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One-step synthesis of dispersed bimetallic carbides and nitrides from transition metals hexamethylenetetramine complexes

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Abstract

Bimetallic nitrides and carbides Co(Ni)–Mo were obtained from the decomposition of transition metals complexes with hexamethylenetetramine (HMTA) under inert atmosphere. The precursor complexes were prepared by means of aqueous precipitation of ammonium molybdate with cobalt nitrate or nickel nitrate and HMTA. During the decomposition, HMTA acts at once as a reducing agent and as a source of carbon and nitrogen. The precursor's composition and the decomposition conditions are the key parameters to influence the nature of the obtained phases. The method developed provides a simple one-step way to highly divided bimetallic nitrides and carbides.

Keywords: Nitride; Cobalt; Molybdenum; Molecular precursor

1. Introduction

Transition metal carbides and nitrides are used in a wide range of applications due to their unique physical and chemical properties [1]. They are known for their hardness and very high melting points (Mo_2N, mp = 2223 K). They also exhibit high catalytic activity in different reactions including hydrogenation [2–4], hydrodesulfurization and hydrodenitrogenation [5–9]. Numerous methods for the synthesis of monometallic compounds have been developed but only few have been devoted to the synthesis of bimetallic transition metal nitrides and carbides.

The approaches, applied earlier to prepare bimetallic nitrides include: the reactions of a metal nitride with a metal or another metal nitride (usually Li_3N) at 1073–2073 K [1], decomposition of alkanolamine complexes precursors [10,11], that of the precursors resulting from freeze-drying of aqueous solutions of metal salts [12] or nitridation of metal oxides under reducing conditions (H_2/N_2) at 1273 K [13]. Bimetallic transition metal nitrides can also be obtained by ammonolysis of bimetallic metal oxides or chlorides at relatively low temperature. Thus, Bem et al. [14] prepared the bimetallic nitrides Fe_3Mo_3N and Ni_3Mo_3N from the oxides $FeMoO_4$ and $NiMoO_4$ at 973 and 1073 K. The ammonolysis of $FeWO_4$ and $MnMoO_4$ resulted in the synthesis of layered hexagonal bimetallic nitrides $FeWN_2$ and $MnMoN_2$ [15]. Yu et al. prepared new bimetallic oxynitrides with a cubic face centered structure using this method [16]. Mc Candlich et al. [17] decomposed precursors obtained from molybdic acid and ethylenediamine under an inert atmosphere which resulted in the formation of a molybdenum oxycarbonitrides. Kugler et al. [18] also used this method to prepare ETA phase of bimetallic nitrides and carbides $X_6Y_6Z_a$ (X = Mo, W; Y = Co, Ni, Fe, Z = C, N; $1<a<2$). All these techniques lead to the bulky materials with low specific surface areas.

Recently in our laboratory, highly dispersed Mo_2N was prepared by decomposition of a molybdate hexamethylenetetramine (HMTA) precursor [19]. This approach was also recently extended to the preparation of bulk and supported

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bimetallic molybdenum nitrides [20]. We are studying the preparation of highly dispersed bimetallic transition metal nitrides and carbides using this route for eventual catalysis applications. The precursors are cobalt and nickel molybdenum complexes with HMTA which is used as a nitrogen and carbon source. In the present work, we focus the discussion on the influence of the precursor and the decomposition conditions on the properties of the obtained materials.

2. Experimental

2.1. Synthesis of the precursors

Precursor complexes were obtained by combining aqueous solutions of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) with cobalt nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$), or cobalt acetylacetonate hydrate ($Co(C_5H_7O_2)_2\cdot xH_2O$) and HMTA ($N_4(CH_2)_6$) under stirring. Table 1 gives the conditions of preparation and the composition of the complexes synthesized. The ligand content can not be determined in the CoMo complexes prepared from cobalt acetylacetonate as C and N in the samples also come from acetylacetonate ($C_5H_7O_2$) and from ammonium cations (NH_4^+), respectively. As a consequence the carbon to molybdenum and cobalt ratio (C/(Mo+Co)) is used to perform comparison between samples instead of the HMTA to molybdenum and cobalt ratio (HMTA/(Co+Mo)). Complexes synthesized from cobalt nitrate or nickel nitrate were prepared as follows. The solutions were kept under stirring for 24 h at room temperature and then centrifuged at 4000 rounds/min during 10 min to separate the precipitates. The precipitates were washed with distilled water and dried under nitrogen flow overnight at 373 K. The CoMo complex synthesized using cobalt acetylacetonate precursor instead of nitrate were also stirred for 24 h and the precipitates thus obtained were filtered under vacuum and washed with water instead of being centrifuged. The samples were then dried under vacuum at room temperature.

2.2. Synthesis of the dispersed bimetallic carbides and nitrides

Nitrides and carbides were prepared by thermal decomposition of the precursors under flowing nitrogen. Approximately, 1 g of the precursor was placed in a quartz reaction tube. The precursor heated in a gas flow from

Table 1
Composition of the precursors and properties of the materials obtained by their decomposition under nitrogen at different temperatures

Sample	Precursor	Atomic ratios in solution		Atomic ratios in the solid		T (K)	XRD phases	S_{BET} (m^2/g)
		X/Mo	C/(X+Mo)	X/Mo	C/(X+Mo)			
$CoMo_1$	$Co(NO_3)_2$	0.5	24	0.5	2.4	823	Amorphous	132
						923	Mo_2N, Co_3Mo_3N	90
						1073	Mo_2N, Co_3Mo_3N	8
$CoMo_2$	$Co(NO_3)_2$	1	8.2	0.76	1.2	823	Amorphous	120
						923	Co_3Mo_3N, εMoO_2	110
						1073	Co_3Mo_3N, εMoO_2	8
$CoMo_3$	$Co(NO_3)_2$	1	15	1	3.24	923	Co_3Mo_3C, Co, Mo_2C	2
						1073	Co_3Mo_3C	—
$CoMo_4$	$Co(NO_3)_2$	1	24	1	5	923	Mo_2C, Co	—
						1073	Co_3Mo_3C, Mo_2C, Co	—
$CoMo_5$	$Co(NO_3)_2$	3	36	2.4	15.6	923	Co, Mo_2C	34
						1073	Co, Mo_2C	—
$CoMo_6$	CoAcac	1	15	0.99	3.5	823	Co	—
						923	Co_3Mo_3N, εCo	120
						1073	Co_3Mo_3N	—
$CoMo_7$	CoAcac	1	30	1	5.8	923	Co, Mo_2C, Co_3Mo_3N	39
						1073	Co_3Mo_3C, Co_3Mo_3N	—
$NiMo_1$	$Ni(NO_3)_2$ (solution not stirred)	0.5	32	0.25	1.44	823	Amorphous	167
						923	MoO_2,	112
						1073	Mo_2N,Ni_2Mo_3N	14
							MoO_2, Mo_2N,Ni_2Mo_3N	
$NiMo_2$	$Ni(NO_3)_2$	0.5	32	0.47	2.2	823	Amorphous	119
						923	Ni_2Mo_3N, Mo_2N	
$NiMo_3$	$Ni(NO_3)_2$	0.66	78	0.60	5	923	Ni_2Mo_3C, Mo_2C	10

(X = Ni, Co); CoAcac = cobalt acetylacetonate.

room temperature to 823, 923 or 1123 K (heating rate 10 K/min). The temperature was held at the target temperature for 2 h, and then the material was cooled quickly by removing the quartz tube from the furnace. After being cooled, the material was passivated for 2 h in a flowing stream of nitrogen saturated with water. Passivation was performed to prevent bulk oxidation of the materials.

2.3. *Characterization of solids*

X-ray diffraction (XRD) patterns were obtained on a BRUKER diffractometer using Cu$K\alpha$ emission. The diffractograms were analyzed using the standard JCPDS files. Surface area was measured using low temperature adsorption of nitrogen and calculated according to BET equation. Scanning electron microscopy (SEM) images were obtained on a Hitachi S800 device, at the center of electronic microscopy of Claude Bernard University (Lyon). High resolution transmission electron microscopy (HREM) was done on a JEOL 2010 device, using 200 kV accelerating voltage.

The gases emitted during the decomposition were monitored using a quadrupole mass spectrometer (VG Quadrupole Fisons Instruments) working in the Faraday mode. Ammonia and water were qualitatively analyzed at $M/z = 15$ and 18, respectively. Since the OH fragment has the same M/z value as molecular ion of ammoniac, the last was identified by the signal at $M/z = 15$. Nitrogen and carbon monoxide were monitored by $M/z = 28$. The emission of nitrogen could be distinguished from that of CO by the different intensity of signal with $M/z = 14$ and by the presence the isotope 29 of nitrogen. Carbon dioxide and nitrogen monoxide were analyzed by $M/z = 44$ and 30, respectively.

Thermal analysis was carried out on an SETARAM, Setsys Evolution 12 Model device under nitrogen. Chemical composition of the complexes and decomposition products was determined by plasma atomic emission method (ICP). Laser Raman spectra were measured on an HORIBA spectrometer using the 514.53 nm line of an Ar laser. The power on samples was 1 mW. The spectra were recorded at room temperature. The decomposition was undertaken in an in situ cell heated under nitrogen.

3. Results and discussion

Mixing of the ammonium heptamolybdate, cobalt or nickel salt and HMTA solutions leads to the immediate precipitation of pink-purple (cobalt) or light-green (nickel) powders of the complexes. These solids (precursors) are all sparsely soluble in water and contain submicrometric size crystallites of variable shape. The quality of the XRD patterns did not allow indexing of the elementary cells of these complexes. However, it can be inferred from the XRD that the solids do not contain any (known) monometallic Co(Ni) and Mo complexes with HMTA, neither any other known compounds of these elements. The solids obtained represent therefore new compounds containing mixed complexes of VIII and VI group metals with HMTA.

Chemical composition of the precipitates depends on the X/Mo (X = Co, Ni) ratios and on the C/(X+ Mo) ratios in the solutions (Table 1). Complexes with X/Mo ratio 1 for Co and that of 0.66 for Ni were at first of the principal interest since the metals atomic ratios in them correspond to those in the known bimetallic carbides and nitrides like Co_3Mo_3N, Co_3Mo_3C, Ni_2Mo_3N and Ni_2Mo_3C. Organic precursors with such X/Mo would lead to pure bimetallic nitride.

It was one of our main goals in this study to obtain pure phases. Therefore, it was important to get stoichiometric (Ni)Co/Mo ratios in the precursors. We observed that at sufficiently large HMTA excess, both elements are quantitatively bound within the precipitate. Therefore, the composition of the precipitate corresponds well to that of the reaction mixture. Therefore, 1:1 Co:Mo or 2:3 Ni:Mo ratios in the complexes were obtained with good precision of the elements stoichiometry.

We did not carried out a special study of the influence of aqueous Co and Mo concentrations on the precipitate composition. However, a brief preliminary study showed that the contents should be high enough to provide good precipitation yields. The, higher is the content the better is the yield. As follows from the results of chemical analysis, both transition metals introduced in the reaction mixture at 0.1 M concentration were quantitatively bond within the precipitate by the excess of HMTA. The Raman spectra of a CoMo complex ($CoMo_1$), and HMTA are presented in Fig. 1. The LRS spectra of the complexes show the bands characteristics of the ligand HMTA and the band at 1050 cm^{-1} which can be ascribed to the N=O vibrations in the NO_3^- anions. Other bands are observed between 800 and 1000 cm^{-1} which correspond to the Mo=O double bond vibrations of molybdates. The presence of the Anderson phase $(NH_4)_3H_6NiMo_6O_{24}$ is observed in the case of the NiMo complexes (not reported here) ascertained by the presence of the band at 580 cm^{-1} characteristic of ν(Ni–O–Mo) vibration. It can be concluded from these characterizations that the bimetallic complexes are new compounds not studied before.

3.1. *Bimetallic nitrides Co–Mo–N and Ni–Mo–N*

The decomposition of complexes was conducted under argon or nitrogen atmosphere. It has been ascertained that N_2 does not act as a nitriding agent at the temperatures used here. Indeed, the comparison of the chemical composition of nitrides prepared under nitrogen and those prepared under argon does not show significant differences. Table 1 gives phase composition and BET surface areas of the solids obtained by decomposition of various complexes. It appears that depending on the processing conditions and the complex composition, the

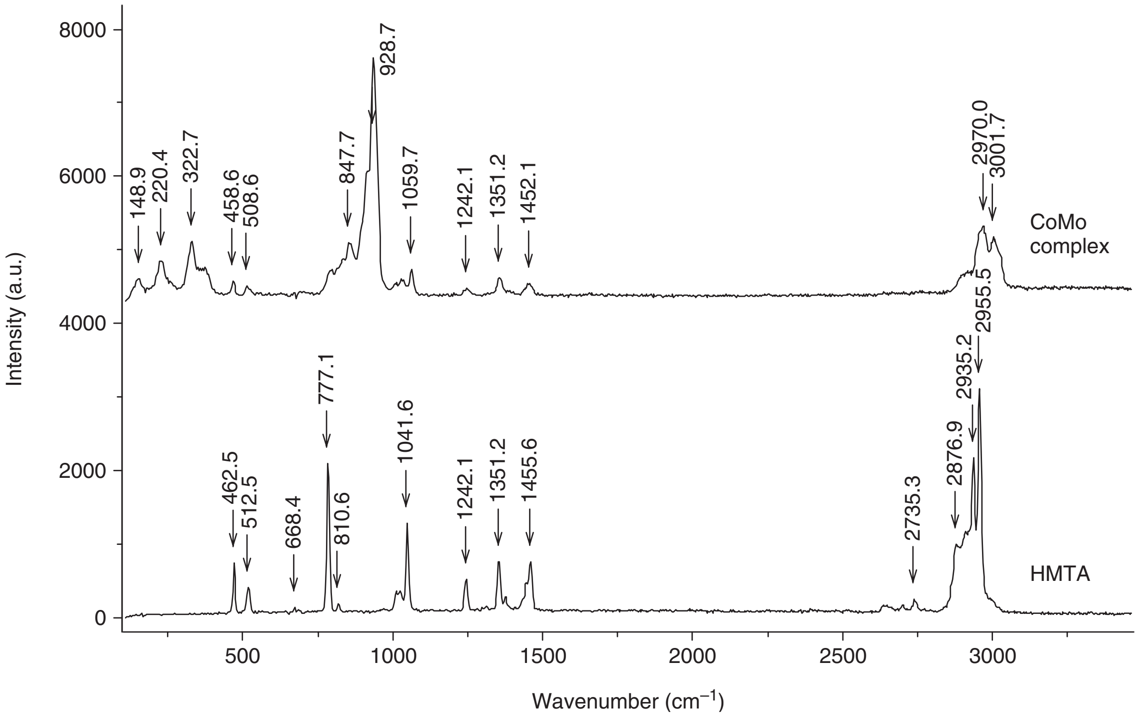
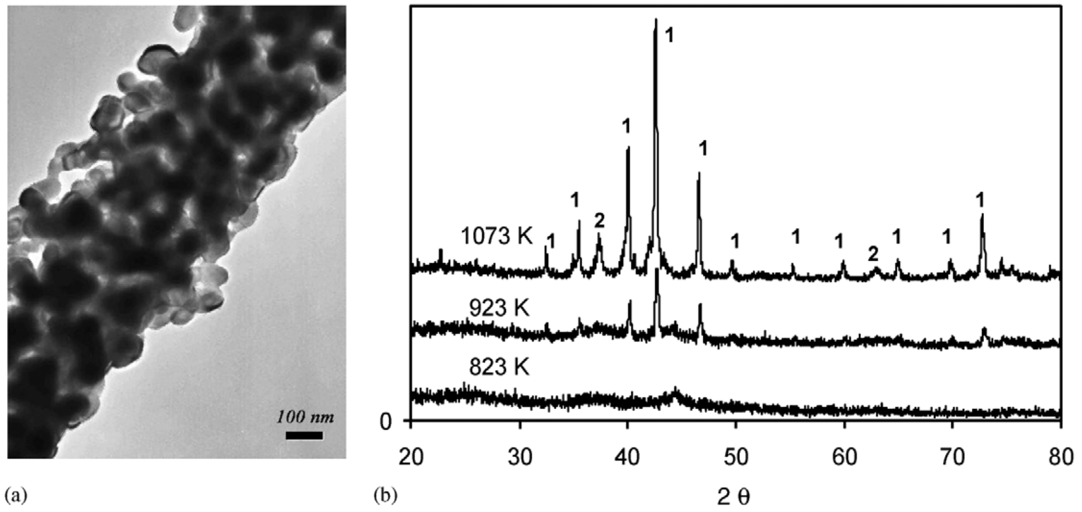


Fig. 1. Raman spectra of hexamethylenetetramine ligand (HMTA) and a bimetallic complex ($CoMo_1$).



(a) (b)

Fig. 2. TEM micrograph of the nitrides prepared at 1073 K (a) and XRD patterns of the solids obtained by decomposition of $CoMo_1$ at 823, 923 and 1073 K. Peaks labels: (1) Co_3Mo_3N; (2) Mo_2N.

decomposition of complexes enables the formation of bimetallic nitrides or carbides.

The synthesis of bimetallic CoMo nitrides with high surface area could be achieved by decomposition of a CoMo complex prepared from cobalt nitrate ($CoMo_1$, Table 1) which yielded a mixture of Co_3Mo_3N and Mo_2N as evidenced by XRD (Fig. 2). Chemical compositions of the specimens prepared at various temperatures (823, 923 and 1073 K) are shown in Table 2. This table reveals that carbon and nitrogen contents decrease with increasing temperature, the impurities contents of nitrides prepared at 923 and 1073 K being very low. SEM images of the precursor $CoMo_1$ showed rodlike particles (Fig. 3). After decomposition the large scale morphology of the particles remained unchanged. Co_3Mo_3N particles could be observed by TEM and distinguished from those of Mo_2N by EDX analysis. Mo_2N particles are difficult to observe because of their small size (3–4 nm) (Fig. 4a) and could only be identified on the periphery of bigger Co_3Mo_3N particles which have sizes up to 30–40 nm (Fig. 4b) (Fig. 5).

Ni–Mo–N nitride was obtained by the decomposition of a NiMo complex prepared from nickel nitrate with Ni/Mo = 0.25 (Table 1, NiMo1 solid). The decomposition led to a mixture of Ni_2Mo_3N, Mo_2N and MoO_2, as shown by

Table 2
Chemical composition of bimetallic nitrides obtained from the decomposition of CoMo1 at various temperatures under nitrogen (10 K/min, dwell 2 h)

T (K) of decomposition	N (wt%)	C (wt%)	XRD	Composition
823	4.38	3.59	Amorphous	$MoCo_{0.53}C_{0.52}N_{0.55}O_x$
923	3.82	<0.3	Co_3Mo_3N	$MoCo_{0.53}C_{0.03}N_{0.38}O_x$
1073	3.76	<0.3	Co_3Mo_3N,Mo_2N	$MoCo_{0.52}C_{0.03}N_{0.36}O_x$ $(Co_3Mo_3N)_{0.18}(Mo_2N)_{0.23}$ $C_{0.03}O_x$

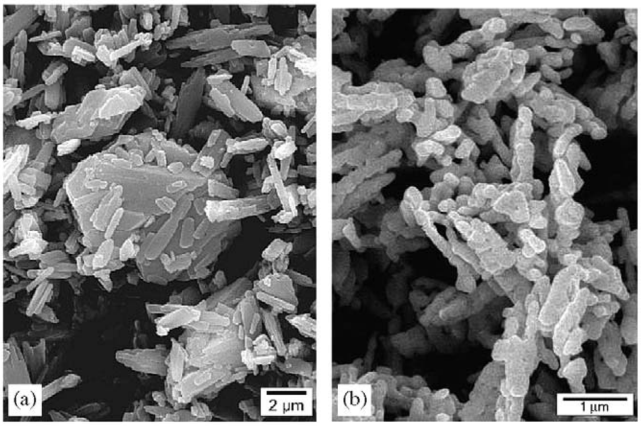


Fig. 3. SEM image of the precursor $CoMo_1$ (a) and SEM image of nitrides Co_3Mo_3N and Mo_2N obtained after decomposition of $CoMo_1$ under argon at 923 K (b).

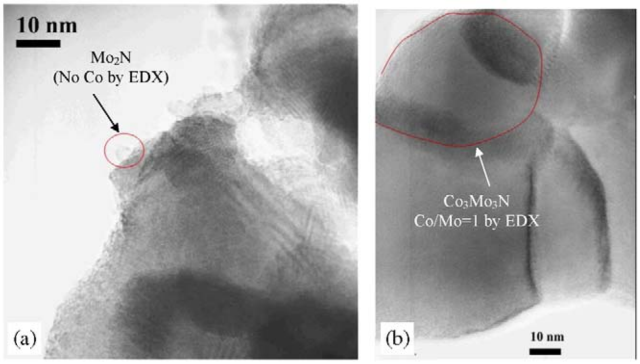


Fig. 4. TEM micrographs of nitrides obtained by decomposition of $CoMo_1$: Mo_2N particle (a) and Co_3Mo_3N particle (b).

XRD (Fig. 6). Similarly to the behavior observed for Co–Mo–N nitrides, the carbon and nitrogen contents decreased as the temperature of decomposition increases (Table 3). The particles of Ni_2Mo_3N could be observed by TEM, as shown in (Fig. 6a), and identified with EDX analyses. These particles are bigger (80–60 nm) than MoO_2 and Mo_2N particles (10–20 nm) (Fig. 7b).

Fig. 6 shows a TEM micrograph of the bimetallic nitrides (big particle) dispersed among monometallic nitrides (small particle).

Overall, dispersed bimetallic nitrides are obtained in both cases from complexes prepared on the base of nickel and cobalt nitrates, but the X/Mo (X = Co or Ni) atomic ratios in the corresponding precursors do not allow obtaining pure Ni_2Mo_3N and Co_3Mo_3N phases. To prepare single phase specimens of target bimetallic nitrides, acetylacetonate precursors should be applied (CoMo6) which led to the Co_3Mo_3N as a single phase at 1023 K. However, the decomposition at lower temperature (923 K) gave a mixture of metal cobalt and bimetallic nitride Co_3Mo_3N (Fig. 8). The formation of pure Co_3Mo_3N is achieved at higher temperature when using cobalt acetylacetonate instead of cobalt nitrate. The chemical analysis (Table 4) shows that the carbon level in this material is higher than the carbon content in the nitrides obtained from $CoMo_1$. It seems likely that a high carbon content prevents the formation of Co_3Mo_3N explaining thus the presence of metal cobalt at 923 K. SEM images of the complex before and after thermal decomposition showed a significant modification of the precursor after decomposition (Fig. 9). TEM micrographs of the bimetallic nitride Co_3Mo_3N prepared at 1073 K present well-crystallized agglomerated bulky particles (Fig. 9). Analysis of the interplane distances and numeric diffraction on the HREM images confirm that the particles observed are those of Co_3Mo_3N compound.

3.2. Bimetallic carbides Co–Mo–C and Ni–Mo–C

Decomposition of other complexes obtained from cobalt nitrate and nickel nitrate ($CoMo_3$, $CoMo_4$, $CoMo_5$ and $NiMo_3$, Table 1) as well as from cobalt acetylacetonate ($CoMo_7$, Table 1) gave rise to the formation of bimetallic carbides Co_3Mo_3C and Ni_2Mo_3C, monometallic carbide Mo_2C and metallic cobalt or nickel with low surface areas instead of the nitrides previously observed. Fig. 10 shows the HREM micrograph of a Co_3Mo_3C particle, allowing to identify this phase from the numeric diffraction. The nature of the phases prepared depends on 2 parameters: the temperature of the thermal decomposition and the ligand loading in the starting material.

Thus, the decomposition of $CoMo_3$ at 923 K gave rise to the formation of a mixture of Co_3Mo_3C, Mo_2C and Co. The same precursor yielded pure Co_3Mo_3C when heated to 1073 K. From the XRD study it follows that metallic cobalt reacts with monometallic carbide Mo_2C to form the bimetallic carbide Co_3Mo_3C.

When comparing the decomposition of complexes with the same ratio Co/Mo (Co/Mo = 1), it appears that the nature of the phases obtained at a specified temperature depends also on the ligand content in the precursor (Table 1). Thus, the decomposition of $CoMo_3$ (Co/Mo = 1, C/(Co + Mo) = 3.24) at 923 K yielded 3 phases: Co, Mo_2C, Co_3Mo_3C, whereas CoMo4 (Co/Mo = 1, C/(Co + Mo) = 5) gave rise to the synthesis

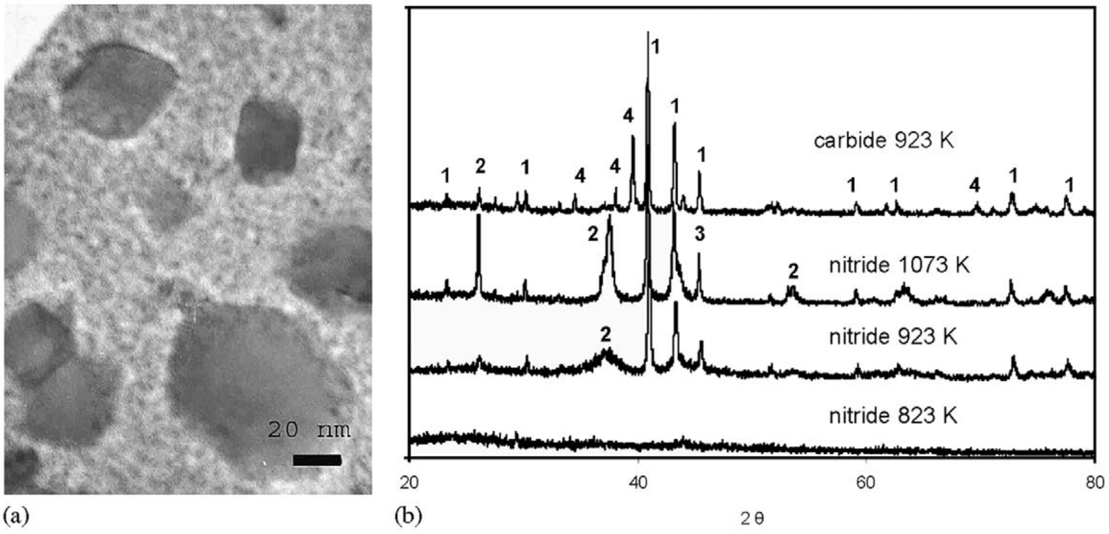


Fig. 5. TEM micrograph of the NiMo nitrides prepared at 923 K (a) and XRD patterns of the NiMo solids: nitrides obtained by decomposition of NiMo1 specimen at 823, 923 and 1073 K and carbides obtained from the $NiMo_3$ solid at 923 K (b). Peaks labels: (1) Ni_2Mo_3N, (2) MoO_2; (3) Mo_2N (4) Mo_2C.

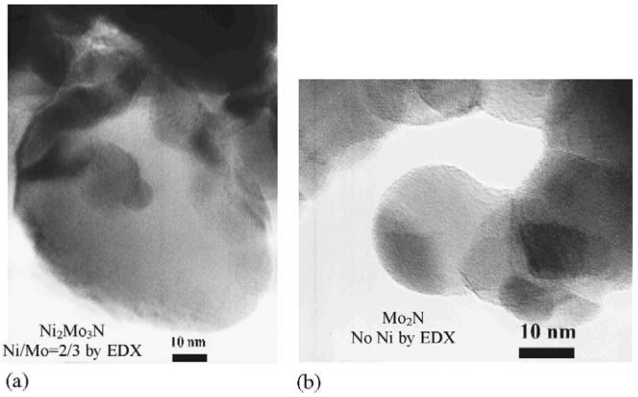


Fig. 6. TEM micrographs of nitrides obtained by decomposition of NiMo1: Ni_2Mo_3N particle (a) and Mo_2N particles (b).

Table 3
Chemical composition of bimetallic nitrides obtained from the decomposition of $NiMo_1$ at various temperatures under nitrogen (10 K/min, dwell 2 h)

T (K)	*N* (wt%)	*C* (wt%)	XRD	Composition
823	4	2.5	Amorphous	$MoNi_{0.3}N_{0.47}C_{0.35}O_x$
923	3.7	3.13	Ni_2Mo_3N,Mo_2N,MoO_2	$MoNi_{0.25}N_{0.38}C_{0.04}O_x$
1073	4	<0.3	Ni_2Mo_3N,Mo_2N,MoO_2	$MoNi_{0.25}N_{0.37}C_{0.03}O_x$ $(Ni_2Mo_3N)_{0.12}(Mo_2N)_{0.25}$ $(MoO_2)_{0.125}C_{0.03}$

of Co and Mo_2C at the same temperature. At 1073 K, $CoMo_3$ led to the formation of Co_3Mo_3C as a single phase whereas $CoMo_4$ decomposed to the mixture of Co, Mo_2C and Co_3Mo_3C.

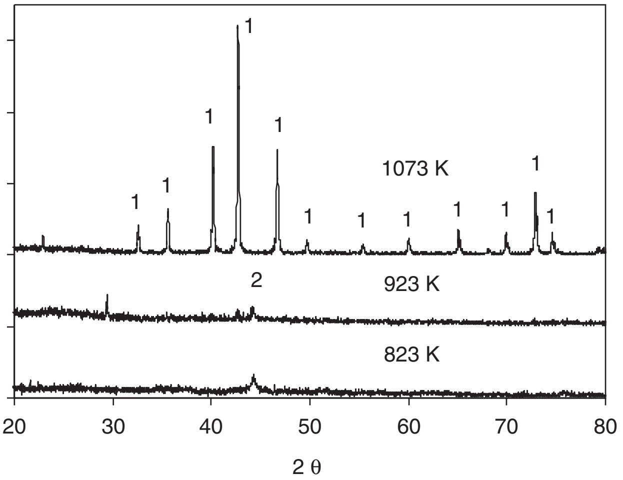


Fig. 7. XRD patterns of (1) Co_3Mo_3N and (2) Co obtained by decomposition of $CoMo_6$ at 823, 923 and 1073 K.

As follows from the XRD study, the mechanism of formation of bimetallic carbides and nitrides seems to be stepwise. First, at relatively lower temperatures, an intimate mixture of poorly dispersed molybdenum carbide (nitride) and the corresponding VIII group metal is obtained. Then, when the temperature is further raised, the solid solid reaction occurs between them, producing bimetallic nitride, as follows:

$$3Mo_2N + 6Co \Rightarrow 2Co_3Mo_3N + 1/2N_2.$$

Such a reaction has been also suggested in the case of the mechanochemical synthesis of the bimetallic nitrides [20].

The temperature at which Co reacts with Mo_2C increases as the HMTA content increases, because more abundant carbonaceous matter prevents the interaction of particles. Therefore, for the precursors with lower HMTA content

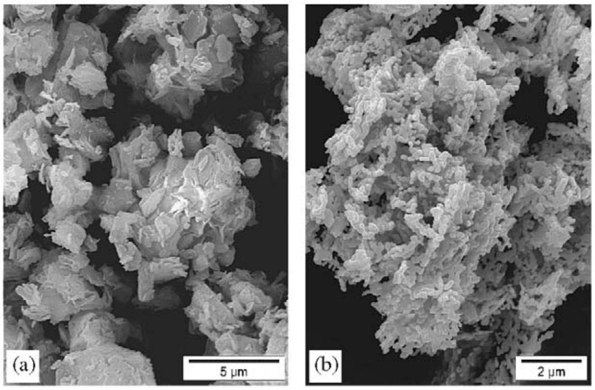
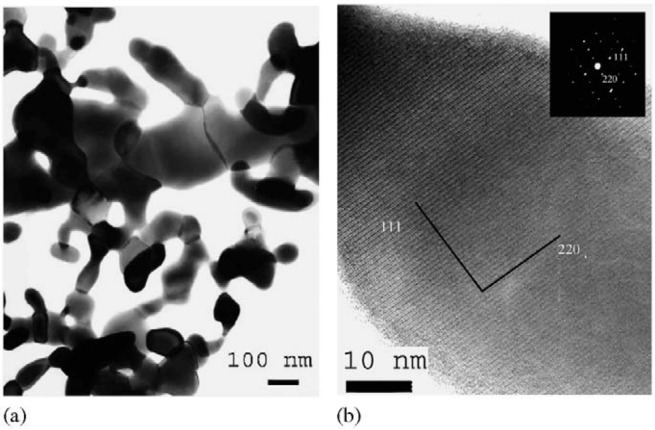


Fig. 8. SEM micrographs of a CoMo complex ($CoMo_6$) prepared from cobalt acetylacetonate before decomposition (a) and after decomposition (b) at 1123 K under N_2.

Table 4
Chemical composition of bimetallic nitrides obtained from the decomposition of $CoMo_6$ at various temperature under nitrogen (10 K/min, dwell 2 h)

T (K) of decomposition	N (wt%)	C (wt%)	XRD	Composition
823	2.3	5.2	Co	$MoCoC_{0.95}N_{0.35}O_x$
923	2	2.5	Co_3Mo_3N,Co	$MoCoC_{0.4}N_{0.29}O_x$
1073	2.8	<0.3	Co_3Mo_3N	$MoCoC_{0.03}N_{0.3}O_x$ $(Co_3Mo_3N)_{0.3}C_{0.03}O_x$



(a) (b)

Fig. 9. TEM micrographs of Co_3Mo_3N obtained from decomposition of a CoMo complex prepared from cobalt acetylacetonate at 1073 K, 40,000 × (a) and 800,000 × (b).

we observed formation of bimetallic carbide single phase at relatively lower temperatures.

3.3. Decomposition of complexes studied by mass spectrometry, thermal analysis and in situ Raman spectroscopy

Different nature of the phases from the decomposition of HMTA complexes might be related to the change of the decomposition mechanism. To verify whether this is really the case, the decomposition of two bimetallic CoMo complexes ($CoMo_1$ and $CoMo_3$, Table 1) both prepared from cobalt nitrate, have been followed by mass spectrometer and TGA-DTA. The curves relative to the decomposition of $CoMo_3$ (Co/Mo = 1) yielding Co_3Mo_3C at

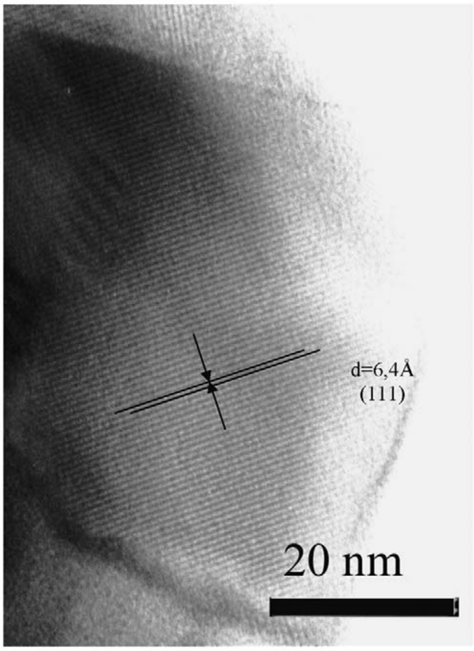


Fig. 10. TEM micrograph of Co_3Mo_3C obtained at 1073 K; 800,000 × .

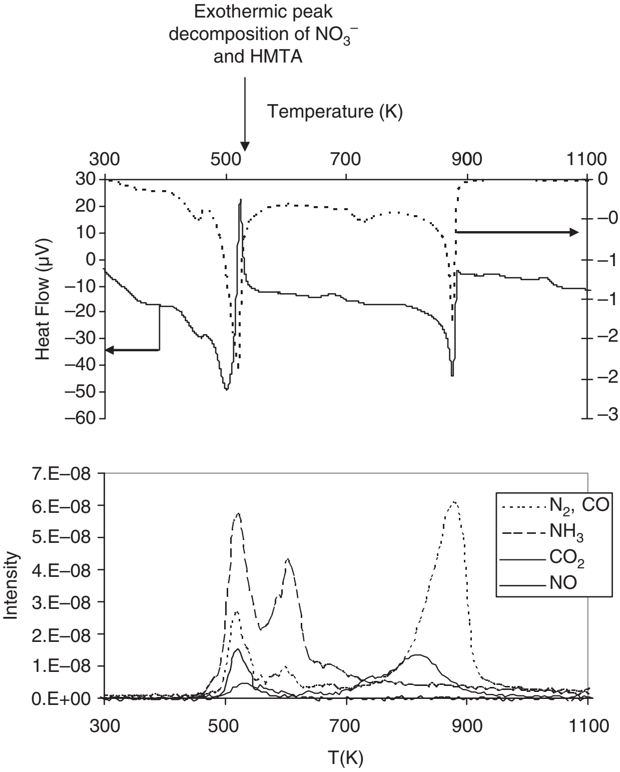


Fig. 11. Thermal decomposition of $CoMo_3$ at 10 K/min followed by mass spectrometry, TGA and DTA.

1073 K are given Fig. 11. An endothermic peak is observed at 470 K attributed to small the formation of quantities of H_2O, not observed by mass spectrometry. The decomposition of HMTA is observed with an endothermic peak at 505 K and is followed by the exothermic decomposition of NO_3^- at 525 K with a rapid weigh loss. Mass spectrometry shows the simultaneous emission of NH_3, CO, N_2 and NO. The final weight loss (endothermic peak at 820 K) can be ascribed to the emission of CO and CO_2 and to crystallization of the sample.

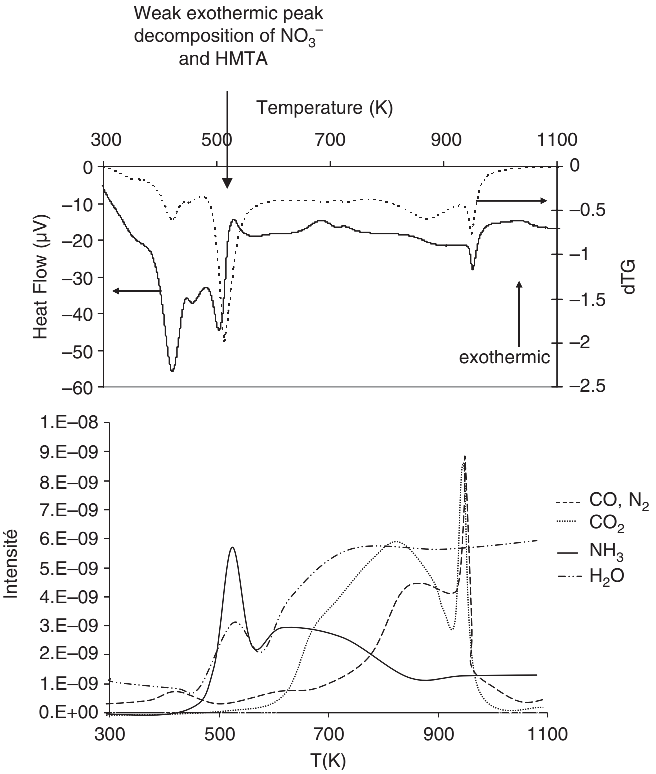


Fig. 12. Thermal decomposition of $CoMo_1$ at 10 K/min followed by mass spectrometry, TG and DTA.

The DTA curves of the decomposition of a CoMo complex ($CoMo_1$,Co/Mo = 0,5) (Fig. 12), leading to Co_3Mo_3N and Mo_2N at temperatures higher than 923 K, also show endothermic peaks at 425 and 460 K attributed to the release of small amount of H_2O, which is not observed by mass spectrometry. Decomposition of HMTA is again observed with an endothermic peak at 507 K and the emission of NH_3 and CO_2 with rapid weigh loss. However, contrarily to the $CoMo_3$ specimen, only a small exothermic peak is then observed at 535 K and no emission of NO is seen by mass spectrometry (Fig. 12).

The decomposition of the $CoMo_3$ complex was also followed by in situ Raman spectroscopy under N_2 (Fig. 13). The spectra showed that the intensity of LRS lines of the CoMo complex drops down abruptly between 423 and 523 K, which is in good agreement with the phenomena observed by TGA and mass spectrometry. After decomposition, we can observe a large band between 1200 and 1600 cm^{-1} probably due to the vibrations of C–N or C–H bonds in the material. At the same time the intensity of the lines in the region 800–1000 cm^{-1} dropped down, due to both decrease of the material crystallinity and

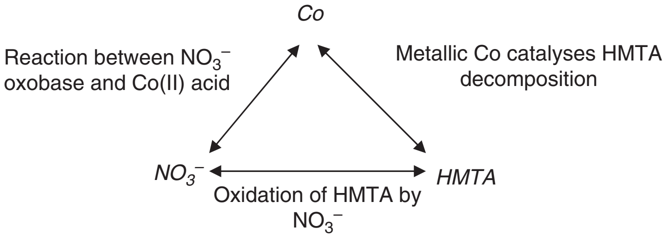


Fig. 14. Scheme illustrating triple interaction between HMTA, NO_3^- and Co during the decomposition.

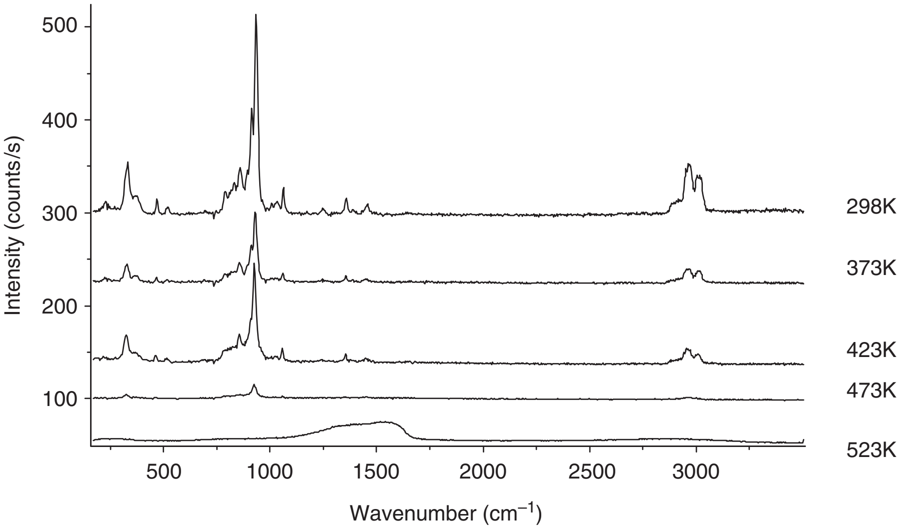


Fig. 13. In situ Raman spectra obtained during decomposition of a CoMo complex prepared from cobalt nitrate.

the reduction of Mo(VI) species to Mo(IV) and further to the nitride (Fig. 14).

3.4. Parameters governing the decomposition

From the results described above, it follows that either bimetallic nitrides or carbides can be obtained from the thermal decomposition of bimetallic complexes with HMTA. During the decomposition, reduction of the molybdenum and cobalt (nickel) species occurs with the decomposing HMTA moieties. The last compound contains both nitrogen and carbon. Which one of these elements remains in the solid at high temperatures, depends on the conditions and on the precursor composition. The mechanism of decomposition very probably influences the nature of the phases obtained. As shows the thermal analysis study, the decomposition of a complex leading to carbide ($CoMo_3$) takes place at lower temperature than that yielding to nitride ($CoMo_1$). Table 5 summarizes the temperature of decomposition of NO_3^- and HMTA as studied by thermal analysis.

It seems that the intensity of NO_3^- decomposition peak is directly correlated to the nature of phases obtained. Indeed, the precursors with low cobalt nitrate content and $Co/Mo = 0.5$ yield nitrides, whereas precursors with high nitrate content and $Co/Mo = 1$ lead to the carbides. It seems that nitrate reacts with HMTA and modifies the decomposition. Indeed, nitrates are oxidizing compounds which can react with organic molecules like HMTA at low temperatures. At the same time, nitrates are oxo bases which can react with the oxoacid Co(II). For example, $Co(NO_3)_2$ decomposes at 473–523 K under an inert atmosphere. Moreover, cobalt particles formed by decomposition of the precursor can also catalyse the decomposition of HMTA by mechanism of catalytic cracking. As a result of all these effects, high loading of cobalt nitrate leads to the release of the most part of nitrogen contained in the precursor already at low temperatures. Residual carbon then reacts to produce carbides. These observations are confirmed by the obtention of pure Co_3Mo_3N when using a cobalt acetylacetonate precursor (CoMo5) which could not be obtained when using a cobalt nitrate precursor.

A second key parameter which can switch between carbide and nitride products is an HMTA ligand content in the material. From Table 1, we can see that if the carbon to metals ratio was higher than 3.2, decomposition of precursors prepared from cobalt nitrate always led to the corresponding carbides. We can observe that an increase of the carbon content for complexes obtained from acetylacetonate cobalt which have the same Co/Mo ratio also favors the formation of carbides instead of nitrides.

Overall, two key parameters govern the decomposition of CoMo complexes: the ligand loading, and the nature of precursor. An increase of the ligand loading favors the formation of carbide. As with the cobalt precursor, cobalt nitrate is less suitable than cobalt acetylacetonate due to its oxidizing properties. To obtain pure and high surface area nitrides, acetylacetonate compexes with moderate amount of HMTA should be utilized. As with carbides, both nitrate and acetylacetonate can be used, with high amount of HMTA included. Note with this respect that this work was first of all targeted on the fundamental understanding of the phase's genesis in this kind of systems. Further optimization of the properties of such systems is of course possible, by variation of gas atmosphere and the composition of precursor. Thus, a brief preliminary study showed that sulfate and acetate derivatives can be successfully used to prepare bimetallic nitrides and carbides according to the same approach.

4. Conclusion

New bimetallic Co–Mo and Ni–Mo complexes with HMTA are obtained using simple aqueous precipitation. Decomposition of these compounds leads to the formation of bimetallic nitrides and carbides under relatively mild conditions. The nature of phases obtained depends on the precursor composition and the nature of gas used during decomposition. Using of nitrate complexes led to the bimetallic carbides, whereas acetylacetonate precursors are more suitable for the preparation of nitrides. The advantage of the technique is that the solids are obtained in highly divided state, with high specific surface areas suitable for the applications in catalysis.

Table 5
Temperature of decomposition of hexamethylenetetramine (HMTA) and nitrate anions for $CoMo_1$ and $CoMo_3$

Complex	T (K) decomposition of NO_3^-	T (K) decomposition of HMTA
CoMo1 ↓ $Co_3Mo_3N+Mo_2N$	535 K no emission of NO observed very weak exothermic peak	480–600 K emission of NH_3, N_2, CO rapid weigh loss
CoMo3 ↓ Co_3Mo_3C	525 K emission of NO strong exothermic peak	475–580 K emission of NH_3, N_2, CO, CO_2 rapid weigh loss

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