of the nanoparticles might have induced the aforementioned reaction at a lower temperature than the usually reported for bulk materials.

H₂O was also detected and three signals could be appreciated. The first peak, although weak, started at 190 °C until 350 °C and might be associated with the formation of the molybdenum bronze and subsequent oxidation of the CH₄ to form CO₂ and H₂O. The second peak evolved between 350-460 °C, while the third one started at 520 °C, reaching a maximum at around 570 °C, which coincides with the first detection of the carbide in the XRD patterns. One interesting observation is the fact that the second peak of H₂O began to appear when the slope of the CO₂ signal began to decrease, indicating that the reduction of the MoO₃ was concluding and the reaction shifted to the removal of the lattice oxygen from the MoO₂.

Starting at about 550 °C the rest of the signals, CO, C₂H₃, CH₃ and CHO showed an increase in intensity as the carburization progressed and CO and C₂H₃ showed a successive increment until the reaction was completely finished. On the other hand, the fact that the m/z = 29 signal was detected and did not show the same slope as signals m/z = 28 and 27 indicates that formaldehyde

was being formed as a product of the reaction of CO and H₂ (or another side reaction) over the Mo₂C that was crystallizing. It has been reported by several authors the capabilities of Mo₂C to catalyze the hydrogenation of CO, dehydrogenation of ethane²⁵, ethane hydrogenolysis²⁶, etc; to produce several components like CH₃OH, H₂O, CH₄²⁷⁻²⁹ (which explains the increase in the signal m/z = 15) and CH₂O³⁰. Interestingly enough, the signals for CO and C₂H₃ exhibited a similar trend although not with the same slope. It is worth to point out that CH₃OH was not detected in our experiments.

3.2.2.- Treatment under 10 % CH₄/H₂ (commercial MoO₂)

The gases evolved from the experiment using the commercial MoO₂ (Fig 14) exhibited the same behaviour as the MoO₂ nanoparticles (at high temperature) excepting that CH₄ was not produced. In contrast, the only difference is the temperature at which each of the processes occurred. The formation of CO₂ was first detected at 280 °C reaching a maximum at about 350 °C and decreasing in intensity until the temperature was 480 °C, coinciding with the conversion of MoO₃ into MoO₂. H₂O showed two peaks, one starting at about 420°C and ending at 505 °C (maximum at 462 °C) and the last one starting at 560 °C until the end of the experiment, with a maximum located at 720 °C.

CO and C₂H₃ began to increase when the temperature was about 630 °C, suggesting that the carburization started at this temperature; long before any detection of the phase occurred with XRD. At 665 °C the CHO fragment was first detected. CO, C₂H₃ and CHO shared the same maximum at 732 °C. At about 620 °C, H₂ consumption began and the maximum was reached at 720 °C, coinciding with H₂O formation.

Fig 14: Mass spectrometry results of commercial MoO_2 carburized under 10 % CH_4/H_2 .

3.2.3.- Treatment under 10 % CH_4/H_2 (MoO_2 nanoparticles, TPR with isothermal stages)

Fig. 15 shows all the signals monitored in every step of the temperature programmed experiment with isothermal stages. At first glance there is not a substantial difference in any of the signals along the heating process excepting the evolution of CO_2 . CO_2 started to appear at about 180 °C, as occurred during the ramp up carburization, and disappeared at about 370 °C; as opposed to the 420 °C previously determined. Again, this indicates the oxidation of CH_4 or the reduction of the surface MoO_3 most likely present in the nanoparticles.

The fact that no CO evolution was recorded was probably due to its extremely low concentration and by the fact that carburization was occurring slowly as determined by the XRD patterns (Fig.9).

Fig 15: Mass spectrometry results of the MoO₂ nanoparticles carburized under 10 % CH₄/H₂ during the temperature programmed experiment with isothermal stages.

3.2.4.- Treatment under 20 % CH₄/H₂ (MoO₂ nanoparticles)

When the CH₄ concentration was increased to 20 % (Fig. 16) neither the first H₂O peak nor CO₂ were detected as in the case of the commercial MoO₂ or the nanoparticles when 10% CH₄/H₂ was used. H₂O production started at 570 °C until the end of the experiment, with a maximum at about 690 °C. At this same temperature the maxima for H₂ (consumption) and CHO were located. H₂ began to be consumed at 590 °C while CHO began to appear at 600 °C.

CO was first detected at 645 °C which coincides with the detection of the Mo₂C phase (see Fig. 10) with its maximum at 707 °C. C₂H₃ exhibited the same behaviour as CO indicating that these two species were interrelated as previously seen. CH₄ was formed at about 610 °C and until 730 °C with its maximum at 672 °C.

Fig 16: Mass spectrometry results of MoO₂ nanoparticles carburized under 20 % CH₄/H₂.

4.-Conclusions

The primary aim of the present work was to determine if the onset temperature for the formation of molybdenum carbide could be reduced if nanoparticles of MoO₂ were used as starting material. As the results indicated, the presence of the amorphous phase seemed to have a bigger impact on the reduction of the carburization temperature than the size of the crystalline MoO₂. Nonetheless, it cannot be discarded the idea that the size of that amorphous phase is the one responsible for the decrease in the carburization temperature and that its transformation catalyzed the conversion of the crystalline MoO₂. Nanoparticles of MoO₂ are not difficult to synthesize and, as many other works have published in the literature, the main challenge resides in the transformation into Mo₂C. The chemistry of the MoO₂ → Mo₂C transformation is extremely

complex to an extent that many variables influence the formation of the molybdenum carbide. There are many parameters that must be taken into consideration such as carburizing agent, C/Mo ratio, heating rate, oxygen vacancies, isothermal treatment, H₂ content, incorporation of H₂ into the structure, etc, since they affect such transformation. In addition, on top of the parameters mentioned above, indications were found that the stacking or not of certain planes of the MoO₂ seem to have an influence as well and, as explained before, it has to be with the type of oxygen that can be easily removed. As reported by Vitale et al.³¹, such influence has been seen with previously with MoO₃, and extrapolating this behaviour to MoO₂ is plausible if the model proposed by Lalik³² is correct.

On the other hand, decreasing the reaction temperature has an extra cost during the carbide formation, while using low temperatures of synthesis the reaction time has to be substantially increased as the results from the TPR experiments done in this work showed, as well as from previous findings⁷. At this point, it is not clear how much time would be required to fully carburize the nanoparticles of MoO₂ using CH₄ as carbon source or if other choice as toluene, for example, would have a more positive impact. Nonetheless, it is clear that under the ranges of temperatures studied thus far the process becomes a matter of kinetics; for instance, there is still room for improvement if all the parameters that are known to affect the formation of the carbide are fine-tuned as to produce the desired material at low temperature, in a reasonable length of time and with a high surface area as to become competitive in the market place.

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6.-References

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