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Surface Studies of Passivated Molybdenum Oxynitride

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Molybdenum oxynitrides are very sensitive and attention should be paid to their storage and pretreatment in order to get accurate and reproducible physisorption or chemisorption results. This work showed that storage of these compounds in air leads to loss of accessibility of the surface area, illustrated by an apparent decrease of the specific surface area and pore volume. This phenomenon is due to the high affinity of these materials for oxygen, which diffuses into their lattice. Furthermore, oxygen, ammonia, and water, present on the surface of molybdenum oxynitrides after preparation and passivation, can block the access of probe molecules to pores or active sites. A method of storage and pretreatment before physisorption or chemisorption experiments is presented. CO chemisorption experiments in static and dynamic pulsed conditions were performed and led to similar results as in experiments performed with samples without any residual oxygen contamination. Low CO uptakes were interpreted in terms of nonstoichiometry of the compounds. © 1997 Academic Press

INTRODUCTION

Insertion of nitrogen in a molybdenum lattice leads to compounds with catalytic properties close to those of noble metals (1–5). Nitridation of molybdenum trioxide is often not performed to completion and oxygen is present in the lattice. Furthermore, because these materials are pyrophoric, a passivation step is performed after nitridation which can introduce oxygen into the lattice as well (6). Therefore, these solids are called oxynitrides of molybdenum.

It is of great interest to compare these compounds to commercial catalysts on the basis of turnover rate. To accomplish this, it is necessary to count the metallic active sites and determine the total specific surface area (S_g).

It is essential to perfectly clean the surface of a solid before any specific surface area measurements or chemisorption studies using molecular probes. Only such a pretreatment will lead to accurate and reproducible results. Typically, desorption of adsorbed species is done in vacuum at high temperature. For nitrogen physisorption at 77 K, a pretreatment in a vacuum of 0.1 Pa is adequate. For chemisorption measurements (CO at room temperature for instance) a lower vacuum of 1×10^{-5} Pa is adequate. The temperature of pretreatment, generally lower than the temperature of preparation of the material, must be chosen carefully. Indeed, the thermal pretreatment must clean the surface without altering the bulk structure of the material.

In the present study, it became evident that even after the above usual pretreatments at high temperature in vacuum, still species remained adsorbed on the surface of molybdenum oxynitride (MoO_xN_y). It appeared that a suitable pretreatment was necessary for these compounds having a high affinity for oxygen. Furthermore, a storage in vacuum of these compounds was proposed to avoid the apparent decrease of their specific surface area versus time of storage, as observed by Gouin *et al.* (7).

Another problem is the reproducible titration of metallic active sites. For this purpose, CO chemisorption, a technique usually performed on metal catalysts (8), was used. Dynamic and gravimetric CO chemisorptions were compared.

The aim of this paper is to define a procedure for determining both specific surface areas and the number of metallic active sites in either static or dynamic conditions.

EXPERIMENTAL

Materials

The gases used were H_2 (Air Liquide, Custom grade, 99.95%), He (Air Liquide, Custom grade, 99.5%), O_2 (Air Liquide, Custom grade, 99.5%), and NH_3 (Air Liquide, Custom grade, 99.5%), without prior purification, except 9.9 vol% CO/He (Air Liquide, N55 grade, 99.9995%) used for dynamic CO chemisorption experiments. It was deoxygenated and dried over Chrompack gas clean filters.

MoO_3 (Janssen-Acros, 99.998%) was used as the precursor of the molybdenum oxynitride (MoO_xN_y). It has an orthorhombic structure and its specific surface area is about 0.7 $m^2\ g^{-1}$. Molybdenum oxynitride was prepared from MoO_3 powder nitrided in pure flowing ammonia (5) at a volume hourly space velocity (VHSV) of about 37500 h^{-1}.

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The preparation followed Volpe and Boudart's work (9): the temperature was increased in three steps, first rapidly from 293 up to 633 K (17 K min^{-1}), then more slowly from 633 up to 733 K (33 K h^{-1}), and finally from 733 up to 973 K (100 K h^{-1}). The temperature was held at 973 K for 3 h. The system was then cooled to room temperature (RT) in flowing NH_3 and flushed in helium for one-half hour. All sample were passivated by flowing 1% O_2/He (v/v) to avoid a strong bulk oxidation.

Techniques

Specific Surface Area (S_g) and Pore Size Distribution Measurements

A Quantachrome-Quantasorb Jr. was used for the surface measurements in dynamic conditions. After pretreating the passivated molybdenum oxynitride *in situ* in flowing nitrogen at 643 K for 1.5 h, the amount of nitrogen adsorbed at 77 K and desorbed at RT was determined using a catharometer detector. The specific surface area value was obtained from the nitrogen desorbed at different partial pressures by means of the BET method. A pretreatment in flowing hydrogen at 723 K could also be performed separately in a quartz reactor which could be adapted to the Quantachrome-Quantasorb Jr. apparatus without exposing the sample to air. A Carlo Erba sorptomatic serie 1800 was used to determine the pore size distribution of the molybdenum oxynitride, from equilibrium isotherms of adsorption and desorption of N_2, measured at liquid nitrogen temperature. This apparatus could degas samples at 6.6 Pa and temperatures as high as 523 K.

Temperature-Programmed Desorption (TPD)

TPD in vacuum. Typically, 100 mg of passivated molybdenum oxynitride was placed in a quartz reactor connected to a quadrupole mass spectrometer (Delsi Nermag Anagaz 200). The vacuum in the reactor was performed by a primary pump ELNOR Model 350 C (1 Pa) and by a turbomolecular (10^{-6} Pa) pump (BALZER) in the spectrometer. The temperature of the furnace was controlled with a programmable temperature controller (Setaram TGC 85) and a TPD was conducted up to 1173 K at a heating rate of 7.5 K min^{-1}. The desorbed species molecules were leaked into the spectrometer via a microvalve. Mass scanning, between 1 and 200 (*m/e*) was carried out every 9 s. The data were saved, processed, and plotted as desorption curves for all the characteristic fragments included in the selected range.

TPD in nitrogen or hydrogen flow. The same quartz reactor, with a new sample, was flushed under nitrogen (6 L h^{-1}) or hydrogen (1.5 L h^{-1}) and temperature controlled as described above. A gas chromatograph (IGC 12 M Intersmat Delsi) with a catharometric detector and a porapak N column (3 m length, 1/8 in. in diameter) was used for separation and analysis of the evolved gases.

Powder X-Ray Diffraction (XRD)

A Siemens D500 automatic diffractometer with a Cu$K\alpha$ monochromatized radiation source was used to check the stability of the molybdenum oxynitride crystalline structure versus time. The pattern of a freshly passivated molybdenum oxynitride was found to be close to that of a γ-Mo_2N.

Transmission Electron Microscopy

A Jeol JEM 100 CX II was used for characterizing the passivated molybdenum oxynitride particles versus time of storage. The powder was dispersed ultrasonically in xylene and deposited on a copper grid, previously coated with a carbon film.

Elemental Chemical Analysis

Elemental analysis of the solids for oxygen, nitrogen, carbon, hydrogen, and molybdenum content was performed by the Service Central d'Analyse du Centre National de la Recherche Scientifique in Vernaison (France). Oxygen, nitrogen, carbon, and hydrogen amounts were determined using a combustion method and subsequent analysis of the effluent gases. Molybdenum analysis was performed by plasma emission spectroscopy. For samples stored in vacuum, analyses were performed in an inert gas.

X-Ray Photoelectron Spectroscopy (XPS)

A Kratos XSAM 800 apparatus at Shell KSLA was used for X-ray photoelectron analysis using an Al$K\alpha$ monochromatized radiation source. As the N1*s* and Mo3$p_{3/2}$ signals overlapped, estimation of nitrogen present on the surface has been made by integration of the N (Auger) signal at ca. 1000 eV. Integration of the O1*s* signal was used to calculate the amount of superficial oxygen. Mo IV and Mo VI ratios were calculated by deconvolution of the Mo3$d_{3/2}$ and 3$d_{5/2}$ signals.

Dynamic CO Chemisorption—Pulsed Technique

Samples of molybdenum oxynitride (80 mg), were first purged by flowing helium in a quartz reactor. A pretreatment at 693 K for 1 h in hydrogen and 0.5 h in helium at 693 K was used and then followed by a quenching of the sample at 273 K in flowing helium. CO chemisorption, using a 9.9% CO/He (v/v) mixture was performed in situ at 273 K by pulsing in intervals, via an automatic valve, a well-known quantity of CO (4.42 μmol of CO). A catharometric cell detected the remaining nonadsorbed CO at the outlet of the reactor. After completion of a CO monolayer on the surface of the compound the following CO peaks recorded corresponded exactly to the CO amount of each pulse. The data were saved and processed and the number of micromoles of CO chemisorbed per gram of sample could be determined.

Static CO Chemisorption—Thermogravimetric Measurements

The quantity of CO chemisorbed on the surface of the molybdenum oxynitride was determined by thermogravimetric analysis (TGA). The apparatus was equipped with a Setaram MTB 10^{-8} micro balance. The glass vacuum system, connected to a turbomolecular pump (Leybold Turbovac 50) and a primary pump (Trivac), could achieve a static vacuum of 10^{-2} Pa. A furnace could be raised around the sample placed in the vertical glass tube of the balance and the temperature was controlled with a programmed temperature controller (Setaram RT 3000). The sample (500 mg) was placed in a platinum pan suspended in the thermobalance. After a pretreatment in hydrogen at 693 K for 1 h and degassing (10^{-2} Pa) at 693 K for 0.5 h, the temperature was slowly decreased to 273 K in vacuum. At this temperature, a partial pressure of 7.2×10^3 Pa of CO was introduced into the balance, a given quantity of CO chemisorbed and the weight registered versus time of adsorption. The system was then evacuated at RT to desorb CO reversibly chemisorbed. The irreversible CO could be completely desorbed by evacuating at 673 K for 1 h.

RESULTS

In order to determine the density of the metallic active sites (Mo atoms per m^2), it is necessary to very precisely measure S_g of the molybdenum oxynitrides. For this purpose, a systematic study of the specific surface areas was performed as a function of storage conditions and time.

Evolution of the Specific Surface Area: Effect of Storage

In a previous study on molybdenum nitride by Gouin *et al.* (7), a decrease of S_g versus time of storage was observed, even after degassing the samples at high temperature before BET measurements. The authors could almost entirely recover the specific surface area only after a reducing pretreatment at 673 K for 10 h in hydrogen, but no explanation of this phenomenon was given.

The same tendency was observed for the present molybdenum oxynitrides and Figure 1a reports S_g values versus time of storage. For a sample stored in air, which did not undergo any hydrogen pretreatment at high temperature before BET measurements, the apparent values of the specific surface area are clearly decreasing with time of storage. In contrast, for a sample stored in vacuum (Fig. 1b) and whose specific surface area was measured under the same previous conditions, this decrease is only 11% in 3 months compared to 53% for the sample stored in air. Pore size distribution (Fig. 2) confirms this tendency, with a loss of pore volume for the sample stored a long time in air (3 years). Neither modification of the initial crystalline structure nor variation of the initial texture were observed in XRD patterns and TEM micrographs, respectively, for compounds stored for a long time in air. Thus, the decrease in porosity is not a textural feature. Indeed, a treatment in hydrogen at 723 K for 15 min can restore most of the surface (Fig. 1, point c). XPS (Table 1) and elemental chemical analysis (Table 2) results indicate an increase of the oxygen amount for samples stored in air.

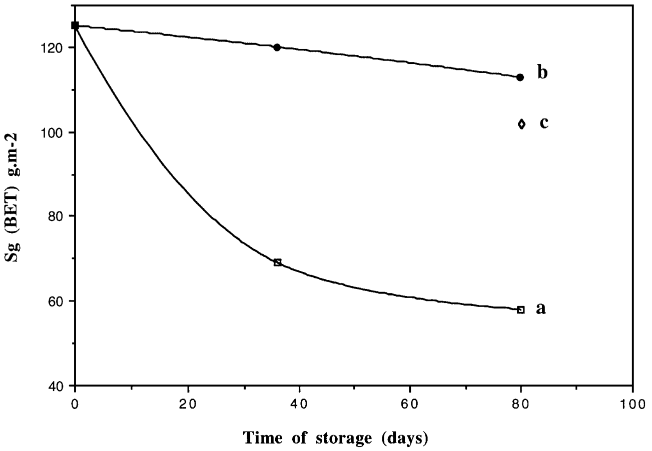

FIG. 1. Evolution of the specific surface area versus time and condition of storage for passivated molybdenum oxynitrides pretreated in N_2 at 643 K for 1.5 h. (a) Sample stored in vacuum; (b) sample stored in air; (c) sample stored in air and pretreated in hydrogen at 723 K, 15 min.

Choice of a Suitable Pretreatment before S_g Measurements and CO Titration of Metallic Sites

Molybdenum oxynitrides must be pretreated to remove any chemisorbed species still present on the surface after preparation. These species are mainly H_2O, NH_3 (after nitridation step) and oxygen (after passivation step). On such clean compounds, S_g measurements and CO chemisorptions can be performed.

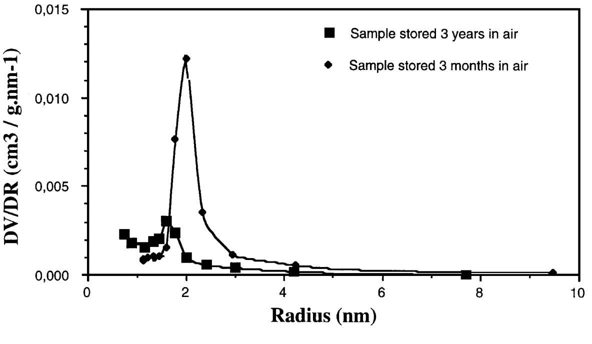

FIG. 2. Pore size distribution of a passivated molybdenum oxynitride stored for 3 years in air compared to a passivated molybdenum oxynitride stored for 3 months in air.

TABLE 1

XPS Spectroscopy

Samples	O	N
A	0.58	1.90
B	0.27	2.47

Note. O and N surface chemical composition of passivated molybdenum oxynitrides (mole per mole of molybdenum). A, stored in air for 2 months; B, stored in vacuum for 2 months. For a stoichiometric Mo_2N, molar ratio N/Mo = 0.5.

TPD was used to determine the conditions of pretreatment and monitor surface species desorption. Several kinds of pretreatments were performed and subsequently followed by BET measurements. The data can be found in Table 3.

Figure 3 shows results from a TPD in nitrogen. It can be seen that ammonia was completely removed from the surface of the sample at 643 K, but some water still remained even at that final temperature. The corresponding pretreatment in flowing nitrogen at 643 K increased the value of S_g by only 6% compared to the pretreatment at 423 K (Table 3). This is not a significant increase because the relative error is 5%.

Second, a TPD in vacuum (Fig. 4) shows that at 643 K, both ammonia and water could be completely removed. The corresponding static pretreatment in vacuum at only 523 K for 1 h was then performed and the value of the specific surface area increased by 27% (152 $m^2\ g^{-1}$, Table 3). Between 643 and 1073 K (Fig. 4) nitrogen was detected. Furthermore, hydrogen was observed between 873 and 1273 K and γ-Mo_2N and MoO_2 were detected by XRD at this final temperature.

Reduction of surface oxygen (from passivation) by flowing hydrogen was studied by analysis of gases evolved during treatment in hydrogen at atmospheric pressure (Fig. 5). For the sake of comparison, analysis of gases evolved in flowing helium at atmospheric pressure (Fig. 6) was also performed.

TABLE 2

Elemental Chemical Analysis

Samples	O	N
A	0.65	0.88
B	0.58	0.83
C	0.55	0.75

Note. Bulk chemical composition of passivated molybdenum oxynitrides (mole per mole of molybdenum). A, stored in air for 2 months; B, stored in vacuum for 2 months; C, pretreated at 673 K, for 1 h, at 130 Pa and stored in vacuum. For a stoichiometric Mo_2N, molar ratio N/Mo = 0.5.

TABLE 3

Specific Surface Areas Following Various Pretreatments of a Passivated Molybdenum Oxynitride Stored in Air for a Few Hours

Pretreatment:	423 K, 1 h, N_2	643 K, 1.5 h, N_2	523 K, 1 h, 6.6 Pa
S_{BET} ($m^2\ g^{-1}$):	111	118	152

The ammonia and water peaks at low temperature in flowing hydrogen (Fig. 5) were also observed when helium was used as carrier gas (Fig. 6). However, a second water peak can be observed in flowing hydrogen at about 593 K in Fig. 5. If the reducing treatment was continued above 773 K (Fig. 5), the molybdenum oxynitride was completely reduced to molybdenum metal.

According to these results and as will be discussed later, a pretreatment under hydrogen at 693 K for 1 h was chosen before any S_{BET} measurement or CO chemisorption on passivated molybdenum oxynitride.

To check the state of the surface of the material prereduced as described above, a TPD in vacuum was done: it showed neither ammonia nor water desorption, up to 693 K.

Counting of Metallic Active Sites by CO Chemisorption

Carbon monoxide is commonly used as a molecular probe to count metallic sites. Haddix *et al.* (10) have shown that molybdenum nitride (γ-Mo_2N) chemisorbs CO without dissociation and have assumed a 1 : 1 stoichiometry for Mo : CO. The amount of CO chemisorbed was used to determine the number of accessible surface molybdenum atoms considered to be the metallic active sites on the molybdenum oxynitride. In this work, CO chemisorption was measured, as described under Experimental, in either dynamic or static conditions. The previously described pretreatment in hydrogen at 693 K for 1 h was performed. It is noteworthy that in the case of the pulse method, the sample must be quenched at 273 K after its pretreatment in order to observe CO chemisorption. Once these pretreatments were performed, the molybdenum oxynitride surface was clean

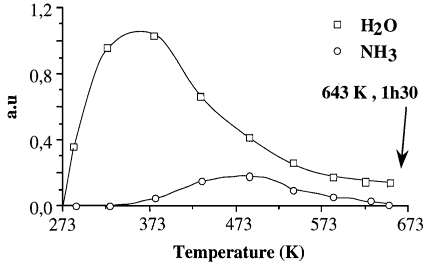

FIG. 3. Temperature-programmed desorption in nitrogen of a passivated molybdenum oxynitride stored in vacuum and analysis of gases evolved using a catharometric detector.

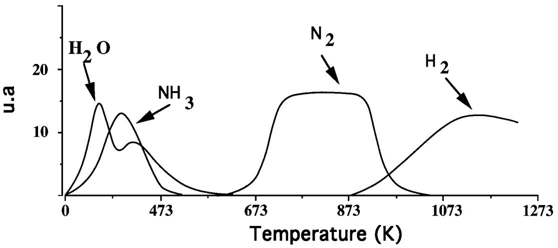

FIG. 4. Temperature-programmed desorption in vacuum of a passivated molybdenum oxynitride stored in vacuum and analysis of gases evolved using a quadrupolar mass spectrometer.

and CO molecules could have access to surface molybdenum atoms.

Table 4 presents the CO chemisorption data obtained on molybdenum oxynitride using the two techniques. The data correspond to CO irreversibly chemisorbed. The different techniques give results that are in quite good agreement which each other. The best MoO_xN_y sample irreversibly chemisorbed 270 mmol of CO per gram of oxynitride.

DISCUSSION

Passivated Samples

The results indicate that water, ammonia (Figs. 3–6), and oxygen (Tables 1 and 2) are present on the surface of a passivated molybdenum oxynitride. They can prevent accurate measurements of S_g (Table 3) and CO uptake. Indeed, for a sample on which water and ammonia are still present, S_g is lower (111 or 118 m^2 g^{-1}) than for a sample degassed at high temperature (152 m^2 g^{-1}). Thus, ammonia and water, chemisorbed on the surface after nitridation can block access to pores.

But the results show that oxygen should not be neglected either, as it can lower S_g measurements as well (Fig. 1a compared to Fig. 1c). Previous works agree with such a behavior. For example, Volpe and Boudart (9) observed that the specific surface area of a passivated molybdenum nitride is 23% lower than that of a nonpassivated one. Choi *et al.* (11) also reduced their passivated molybdenum nitrides in order to obtain higher specific surface areas.

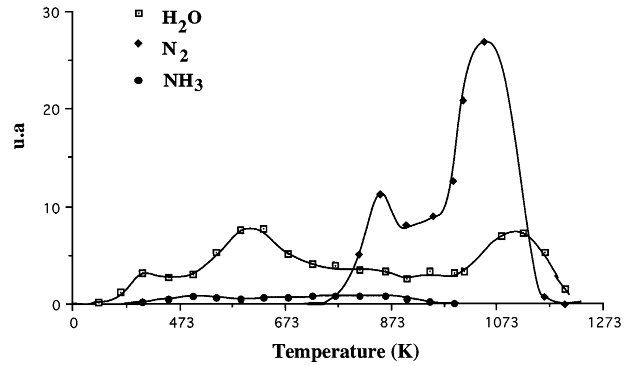

FIG. 5. Temperature-programmed desorption in hydrogen at atmospheric pressure of a passivated molybdenum oxynitride stored in vacuum and analysis of gases evolved using a catharometric detector.

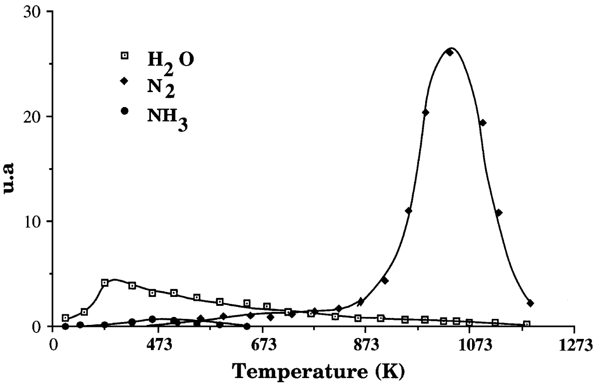

FIG. 6. Temperature-programmed desorption in helium at atmospheric pressure of a passivated molybdenum oxynitride stored in vacuum and analysis of gases evolved using a catharometric detector.

Since oxygen can only be removed as water, as shown in our results (Fig. 5), it is highly recommended that passivated molybdenum oxynitrides be pretreated at 693 K for 1 h in hydrogen before physisorption or chemisorption experiments in order to get accurate and confident data. As shown in this paper, this pretreatment cleans the surface without altering the compounds. Reduction in flowing hydrogen at atmospheric pressure (Fig. 5) shows that the first water peak corresponds to the desorption of

TABLE 4

CO Chemisorption Data Obtained on a Passivated Molybdenum Oxynitride with Two Different Techniques: TGA and Pulsed Technique

Sample:	Molybdenum oxynitride	Molybdenum oxynitride	Molybdenum oxynitride
m_i(g):	0.518	0.08	0.08
S_g (m^2 g^{-1}):	103	120	120
Technique:	Thermogravimetric	Pulsed	Pulsed
Pretreatment:	693 K, 1 h, H_2 + vacuum 10^{-6} Pa at 693 K, 1/2 h	693 K, 1 h, H_2 +693 K 1/2 h, He +quench at 273 K	693 K, 1 h, H_2 +693 K 1/2 h, He +slow decrease of temperature to 273 K in helium
mmoles CO_{irr}/ g catalyst:	262	270	0
Atoms of CO_{irr}/cm^2:	1.5×10^{14}	1.4×10^{14}	0
$100 \times n$CO/nMo^a:	13	12	0

[a] Ratio of CO experimentally chemisorbed versus Mo atoms theoretically exposed on the surface, in the case of a stoichiometric fcc lattice.

physically adsorbed water, whereas the second one corresponds to the reduction of the surface oxygen due to passivation. No decomposition of the oxynitride will occur if the temperature is below 760 K. Above this temperature, Fig. 5 shows that the oxynitride decomposes into N_2 and H_2O due to the reduction of the bulk. In the case of TPD in vacuum (Fig. 4), the first water peak corresponds to physically adsorbed water (as for treatment under hydrogen, Fig. 5) but the second water peak can be considered to be either chemisorbed water, a dehydroxylation of the surface, or a reduction of surface oxygen by hydrogen still present in the bulk as shown by the hydrogen desorption peak at high temperature (Fig. 4). This hydrogen remained in the bulk (at room temperature) and is probably due to ammonia decomposition during nitridation step.

Therefore, the decrease in S_g measurements for samples stored in air is not only due to ammonia and water adsorbed on the surface but also to the presence of oxygen since only a treatment in hydrogen at high temperature can regenerate most of the specific surface area.

Samples Stored in Vacuum

XPS and elemental analysis data are in agreement with increasing oxygen for samples stored in air (Tables 1 and 2). Carbides and nitrides of transition metals are well known for their high affinity for oxygen (12). Ambient oxygen can then adsorb strongly on the molybdenum oxynitride and progressively decrease the surface area and porosity (Fig. 2). However, this apparent disappearance of pores is not effective since the TEM micrographs still show a porous texture. Filling of micropores and mesopores by oxygen is a more likely explanation. Brennan *et al.* (13) have observed a decrease of the accessible surface linked to mesopore blockage by oxygen. To avoid this phenomenon, the compounds were stored in vacuum and Fig. 1b shows that this perfectly preserved the accessibility to the surface area.

Pulsed and Static Techniques for CO Chemisorption

This very high affinity for oxygen was also observed during dynamic CO chemisorption experiments. Indeed, after the high temperature reducing treatment, it was necessary to quench the samples at 273 K before starting CO uptake experiments, instead of decreasing the temperature slowly from 693 to 273 K under helium, which led to no CO uptake (Table 4, column 4). In fact, oxygen and water impurities could still be present in helium even after its purification and prevent CO chemisorption on metallic active sites. Thus, the whole pretreatment procedure must be performed very carefully and the quenching step must be done. Under these conditions, both dynamic (pulsed technique) and static (TGA) measurements following vacuum pretreatment without any oxygen contamination are in good agreement (Table 4, columns 2 and 3). Nevertheless, only a fraction of surface Mo atoms seems to be titrated. Assuming a stoichiometric fcc lattice structure ($a_0 = 0.418$ nm), a density of 1.14×10^{15} Mo atoms per square centimeter was theoretically estimated. From CO chemisorption data, only 0.135×10^{15} active sites per square centimeter were measured. This discrepancy means that only 13% of surface molybdenum atoms chemisorbed CO. Previous work on CO chemisorption over molybdenum nitride compounds has led to the same results. Indeed, Ranhotra *et al.* (14) report accessing 16% of surface molybdenum atoms, Oyama and Schlatter 17% (15), Oyama *et al.* 12% (16), and Boudart and Volpe 23% which is the highest reported value (9). Similar observations have been made by Ranhotra *et al.* (14) for hydrogen chemisorption on γ-Mo_2N, as studied by NMR. Only 10% of the molybdenum atoms are titrated by hydrogen atoms (dissociative chemisorption). More recently, Choi *et al.* (11) have shown that over a reduced molybdenum nitride, 21% of the surface molybdenum atoms are covered over by atomic oxygen.

However, molybdenum oxynitrides are considered to be nonstoichiometric compounds. From elemental analysis of a molybdenum oxynitride pretreated in vacuum at high temperature (Table 2, sample C), it was found that the atomic ratio Mo/(N + O) was equal to 1/1.3. Because the XRD pattern of a molybdenum oxynitride (similar to γ-Mo_2N) is distinct from any other molybdenum nitride, there is, without any doubt, a lack of molybdenum atoms in the metal fcc lattice, as well as in the sublattice of the nonmetallic element (N). This has been observed by Gouin *et al.* (7) who determined a lower density for the MoO_xN_y ($d = 7$ g cm^{-3}) than for the stoichiometric γ-Mo_2N ($d = 9.48$ g cm^{-3}). A model for the structure of molybdenum oxynitride has been proposed in recent papers (17, 18). The nonstoichiometry in the metal lattice (lack of Mo atoms) can explain the low CO uptake observed in this and other works.

CONCLUSION

Because molybdenum oxynitride is a pyrophoric compound, a passivation step is necessary after nitridation to avoid bulk oxidation when contacting with air. However, passivated molybdenum oxynitrides have a high affinity for oxygen. Indeed, oxygen can diffuse into the pores and an apparent loss of the specific surface area is observed. Storage in vacuum is highly recommended for such compounds.

As illustrated in this work, water, ammonia, and oxygen, present on the surface, can lead to the same loss of accessibility of the surface area when physisorption (N_2) or chemisorption (CO) experiments are performed. To avoid such phenomena and recover all the specific surface by removing not only water and ammonia but also oxygen, a standard pretreatment in hydrogen at 693 K for 1 h was shown to be efficient.

Furthermore, this work showed clearly that both static (TGA) and dynamic (pulsed) techniques for CO chemisorption led to the same results under oxygen-free conditions. Indeed, even a very low concentration of oxygen (in pretreated helium, for instance) was found to suppress CO chemisorption.

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