

New Synthesis of Mo₂C 14 nm in Average Size Supported on a High Specific Surface Area Carbon Material

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A molybdenum carbide supported on active carbon for catalytic hydrotreating was prepared by temperature-programmed reaction (TPR) in flowing H₂ of an active carbon impregnated by an heptamolybdate. TPR led at 973 K to the formation of supported Mo₂C. This new method of preparation avoids the use of methane as carburizing reactant and allows *in situ* preparation of supported molybdenum carbide without any contact of this pyrophoric material with air between preparation and catalytic run. The various steps of the carburization process were studied by trapping the solid intermediates at different temperatures during TPR. Two successive reactions were evidenced: the partial reduction by H₂ of the initial molybdenum precursor to MoO₂, and its subsequent carburization to Mo₂C. This last step is mainly due to the reduction of MoO₂ and carburization with native methane evolved from the reaction of the carbon support with dihydrogen. Solid materials were characterized by elemental analysis, X-Ray diffraction, transmission electron microscopy and specific surface area measurements. © 1998 Academic Press

Key Words: molybdenum carbide; active carbon; temperature-programmed reaction; *in situ* preparation.

1. INTRODUCTION

An increasing interest has developed for the use of transition metal carbides as they behave like noble metals (1, 2). Carbides of molybdenum are known for their hardness, thermal stability and surface reactivity (3). The typical method for preparing bulk transition metal carbide catalysts is the temperature-programmed reaction (referred to as TPR in the present paper) between bulk or supported molybdenum precursors, and flowing CH₄/H₂ (20/80) mixture (4, 5).

In the last 10 years there has been a growing interest in the study of carbon-supported Mo and W sulfides because carbon is a more inert support than alumina or silica. Therefore, carbon support leads to a total sulfidation of Mo or W due to a lack of precursor-support interaction (6).

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Carburization instead of sulfidation was considered in the present paper.

For electrochemistry applications, Ross and Stonehart have used carbon black as a support for low specific surface area tungsten carbides prepared by reducing supported tungsten in flowing hydrogen, at 970 K. A subsequent diffusion of carbon into the tungsten metal occurred by only flowing argon for 30 h at a temperature as high as 1270 K (7). The resulting tungsten carbide was WC. Leclercq *et al.* have obtained WC crystals with low specific surface area by reaction between tungsten metal and carbon at still higher temperature (1790 K) (2). Ledoux *et al.* also prepared Mo₂C at very high temperature 1520–1570 K, by reaction between the transition metal vapor oxide and a very high specific surface area active carbon (8–10). All these previous papers have shown it is possible to use carbon to prepare early transition metal carbides.

The present objective is to prepare high specific surface area metallic carbides that exhibit low interaction with carbon support. This paper describes a new route for preparing active carbon supported molybdenum carbides by only flowing H₂ during TPR.

2. EXPERIMENTAL

2.1. Materials and Catalyst Preparation

The molybdenum precursor used in this study was ammonium heptamolybdate Mo₇O₂₄(NH₄)₆·4H₂O from Pro-labo (99.0% purity).

A steam active carbon from NORIT and referred to as SX1 was acid-washed and used for this study. SX1 is a microporous and mesoporous carbon (pore size distribution Fig. 1) with a specific surface area of 900 m²·g⁻¹ and grain size less than 150 μm (97%). The total pore volume was 0.67 cm³·g⁻¹. Elemental analysis (in wt %) of the active carbon is reported in Table 1.

Impregnation and drying steps were carried out as follows. The precursor solution (Mo₇O₂₄(NH₄)₆·4H₂O: 1.10⁻³ mol·L⁻¹ in water) in excess volume was added to the active carbon (7) and mechanically mixed at room

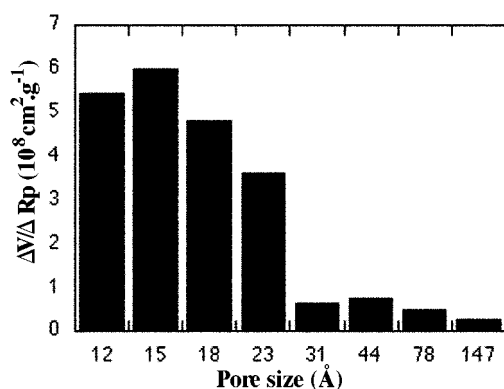


FIG. 1. Pore size distribution of the active carbon SX1 used as support.

temperature for 16 h. The water was then evaporated at 323 K and the remaining solid was dried in air at 383 K for 24 h. A 10 wt% Mo/SX1 sample (which will be referred to later as Mo/SX1) was used to study the carburization process. It presented a total specific surface area of 437 m².g⁻¹.

2.2. X-Ray Diffraction

A Siemens D-500 diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) equipped with a NaI, Tl doped crystal was used to obtain X-ray diffraction (XRD) patterns. The X-ray source was operated at 30 kV and 20 mA and was scanned at a rate of 1.2 deg.min⁻¹ (in 2θ).

2.3. Transmission Electron Microscopy

Transmission electron microscopy was done using a JEOL JEM 100 CXII apparatus. Samples were dispersed ultrasonically in ethanol and then deposited on a TEM copper grid coated with a holey carbon film.

2.4. Elemental Analysis

Elemental analysis were performed at the “Service Central d’Analyse” of the CNRS (Vernaison, France). The analysis were performed by acidimetry and coulometry for C, S, and O, by chromatography for N, and by inductive coupling plasma—atomic emission spectroscopy for Mo.

TABLE 1
Elemental Analysis (in wt%) of the Active Carbon SX1,
Used as a Support for Catalysts

| C | H | N | O | S | C/H | Ashes |
|------|-----|-----|-----|-----|------|-------|
| 85.6 | 1.2 | 0.6 | 5.3 | 0.3 | 71.3 | 5 |

2.5. Specific Surface Area (S_g) Measurements

Specific surface areas were measured on a Quantasorb Jr sorptometer using the BET specific surface area procedure. The samples (10 to 20 mg) were outgassed under flowing nitrogen at 673 K for 2 h and cooled down to room temperature. Adsorption measurements were performed in liquid nitrogen at 77 K with N₂-He mixtures. The samples were then heated up to room temperature and the amount of desorbed nitrogen measured by a thermoconductivity detector (TCD).

2.6. Analysis of Gases Evolved (AGE) during Temperature-Programmed Reactions

Two kinds of AGE experiments were carried out:

2.6.a. In a first device, thermoreactions were performed in a quartz reactor containing a 100-mg sample under flowing (space velocity: 0.016 s⁻¹) pure H₂ (Air Liquide, 99.995%) at atmospheric pressure. The sample was heated from room temperature to 973 K at 33 K.h⁻¹ and hold at 973 K for 2 h. To avoid bulk oxidation of the material, a passivation step was performed at room temperature in an O₂(1 vol%)-He mixture for 2 h. This setup can work either linked to a chromatograph equipped with a TC detector (Intersmat; Porapak Q column, 1/4", 2 m), or to a flame ionization detector (FID) chromatograph (Hewlett Packard, Pona capillary column, 50 m). The first chromatograph was used to detect CO, CO₂, and CH₄, while the second one was used to detect only CH₄.

2.6.b. In a second device gases evolved from the quartz reactor during thermoreactions performed in the same temperature conditions as above were analyzed by mass spectrometry (Delsi-Nermag, Anagis 200).

2.7. Temperature-Programmed Reaction (TPR)

Both reduction and reaction processes occurring during the carburization steps were conducted in a third experimental device equipped with a thermoconductivity detector. TPR was conducted on a 100-mg sample of Mo/SX1 placed in a quartz reactor and heated from room temperature to 1200 K at 450 K.h⁻¹. The reacting gas mixture was H₂ (5 vol%)-Ar (dehydrated on zeolite 3A) and the flow rate was 1.5 L.h⁻¹. Hydrogen consumption and/or production of CO, CH₄ could be detected. After reduction and carburization of the supported precursor, the sample was cooled down to room temperature in flowing argon and finally passivated in O₂ (1 vol%)-Ar mixture for 2 h to avoid bulk oxidation when contacting with air. Identification of the various solid intermediates, during the reduction-carburization process, was done by switching the H₂-Ar mixture to

pure Ar after each significant peak of the TPR curve and quickly cooling the reactor to room temperature; XRD measurements were then carried out after passivation.

2.8. Temperature-Programmed Reaction (TPR) with Mass Spectrometry (MS) (Altamira, AMI 100, Zeton inc.)

A TPR experiment as previously described was carried out in the same experimental conditions (Section 2.7.) and the evolved gases from the reactor were analyzed on line by a quadrupole mass spectrometer in order to monitor both CH_4 and CO production.

3. RESULTS AND DISCUSSION

3.1. Carbon Supported Molybdenum-Precursor Samples

The elemental analysis (weight percentage) of the active carbon SX1 used for the supported carbide catalysts is reported in Table 1. The active carbon contains organic S, N, and O. Some of the oxygen comes from water adsorbed on the carbon. An XRD pattern of the support shows exclusively the diffraction lines of quartz (contained in the ashes at 5 wt%) and no other lines. No H_2S formation was observed during thermal treatment of the active carbon up to 1000 K. The pore size distribution reported in Fig. 1 shows that the active carbon used in this study is mainly a micro and mesoporous carbon; the mean pore radius is about 20 Å.

The molybdenum contents of the dried supported materials before carburization are reported in Table 2. They are in good agreement with theoretical percentages expected following the impregnation of the active carbon by the heptamolybdate. XRD patterns of the impregnated support only showed the reflexion lines of quartz contained in the ashes of the active carbon; no other crystallized species in the samples after impregnation could be detected. High resolution transmission electron microscopy was performed on the dried Mo precursor/SX1 to determine the nature of the intermediate species present after the drying step. Selected area electron diffraction micrographs showed single

TABLE 2
Mo contents (in wt%) of Dried Carbon Supported Materials after Impregnation

| Percentage | Mo/SX1 | Mo/SX1 | Mo/SX1 |
|------------------|--------|--------|--------|
| Theoretical wt% | 5 | 10 | 15 |
| Experimental wt% | 5.35 | 9.77 | 16.35 |

TABLE 3
Total Specific Surface Area S_g ($\text{m}^2 \cdot \text{g}^{-1}$) of SX1, and Mo/SX1 Materials before and after Carburization

| | S_g ($\text{m}^2 \cdot \text{g}^{-1}$) ^a | | | |
|-------------------------------------|---|-------------|--------------|--------------|
| | No metal | 5 wt% metal | 10 wt% metal | 15 wt% metal |
| Mo/SX1 | 846 | 658 | 589 | 437 |
| Mo/SX1 after TPR $\text{H}_2/973$ K | 920 | 844 | 725 | 543 |
| | Average particle size (nm) ^b | | | |
| Mo/SX1 after TPR $\text{H}_2/973$ K | — | 16.8 | 12.5 | 13.2 |

Note. Average Mo_2C particle size (nm) after carburization.

^aCalculated from the BET equation.

^bCalculated from the Scherrer equation.

crystal patterns of MoO_3 . These data show that during drying in vacuum at 323 K, the heptamolybdate thermally decomposed to MoO_3 . The most important feature evidenced by TEM micrographs was the increasing space distribution of the metal-containing particles with the decrease of the average particle size from 20 nm to 5 nm as the amount of molybdenum is decreased from 15 to 5 wt%. The 5 wt% Mo/SX1 precursor sample was therefore selected as a good candidate to proceed to the further carburization step.

Table 3 shows that S_g decreased with increasing heptamolybdate loadings after impregnation. It can be assumed that the impregnated molybdenum precursor blocked a fraction of the pores accessible to nitrogen during S_g measurement by the BET method.

3.2. Attempt to Prepare Molybdenum Nitride Supported on Active Carbon

One of the aims of this study was initially to prepare nitrides supported on active carbon according to Volpe and Boudart method (4).

We first studied the nitridation of the Mo-based sample (10 wt% Mo/SX1) in flowing pure NH_3 by analysis of gases evolved (AGE) during the reaction at 973 K. After reaction, the sample was passivated and then analysed by XRD. Figure 2 reports the XRD pattern of the Mo/SX1 nitrided sample referred to as Mo/SX1-N. The nitride formed during this temperature-programmed nitridation at 973 K was found to be MoN. This result is in agreement with Gouin *et al.* who have shown that MoN forms instead of Mo_2N when the precursor does not contain oxygen (11). Furthermore, some other diffraction lines could be observed in this XRD

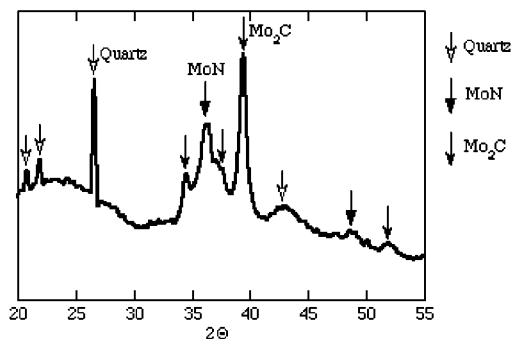


FIG. 2. X-ray diffraction pattern of Mo/SX1-N (temperature-programmed reaction in pure NH₃).

pattern corresponding to the formation of Mo₂C. To explain the formation of Mo₂C, we noted the increasing dissociation of NH₃ to N₂ and H₂ above 673 K as observed by AGE and therefore studied the effect of H₂ in the formation of Mo₂C/SX1.

3.3. Temperature-Programmed Carburization by Flowing Pure Dihydrogen

For the sake of comparison, two AGE at 973 K were carried out during the carburization process of Mo/SX1 to point out the role of hydrogen: the first one was performed by flowing a 10 vol% CH₄ in H₂, a standard gas mixture used for carburization (4), and the second one by flowing pure H₂. The final products (respectively referred to as Mo/SX1-C and Mo/SX1-H) were analysed by XRD (Fig. 3) after passivation by flowing 1 vol% O₂-He gas mixture. The XRD pattern of Mo/SX1-C (Fig. 3a) shows the diffraction lines of quartz from the support, a characteristic line of α-Mo₂C (hexagonal, JCPDS 35-787) at 2θ = 39.4°, and the diffraction lines of well crystallized MoO₂, probably due to the reduction of Mo^{VI} (MoO₃) to Mo^{IV} (MoO₂) by H₂. The XRD pattern of Mo/SX1-H (Fig. 3b) does not show any MoO₂ diffraction lines, but only those of well crystallized Mo₂C. The gases evolved during the temperature-programmed reaction were analysed at the outlet of the reactor by TCD-gas chromatography and the removal of water (reduction of MoO₃) was observed during both experiments: carburization by CH₄/H₂ or by H₂ alone. A light gas evolved above 853 K until the end of the carburization when flowing pure H₂ was used. This light compound is assumed to be either CO or CH₄ and will be identified later by FID gas chromatography and mass spectrometry. Table 4 shows the weight content of C, N, and Mo and the specific surface areas of Mo/SX1-N, -C, and -H. The temperature treatment of Mo/SX1 in flowing pure dihydrogen alone led to a large consumption of the support and the specific surface area was 543 m².g⁻¹.

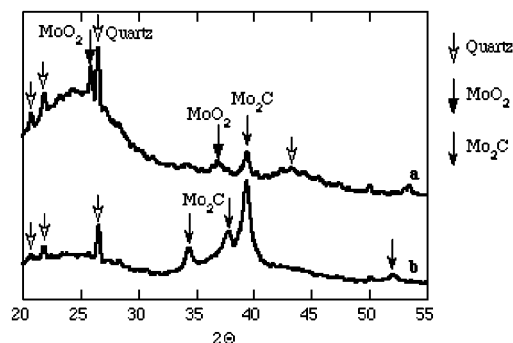


FIG. 3. X-ray diffraction patterns of (a) Mo/SX1-C (temperature-programmed reaction in CH₄ (10 vol%)-H₂ gas mixture); (b) Mo/SX1-H (temperature-programmed reaction in pure H₂).

These data showed that it is possible to prepare molybdenum carbides supported on active carbon by temperature-programmed reaction in flowing pure hydrogen. Furthermore, as a dihydrogen pretreatment is generally preceded before any catalytic run for hydrotreating or reforming, this preparation will allow a new route for *in situ* synthesis of Mo₂C/carbon support, avoiding both the use of a CH₄-H₂ gas mixture, and the passivation step necessary when catalysts have to be stored in air or transferred from the preparation device to the reactor for catalysis. Indeed, in the present experimental conditions, the carburization by flowing hydrogen leads to a well-defined Mo₂C phase (Fig. 3b). Whether or not graphite is formed at the surface of carbide particles remains to be studied, as CO chemisorption on these materials (5 wt% Mo) led to low CO uptake.

Moreover, as seen in Table 3, the specific surface area increases as a result of the hydrogen reduction treatment

TABLE 4
C, N, and Mo Contents (wt%) and Total Specific Surface Area (Sg m².g⁻¹) of Mo/SX1 after Different Temperature-Programmed Reactions

| | Content (wt%) | | | Sg (m ² .g ⁻¹) |
|-----------------------|---------------|-----|------|---------------------------------------|
| | C | N | Mo | |
| Mo/SX1 | 64.2 | 1.2 | 15.8 | 437 |
| Mo/SX1-N ^a | 62.6 | 3.1 | 18.7 | 611 |
| Mo/SX1-C ^b | 65.1 | 0.6 | 16 | 508 |
| Mo/SX1-H ^c | 59.0 | 1.1 | 21.0 | 543 |

Note. Operating conditions: 100 mg of Mo/SX1 precursor heated from room temperature to 973 K at 33 K.h⁻¹ under different flowing gases (2 L.h⁻¹).

^aNH₃.

^bCH₄ (10 vol%)-H₂.

^cPure H₂.

and carburization. This feature is probably due to a cleaning of micropores and not to the formation of new pores; this carbon material has been already treated (activation process of the active carbon to create the pore network) in flowing water vapour at very high temperature. Therefore, low temperature hydrogen treatment must not affect the pore structure.

Table 3 also shows the average Mo_2C particle after reduction-carburization is 14 nm. To get a higher dispersion of the carbide, a previous functionalization of the carbon surface should be investigated before synthesis.

To understand the different steps of the carburization of the heptamolybdate supported on the active carbon in flowing pure hydrogen and to identify the various solid intermediates, various temperature-programmed reactions (reduction-carburization) were performed on the TPR apparatus described in the experimental section (Section 2.7).

3.4. Intermediate Steps of the Carburization Process

Let us first note that a positive signal of the TC detector in relation to the base line on a TPR curve corresponds to a consumption of hydrogen in the gas mixture, whereas a negative signal is observed for the production of gases.

Figure 4 reports the TPR curve of Mo/SX1, where two hydrogen consumption peaks can be seen at 773 K and 973 K, respectively. The curve shows a production of gas at 1033 K and the signal remains under the base line until the end of the experiment at 1200 K. Several TPR were carried out in order to trap the intermediate solid species produced at the top or after each peak of the TPR plot, as described in the experimental section (Section 2.7). XRD patterns were then obtained for each intermediate trapped at room temperature. They can be overlaid to check the evolution of the solid species during the whole TPR process as reported in Fig. 5. The XRD pattern of the initial Mo/SX1 (Fig. 5a) only shows the diffraction line of the quartz present in the support ashes. At 793 K, MoO_2 diffraction lines (Fig. 5b) can be seen; the presence of Mo^{IV} results from the reduction by hydrogen of Mo^{VI} (MoO_3) beginning at 623 K. After the first peak of hydrogen consumption, the lines of MoO_2 present a higher intensity and are narrower (Fig. 5c), indicating further reduction and crystallization processes. After the second peak at 1023 K (Fig. 5d), no new diffraction lines can be seen. Then from 1033 K to 1223 K, the XRD pattern (Fig. 5e) shows the formation of Mo_2C , occurring simultaneously with the consumption of hydrogen and production of a gas.

3.5. Gases Evolved and Reactions Occurring during the Carburization Process

To understand which process occurs after the reduction step of MoO_3 to MoO_2 as well as the formation of the

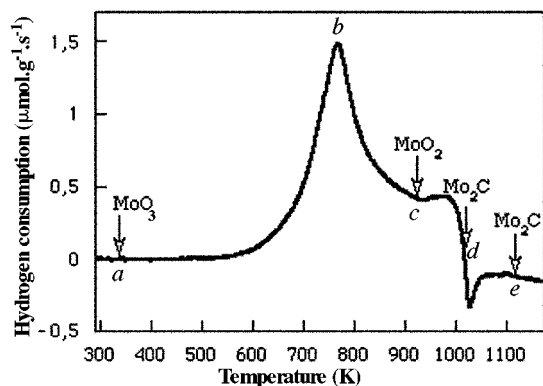


FIG. 4. Temperature-programmed reaction in H_2 (5 vol%)-Ar of Mo/SX1.

carbide, the following two temperature-programmed experiments were performed.

(i) The first (Section 2.6.a) was conducted on Mo/SX1 in flowing hydrogen, up to 823 K, in order to produce MoO_2 as shown by the TPR profile (Fig. 4). The reactor was closed and cooled to room temperature. It was then linked to the MS apparatus (Section 2.6.b) and submitted to another temperature-programmed treatment performed in vacuum up to 1033 K, at $5.4 \text{ K}\cdot\text{min}^{-1}$; the gases evolved were analysed by mass spectrometry (Fig. 6). A first peak occurred at 373 K and water ($m/e = 18$) was detected. The second peak occurred at 480 K and a small quantity of methane ($m/e = 16$) was detected. No additional peaks were recorded up to 900 K, where a peak with two shoulders was observed (960–1000 K and 1013 K). The first shoulder correspond to methane ($m/e = 16$), CO ($m/e = 28$), and CO_2 ($m/e = 44$), whereas the second shoulder was mainly CO ($m/e = 28$). XRD was carried out on the resulting sample after passivation and the diffraction lines of both MoO_2 and Mo_2C could be seen. At 1033 K the carburization process was

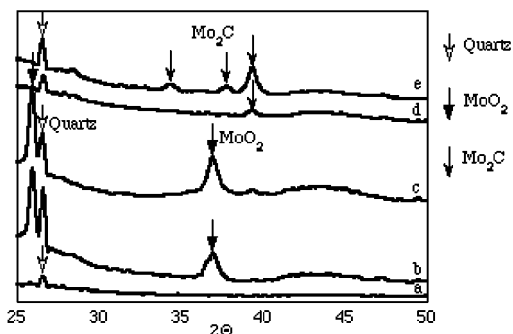


FIG. 5. X-ray diffraction patterns of Mo/SX1 during a temperature-programmed reaction in H_2 (5 vol%)-Ar stopped at: (a) 298 K; (b) 793 K; (c) 973 K; (d) 1023 K; (e) 1223 K.

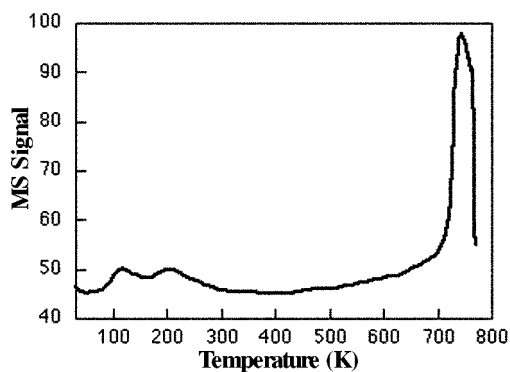


FIG. 6. Temperature-programmed treatment in vacuum of Mo/SX1 after a temperature-programmed reaction in hydrogen up to 823 K.

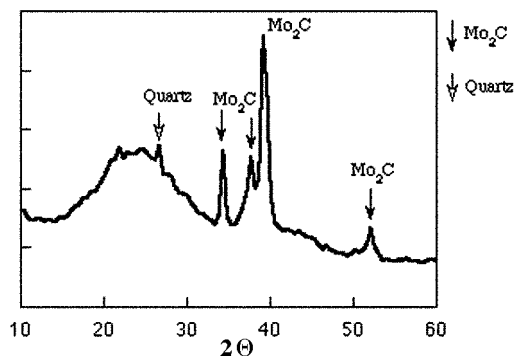


FIG. 8. X-ray diffraction pattern of Mo/SX1 after temperature-programmed reaction up to 1273 K in flowing argon.

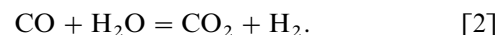
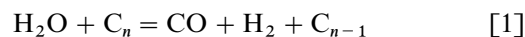
probably not achieved as MoO₂ was still present in the material.

A further TPR was performed and the evolved gases CO and CH₄ were analysed in line by mass spectrometry (Section 2.8.) (Fig. 7).

(ii) A second temperature-programmed treatment of Mo/SX1 in flowing inert gas (argon or helium) up to 1273 K also led to the formation of Mo₂C as shown by XRD (Fig. 8). Thus, without any dihydrogen in the gas mixture, the formation of Mo₂C occurred, but at a higher temperature (1273 K) than in flowing pure hydrogen or 5 vol% H₂ in Ar (973 K); but this experiment proved there is no need for dihydrogen in the flowing gas for carburizing Mo/SX1.

To understand the last carburization step, we have to take into account that water is still present in the support as evidenced by the desorption peak ($m/e = 18$) at 373 K. The active carbon is highly water adsorbing and all water content cannot be removed from the support by quickly heating the sample to 1033 K. A previous study on carbon porosity

has shown that hygroscopic humidity is about 10 wt% with carbon grain size less than 0.2 μm , and the grain size in the carbon SX1 is less than 150 μm (97%) (12). Moreover, let us note that the impregnation of the metallic precursor was performed in aqueous solution, and water could remain in the material. Finally, the reduction of molybdenum oxide produces water as well. All the water adsorbed in the support or produced by reduction of the oxide, as mentioned above, could react with the active carbon to produce carbon monoxide and hydrogen [1]. The carbon monoxide could then react with water [2] to produce carbon dioxide and hydrogen as follows:



A TPD study made on synthetic active carbon has shown that the maximum of CO₂ production rate occurs at 720–770 K and at 1170–1220 K for CO (13).

Reaction [1] is the well-known reaction that occurs during steam activation of active carbon precursor. The equilibrium between CO and CO₂ according to the Boudouart equation can be also considered:



This equilibrium tends to thermodynamically favour CO formation above 1000 K, which can explain why the peak of CO₂ begins at a lower temperature than the CO desorption peak and why we could see CO only at 1013 K.

Methane ($m/e = 16$) can be produced by simple reaction of adsorbed hydrogen with the carbon support,



or by a methanation process between CO and H₂.

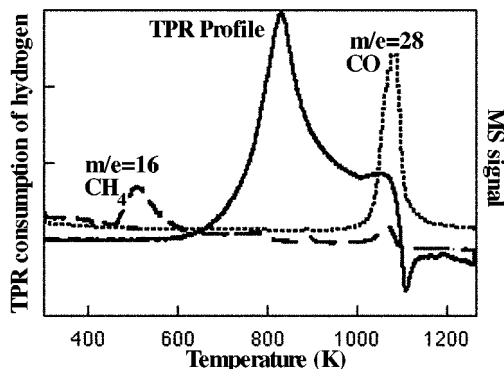
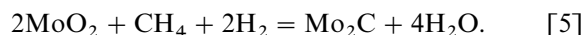


FIG. 7. Temperature-programmed reaction profile of Mo/SX1 and MS signal for $m/e = 16$ and $m/e = 28$ during the experiment.

Reactions [1] and [2] could occur during the temperature-programmed experiment leading to the formation of hydrogen. It can explain why there is no need for dihydrogen in the flowing gas to prepare Mo₂C/SX1. Indeed, MoO₃ can be reduced to MoO₂ by either carbon or H₂ and, at higher temperature, the resulting molybdenum intermediate is carburized. The remaining question concerns the nature of the carburizing gas. Carbon monoxide and methane are both well-known as carburizing gases and they are currently used in carbide preparation.

Methane formed by reaction [4] seems to be the carburizing gas: the last peak of methane occurred at 1000 K and no methane could be detected in the gas phase, due to its consumption for carburization at higher temperatures, whereas CO desorbed until the end of experiment. Moreover, during TPR the carburization occurred while the support adsorbed hydrogen to react and produce methane. A CO/H₂ methanation reaction cannot be excluded.

The global reaction occurring during the carburization can be written as:



4. CONCLUSION

This work reports a new route for preparing molybdenum carbides supported on carbon material with no need for methane in the flowing reacting gas. A temperature-programmed reaction with pure flowing hydrogen, *in situ* in the reactor is sufficient to obtain Mo₂C/active carbon at 973 K. The precursor 5 wt% Mo/SX1 showed good characteristics (homogeneous space distribution, low particle size) to lead to supported carbides. The carburization process was explained by reaction between CH₄, evolved from the support, and the metal reduced intermediate. Hydrogen could be present in the gas mixture or produced by the reaction

between H₂O (adsorbed in the active carbon). Methane was then made by reaction between hydrogen and carbon. The carbon of the support is consumed during the preparation but is stable at lower temperature. This new promising method may find application in hydrocarbon catalysis if the catalyst can be regenerated after use.

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