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Molecular Precursor Route to Bulk and Silica-Supported $Nb_2Mo_3O_{14}$ Using Water-Soluble Oxo-oxalato Complexes

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The catalytically relevant $Nb_2Mo_3O_{14}$ phase has been prepared in bulk and silica-supported forms via the so-called "multiple molecular precursors method" from water-soluble oxo-oxalato complexes of Nb and Mo, $(NH_4)_3[NbO(ox)_3]\cdot H_2O$, and $(NH_4)_2[MoO_3(ox)]\cdot H_2O$. Thermal treatment of the mixed Nb–Mo precursor has been optimized for the formation of the pure $Nb_2Mo_3O_{14}$ phase, either as bulk oxide or a silica-supported phase with high specific surface area. A characterization of the bulk phase obtained via the conventional ceramic route has also been carried out and a comparison has been made with the precursors route. According to this route, the $Nb_2Mo_3O_{14}$ phase is shown to be formed in a pure form at 700 °C (i.e., 100 °C below the lowest temperature reported so far for the formation of the phase by the ceramic method). The supported samples have appreciable specific surface areas of 60–70 $m^2\ g^{-1}$, much larger than those reached in the previous attempts under vacuum in sealed vials. The SEM and EDX analyses reveal a high dispersion of the desired phase on the silica support.

I. Introduction

In recent years, multimetallic Nb-containing oxides have generated considerable interest in many fields because of their attractive physical or chemical properties. One of the most important features of these materials is their promising catalytic behavior in several highly challenging industrial processes, like alkane oxidation or ammoxidation.[1,2] Pure niobium pentoxide itself is a very selective catalyst for propane oxidative dehydrogenation (ODH) even though its catalytic activity is only moderate.[1−4] In recent years, it has been shown that associating niobium with elements such as vanadium, molybdenum, or antimony could considerably improve the catalytic activity while maintaining a high selectivity in such reactions.[2,5−11] Bulk or supported oxides from multicomponent systems such as Nb−V−Mo,[5,6,12] Nb−V−Mo−Sb,[13,14] and Nb(−V)−Mo−Te[7,8,15−18] are still under thorough investigation and huge efforts have been made to optimize their formulations or preparation methods to improve their catalytic performance. These catalysts are in general multiphasic, and the constituent phases are often poorly defined or even unknown. In particular, the Nb−Mo oxide system, investigated by Trunov et al.[19] and Ekström,[20,21] shows several phases of stoichiometries displaying increasing amounts of niobium: $Nb_2Mo_3O_{14}$, Nb_4MoO_{13}, $Nb_{14}Mo_3O_{44}$, Nb_8MoO_{23}, and $Nb_{12}MoO_{33}$. A molybdenum-

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rich $Nb_{0.09}Mo_{0.91}O_{2.80}$ phase is also known but should be considered to be a Nb-doped MoO_3 oxide.[21] Among these niobium and molybdenum-containing phases, the $Nb_2Mo_3O_{14}$ oxide is often detected in Nb−Mo−(M) catalysts, [5,6,12,18] and it was already mentioned in the literature as being moderately active in a bulk form for the ODH of ethane to ethene[5,6,22] or the conversion of propane into acrylic acid.[18] Until now, the $Nb_2Mo_3O_{14}$ phase has been obtained in a pure form typically by a thermal treatment above 700 °C in a closed quartz tube to prevent loss of molybdenum. This process unfortunately leads to a bulk oxide with a very low specific surface area.

This work is dedicated to the development of a novel route allowing the synthesis of the $Nb_2Mo_3O_{14}$ phase in a supported form. The idea is to use preisolated soluble molecular precursors, in which the metals are chelated by organic ligands, so that both metals will be incorporated in the samples. Ideally, these precursors must be compatible with each other, mainly from the point of view of solubility and thermal degradation. The advantages of this so-called multiple molecular precursors method are mainly (i) the formation of homogeneous materials resulting from the mixing at a molecular level of the metals, (ii) the formation of crystalline oxides under conditions significantly milder than those employed in the ceramic route, and finally, (iii) its potential application to the synthesis of supported samples by impregnation of a support with a solution of the starting complexes. Unfortunately, the limited availability of soluble niobium compounds complicates the preparation of Nb-containing bulk or supported phases via these precursor methods. We have recently validated this molecular precursors approach from peroxo complexes in aqueous medium for the syntheses of Nb−Ta, Nb−Ta−V, and Nb−Ta−Bi bulk oxides.[23]

Nb−Mo−O bulk oxides were prepared by Burch et al. from a freeze-dried solution of ammonium heptamolybdate, and niobium oxalate was formed in situ and calcined under the same conditions as in the ceramic method described above.[5,6] The pure $Nb_2Mo_3O_{14}$ phase was prepared by the ceramic route, from the corresponding binary oxides treated above 700 °C in an evacuated sealed quartz tube to prevent loss of molybdenum by volatilization.[12,24] In a previous paper, we described the use of peroxo compounds of niobium and molybdenum with carboxylato ligands as metal sources in an impregnation method for the preparation of silica-supported $Nb_2Mo_3O_{14}$ catalysts in an almost pure form.[24] Small amounts of molybdenum oxide, MoO_3, were still detected in the sample. Moreover, the drastic thermal treatment under vacuum considered in that work, similar to that used by Burch et al., combined with the use of silica, unfortunately resulted in samples with very low specific surface areas. The potential advantages of supporting the pure $Nb_2Mo_3O_{14}$ phase for its use in heterogeneous catalysis were thus lost in the method as used so far.

In the present work, we report the optimization of the previously described molecular precursors route to obtain the pure $Nb_2Mo_3O_{14}$ phase in a bulk form and in a silica-supported form. The improvement of the process concerns both the purity of the samples and, particularly, the preservation of most of the surface area of the silica support. A comparison between the bulk ternary oxide obtained by this precursors method and by the conventional ceramic method will also be given.

II. Experimental Section

Precursors. The molecular precursors used for oxide syntheses correspond to the oxo-oxalato complexes $(NH_4)_3[NbO(ox)_3]\cdot H_2O$ and $(NH_4)_2[MoO_3(ox)]\cdot H_2O$. The synthesis used for the niobium compound is that reported by Mathern et al.,[25] and the preparation method for the molybdenum complex has been adapted from the procedure of Xing et al. for the potassium derivative.[26] Both complexes are soluble in water and stable toward hydrolysis.

Oxalic acid, $H_2ox\cdot 2H_2O$ (Merck), ammonium oxalate, $(NH_4)_2ox\cdot H_2O$ (Merck), ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Acros Organics), and aqueous ammonia (25 wt % solution) were commercial products and were used as received. Niobic acid, $Nb_2O_5\cdot nH_2O$, was supplied from CBMM (Brazil).

Synthesis of $(NH_4)_3[NbO(ox)_3]\cdot H_2O$. Solid niobic acid (1 g) was added to an equimolar solution of $H_2ox\cdot 2H_2O$ (3 g, 21 mmol) and $(NH_4)_2ox\cdot H_2O$ (2.74 g, 21 mmol) in approximately 200 mL distilled water. After the mixture was stirred for 2 h at 80 °C, the solid was dissolved, and the solution was gently evaporated. The excess of oxalate ions precipitated first as the ammonium salt of the hydrogenooxalate. $(NH_4)Hox$ was filtered off and eliminated. The subsequent evaporation yielded a viscous solution (3−4 mL) which was then slowly cooled to room temperature, providing the complex as small white needles. These were filtered off and washed with acetone.

Synthesis of $(NH_4)_2[MoO_3(ox)]\cdot H_2O$. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (5 g, 4.05 mmol) and $(NH_4)_2ox\cdot H_2O$ (2.01 g, 14.2 mmol) were dissolved in 20 mL water and 5 mL ammonia. The clear solution was then stored at 5 °C. The complex appeared after a few days as small white needles, which were filtered off and dried in air.

Bulk $Nb_2Mo_3O_{14}$ Prepared by the Precursors Method. The oxo-oxalato complexes of Nb and Mo were dissolved simultaneously in distilled water according to the appropriate Nb/Mo proportion of 2/3. The resulting clear solution was then stirred at room temperature for 1h. The solvent was removed overnight by a freeze-drying process, and the mixed solid precursor obtained was calcined at different temperatures for several hours in flowing air.

Silica-Supported $Nb_2Mo_3O_{14}$ Prepared by the Precursors Method. The oxo-oxalato complexes of Nb and Mo were dissolved simultaneously in distilled water (Nb/Mo = 2/3). Silica (Merck, 345 $m^2\ g^{-1}$) was then added; the pH was adjusted to 1 with nitric acid (1 mol L^{-1}), and the suspension was stirred at room temperature for 2 h. Three different metal (Nb+Mo)/Si loadings were engaged: 5, 10, and 20 mol %. The solvent was removed overnight by a freeze-drying process, and the solid residue was calcined in flowing air under the optimal conditions determined by the tests carried out with the bulk oxides (i.e., at 700 °C for 2 h).

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Bulk $Nb_2Mo_3O_{14}$ Prepared by the Ceramic Method. The pure bulk $Nb_2Mo_3O_{14}$ phase was prepared by the ceramic route carried out in a closed system to prevent loss of MoO_3 by volatilization. A milled mixture of MoO_3 and Nb_2O_5 was heated at 800 °C for 6 h in an evacuated sealed quartz tube. This method has been described previously.[24]

Analysis. The transformation of the metal oxo-oxalato precursors into metal oxides was analyzed by thermogravimetric analyses using a Mettler Toledo TGA/SDTA851^e analyzer. The sample was heated at 10 °C min^{-1} in air (100 mL min^{-1}). ICP analyses were carried out by Medac LTD (United Kingdom). The bulk and silica-supported Nb−Mo oxides were characterized by X-ray diffraction, surface area measurements, SEM, and EDX analyses. Powder X-ray diffraction (XRD) measurements were carried out on a SIEMENS D-5000 diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å, step width = 0.1°). The samples were placed on quartz monocrystals, and the crystalline phases were identified by reference to the JCPDS-ICDD database. Specific surface areas were measured with a Micromeritics ASAP 2000 analyzer with nitrogen (supported samples) or krypton (bulk samples) at 77 K according to the Brunauer−Emmet−Teller (BET) method. The scanning electron microscopy (SEM) images were obtained on a DSM982 GEMINI microscope with 1 kV accelerating voltage. EDX analyses were performed on the same equipment coupled with energy-dispersive analyzer (accelerating voltage = 15 kV). X-ray photoelectron spectroscopy (XPS) measurements were carried out at room temperature on a SSI-X-probe (SSX-100/206) photoelectron spectrometer from FISONS using the Al Kα radiation ($E = 1486.6$ eV) and a sample holder. Charge effects were avoided by placing a nickel grid above the samples and using a flood gun set at 8 eV. The energy scale was calibrated with reference to the Au4$f_{7/2}$ peak at 84 eV, and the binding energies were calculated with respect to the C−(C,H) component of the C1s peak fixed at 284.8 eV. The intensity ratio I(Mo 3$d_{5/2}$)/I(Mo 3$d_{3/2}$) was fixed at 1.50, and the difference in binding energy between the two components of the Mo 3d doublet was fixed at 3.13 eV.

III. Results and Discussion

Characterizations of the Bulk $Nb_2Mo_3O_{14}$ Prepared by the Ceramic Method. The diffractogram of the sample treated in the sealed quartz vial proves that heating at 800 °C for 6 h under such conditions allows the formation of the dark green $Nb_2Mo_3O_{14}$ phase in pure form (Figure 1). The JCPDS file (number 18−840) used for the indexation refers to the $Nb_2Mo_3O_{11}$ formulation in which molybdenum displays the oxidation state (+IV), while the corresponding publication from Trunov et al.[19] refers to the $Nb_2Mo_3O_{14}$ stoichiometry, implying only Mo(VI). The ambiguity still remains in the literature as for the right formulation of this phase and authors always refer to this JCPDS file whether they mention the one stoichiometry or the other. ICP and XPS analyses of the prepared bulk sample were carried out and allow clarification of that point. The duplicated analyses on the bulk oxide provided mean Nb and Mo contents corresponding to 26.93 and 39.60%, respectively. These experimental percentages are in better agreement with the $Nb_2Mo_3O_{14}$ stoichiometry (Nb, 26.64%; Mo, 41.25%) in comparison with the calculated values for $Nb_2Mo_3O_{11}$ (Nb, 28.60%; Mo, 44.30%). Moreover, the XPS spectrum, illustrated in Figure 2, displays the binding energy range between 225 and 245 eV, in which the 3d photopeaks of molybdenum (+IV), (+V), and (+VI) are assumed to appear. Deconvolution of the spectrum reveals that molybdenum is present in the single oxidation state of (+VI). Observed Mo 3$d_{3/2}$ and 3$d_{5/2}$ binding energies, at 236.4 and 233.2 eV, respectively, are close to those in MoO_3 (235.9 and 232.8 eV). For comparison, the Mo 3$d_{5/2}$ binding energy values are 229.3 eV in MoO_2 and 231.6 eV in Mo_2O_5.[27] Although the XPS technique is a surface analysis method, the absence of any Mo(IV) or Mo(V) at the surface is circumstantial evidence of the $Nb_2Mo_3O_{14}$ stoichiometry.

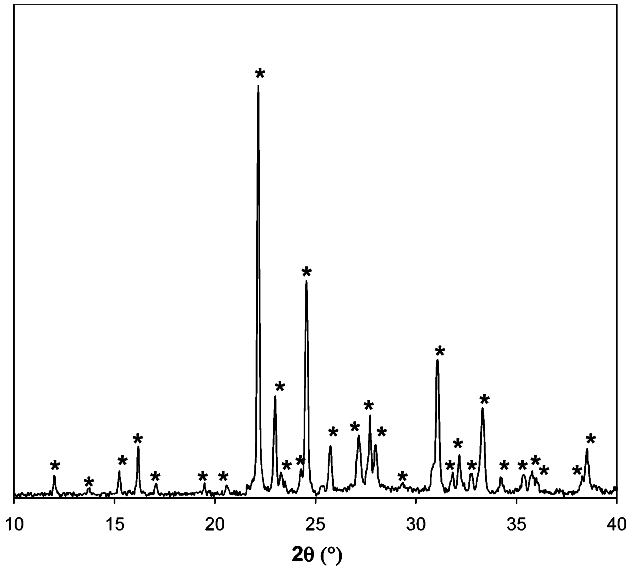

Figure 1. Diffractogram of the bulk oxide prepared by the ceramic route at 800 °C for 6 h: (*) $Nb_2Mo_3O_{14}$ (JCPDS file 18-840)).

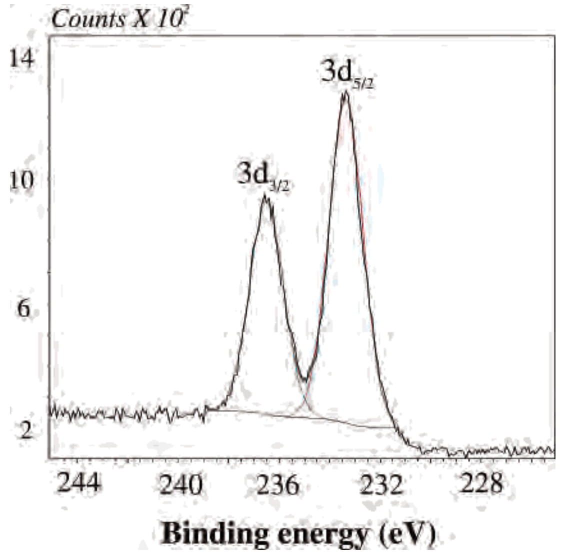

Figure 2. Mo 3d XPS spectrum of the bulk $Nb_2Mo_3O_{14}$ phase prepared by the ceramic route (800 °C for 6 h).

The specific surface area of the $Nb_2Mo_3O_{14}$ oxide prepared by the ceramic route at 800 °C for 6 h was measured with krypton and reaches only 1 m^2 g^{-1}. Figure 3 illustrates the SEM picture of the bulk $Nb_2Mo_3O_{14}$ prepared by the ceramic method (800 °C/6 h). The sample is quite crystalline and is

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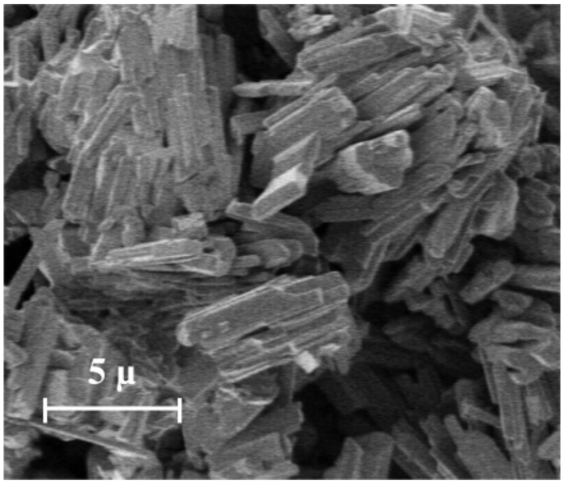

Figure 3. SEM picture of the bulk $Nb_2Mo_3O_{14}$ phase prepared by the ceramic route (800 °C for 6 h).

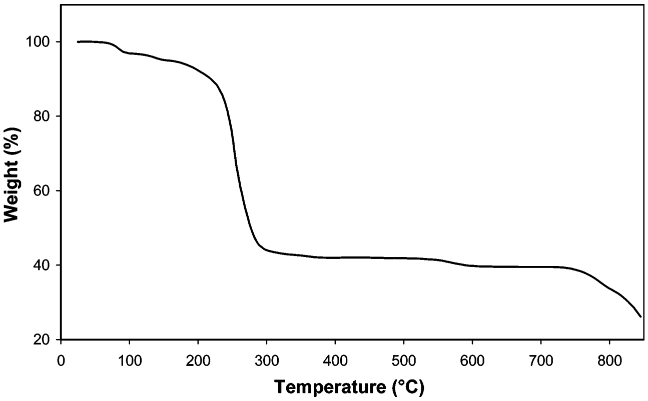

Figure 4. Thermogram under air of the Nb−Mo mixed oxo-oxalato precursor (10° min^{-1}).

Table 1. XRD and BET Results for the Nb−Mo Bulk Oxides Prepared from the Oxo-oxalato Precursors[a]

calcination temp	time	phases observed by XRD				S_{BET} (m^2 g^{-1})[c]
		$Nb_2Mo_3O_{14}$	MoO_3[b]	T-Nb_2O_5	H-Nb_2O_5	
600 °C	6 h	m	M	m	/	1.1
650 °C	6 h	m	M	m	/	1.1
700 °C	2 h	S	/	/	/	1.3
700 °C	6 h	M	/	/	m	1.3
750 °C	6 h	/	/	/	S	1.8

[a] M = major phase, m = minor phase, S = single phase, and / = unobserved phase. [b] MoO_3 often appears to be the major phase probably because of its high crystallinity. Its diffraction peaks are thus very intense in comparison with those occurring from the other phases even if they are present in equivalent amounts in the sample. The quantitative interpretation on the basis of the relative intensity of the peaks should thus be taken with caution. [c] Measurements performed with krypton.

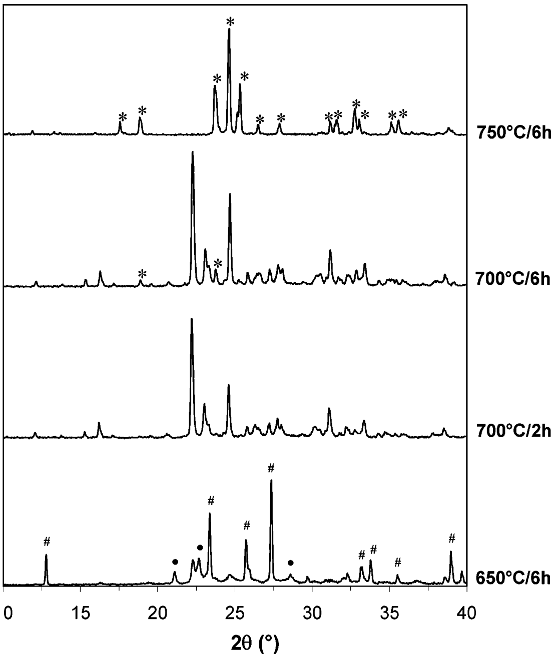

Figure 5. Diffractograms of the bulk Nb−Mo oxides obtained from the oxo-oxalato precursors by thermal treatment at 650 °C for 6 h, at 700 °C for 2 and 6 h, and at 750 °C for 6 h: (#) MoO_3 (JCPDS file 35-609), (*) H-Nb_2O_5 (JCPDS file 37-1468), (●) T-Nb_2O_5 (JCPDS file 30-0873), and the unindexed peaks correspond to $Nb_2Mo_3O_{14}$ (JCPDS file 18-840).

composed of stick-shaped particles of inhomogeneous sizes in the range of 2−5 μm.

Thermal Analyses of the Mixed Precursors. The thermogram of the mixed Nb−Mo oxalato precursor obtained after the freeze-drying process is illustrated in Figure 4. After the dehydration step around 100 °C, the precursor decomposes into oxide until a final temperature of 600 °C. When the temperature reaches ca. 750 °C, a progressive weight loss is observed and continues to 850 °C. This phenomenon is the result of the volatilization of molybdenum oxide in this temperature range. Consequently, the calcination of the mixed precursors was carried out at temperatures between 600 and 750 °C for 2 or 6 h.

Characterizations of the Bulk $Nb_2Mo_3O_{14}$ Prepared by the Precursors Method. Table 1 summarizes the calcination conditions, the crystalline phases observed by XRD for each treatment, as well as the BET specific surface areas determined for our bulk Nb−Mo oxides. Figure 5 displays the diffractograms obtained for each thermal treatment considered and illustrates the combined influence of calcination temperature and time.

Calcination of the mixed precursor at 600 °C yields the desired ternary phase in a small amount, together with both binary oxides, MoO_3 and T-Nb_2O_5 (orthorhombic). This precursor method allows the formation of the mixed $Nb_2Mo_3O_{14}$ phase at a temperature lower than that required by the ceramic method (700 °C minimum for its formation and 800 °C to obtain it in a pure form). When the temperature is raised to 650 °C, the amount of binary oxides decreases and the amount of the ternary phase increases. When the mixture is heated at 700 °C for 2 h, the sample only contains the $Nb_2Mo_3O_{14}$ phase in a pure form. These calcination conditions are thus the optimal ones to prepare the desired phase and will be used for the silica-supported samples.

Moreover, pure monoclinic H-Nb_2O_5 is formed as the thermal treatment continues at 700 °C. When the sample is treated at 700 °C for 2 days or 750 °C for 6 h, the obtained residue is composed of H-Nb_2O_5 only. These results are in agreement with the observations made by TGA which show that the sublimation of molybdenum oxide begins in that temperature region.

In conclusion, the $Nb_2Mo_3O_{14}$ phase is already partially formed when the mixed precursor is totally decomposed (600

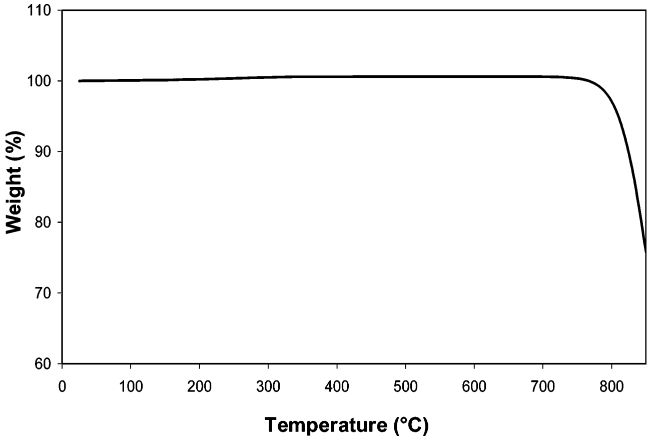

Figure 6. Thermogram under air of the bulk $Nb_2Mo_3O_{14}$ phase prepared by the ceramic method (10 °C min^{-1}).

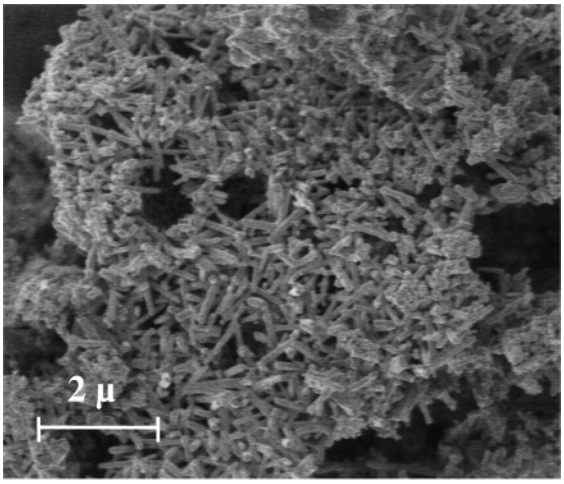

Figure 7. SEM images of the bulk $Nb_2Mo_3O_{14}$ phase prepared from the oxo-oxalato precursors (700 °C/2 h).

°C), and it becomes more and more abundant when the temperature increases up to 700 °C. However, this oxide is quite unstable once formed; it decomposes quite readily into its binary oxides with temperature and time. This was demonstrated by the TGA of the pure $Nb_2Mo_3O_{14}$ phase prepared either by the ceramic route or the precursors method; this oxide undergoes a weight loss near 740 °C, corresponding to its decomposition into *H*-Nb_2O_5 (evidenced by XRD) and MoO_3, which volatilizes (Figure 6).

A SEM image of the sample calcined at 700 °C for 2 h is displayed in Figure 7. The particles observed are smaller (~1 μm) than in the case of the $Nb_2Mo_3O_{14}$ oxide prepared by the ceramic method (Figure 3).

Characterizations of the Silica-Supported $Nb_2Mo_3O_{14}$ Prepared by the Precursors Method. Table 2 lists the XRD and BET results obtained for the silica-supported Nb−Mo samples treated at 700 °C for 2 h under flowing air and with the different metal loadings. Figure 8 illustrates the diffractogramms observed in each case.

The thermal treatment used allows the formation of the $Nb_2Mo_3O_{14}$ phase in a supported form, with a loading of 10 and 20 mol %, corresponding to ca. 25 and 50 wt %, respectively. There was no diffraction line detected in the case of the sample characterized by a loading of 5 mol %. This phenomenon is probably caused by the low amount of active phase on the support, combined with a high dispersion of the active phase.

Table 2. XRD and BET Results for the Nb−Mo Silica-Supported Oxides Prepared from the Oxo-oxalato Precursors Calcined at 700 °C for 2 h

metal loading (mol %)	phase observed by XRD	S_{BET} (m^2 g^{-1})[a]
20	$Nb_2Mo_3O_{14}$	61
10	$Nb_2Mo_3O_{14}$	70
5		275

[a] Measurements performed with nitrogen.

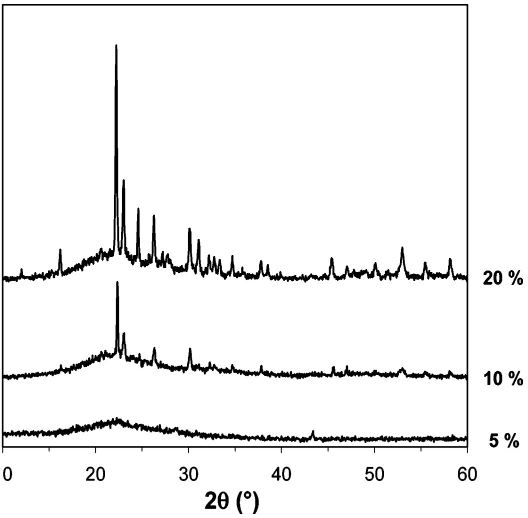

Figure 8. Diffractograms of the silica-supported Nb−Mo oxides obtained from the oxo-oxalato precursors (700 °C for 2 h).

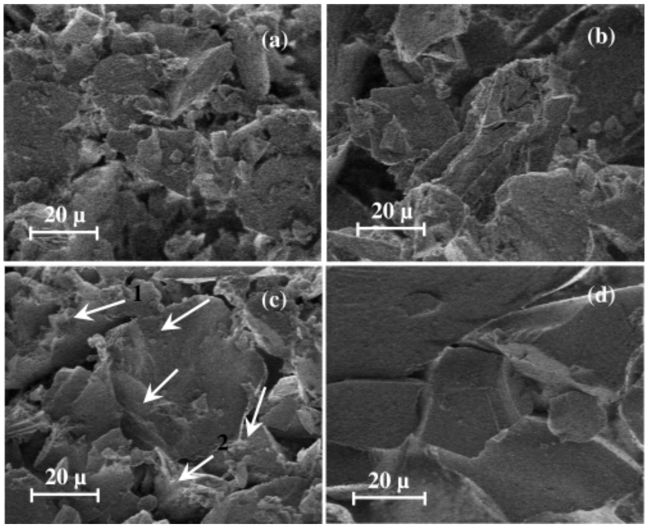

Figure 9. SEM images of the Nb−Mo silica-supported oxides prepared from the oxo-oxalato precursors (700 °C for 2 h) and characterized by a metal loading of (a) 5, (b) 10, and (c) 20 mol % and (d) SEM images of pure silica. Arrows on image c indicate the places where EDX (Figure 10) analyses have been performed.

The supported Nb−Mo oxides display relatively high specific surface areas, but they decrease when the metal loading increases. In the sample with 5 mol % in active metals, the specific surface reaches 275 m^2 g^{-1}. When the loading corresponds to 10 or 20 mol %, it decreases drastically to 70 and 61 m^2 g^{-1}, respectively, as a conse-

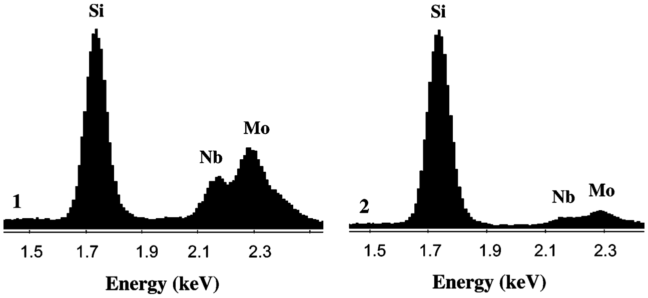

Figure 10. Examples of EDX analyses (Figure 9c, arrows 1 and 2) performed on the Nb−Mo-supported sample with the highest loading (20 mol %).

quence of the large amount of active phase on the support. A decrease in the surface area was expected.

SEM images of the pure silica and supported Nb−Mo samples are shown in Figure 9. The morphology of the oxides is not significantly different despite the loading. No particle with a morphology similar to that observed for the bulk $Nb_2Mo_3O_{14}$ prepared by the same precursors method (Figure 7) is observed on the surface of the support. Moreover, EDX analyses have been carried out at different places, indicated by the arrows in Figure 9c, on the more loaded sample (20 mol %). The EDX spectra displays, for each place analyzed, the simultaneous presence of Si, Mo, and Nb. Only some variations in signal intensity are observed between the spectra. Examples of analyses are shown in Figure 10. These results show the ability of the method used, namely, the multiple molecular precursors method in aqueous medium, to produce a well-dispersed active $Nb_2Mo_3O_{14}$ phase on the support.

IV. Conclusions

The pure $Nb_2Mo_3O_{14}$ phase has been prepared by the multiple molecular precursors method from water-soluble oxo-oxalato complexes $(NH_4)_3[NbO(ox)_3]\cdot H_2O$ and $(NH_4)_2[MoO_3(ox)]\cdot H_2O$. The optimization of the thermal treatment of the mixed Nb−Mo precursor allows the pure $Nb_2Mo_3O_{14}$ phase to be obtained in a bulk or supported form. According to this route, the $Nb_2Mo_3O_{14}$ phase is shown to be formed in a pure form at 700 °C (i.e., 100 °C below the lowest temperature reported so far for the formation of the phase by the ceramic method). The supported samples have appreciable specific surface areas of 60−70 $m^2\ g^{-1}$, much larger than those reached in the previous attempts under vacuum in sealed vials. The formation of this phase in a supported form, displaying, for the first time, a relatively high surface, opens new perspectives to understand its real role in catalytic reactions such as alkane ODH.

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