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Pechini synthesis and characterization of molybdenum carbide and nickel molybdenum carbide

Arnold M. Stux *, Christel Laberty-Robert [1], Karen E. Swider-Lyons

Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5342, USA

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ABSTRACT

Carbides, such as η-Ni_6Mo_6C, are considered as low-cost substitutes for noble metal catalysts for present applications in hydrodesulfurization and for a possible future sulfur-tolerant fuel cell anode catalyst. Most synthesis methods set the carbon content of the carbides by a carbon-based atmosphere or solid carbon in the synthesis. We show here that β-Mo_2C and η-Ni_6Mo_6C can be synthesized using a Pechini process, simply by heating metal acetates mixed with citric acid and ethylene glycol in one step under H_2 with the only source of carbon being the precursor solution. The β-Mo_2C forms when heating a Mo-acetate precursor at 850 °C. When using Ni- and Mo-acetates, β-Mo_2C forms at 700 °C and lower temperatures, while η-Ni_6Mo_6C forms during heating at 800–900 °C. The η-Ni_6Mo_6C has a surface area of 95.5 $m^2\,g^{-1}$ and less than 10 $m^2\,g^{-1}$ when prepared at 800 and 900 °C, respectively. Some Ni_3C, Ni, and NiC impurities are also present in the nanostructured η-Ni_6Mo_6C that was prepared at 900 °C. The η-Ni_6Mo_6C materials made by the Pechini process are compared with those made from a traditional synthesis, using metal organic precursors at 1000 °C under CO/CO_2 mixtures with a carbon activity of 0.011. Our results imply that H_2 and the Pechini process can be used to achieve carbon activities similar to those obtained by methods using gaseous or solid carbon sources.

1. Introduction

Transition metal carbides were traditionally researched for their mechanical hardness and high melting points for steel hardening [1], but they are also now known as catalysts for ammonia synthesis and decomposition, hydrogenolysis, isomerization, methanation, and hydroprocessing [2]. Some molybdenum- and tungsten-carbides can be similar to platinum in their catalytic properties [3,4]. Catalytic activity of the carbides arises from the carbon atoms, which comprise up to 50% of their crystal structure, and which increase the metal–metal distance thus increasing the *d*-band electron density at the Fermi level of the transition metals [5]. The ability of some carbides to mimic Pt has created interest in using them as a noble-metal-free replacement for the Pt/carbon electrocatalyst used in fuel cells [2,6,7].

The η-12 carbides of molybdenum Ni_6Mo_6C, Co_6Mo_6C, and $Co_6Mo_6C_2$, are specific examples of carbides that mimic noble metals and are catalytically active for hydrodesulfurization (HDS) [8]. The $Fd\bar{3}m$ structure of η-Ni_6Mo_6C is depicted by a ball and stick model in Fig. 1 [9]. The η-Ni_6Mo_6C structure has carbon atoms as the center of Mo octahedra with a Mo–C substructure of four other similar octahedra surrounding the central octahedron tetrahedrally so that they are all face-sharing. Another interpenetrating structure is superimposed comprising a diamond lattice of carbon atoms displaced by $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. These other displaced C atoms are then surrounded by tetrahedra of Ni atoms.

Transition metal carbides are traditionally synthesized by several different methods [10]: (a) carbothermal reduction of metal oxides with graphite in an inert environment, (b) electrochemical synthesis, (c) arc melting with graphite, (d) thermal decomposition of diethylnitriamine oxometal compounds, and (e) reduction of oxides by various means, such as H_2, mixtures of H_2 and hydrocarbons as the carburizing gas, or another source of carbon. A critical feature of these processes is that the carbon activity of the environment is thermodynamically favorable for the formation of the carbide phases.

η-Ni_6Mo_6C can be made by a two-step process whereby nickel trisethylene diamine molybdate ($Ni(en)_3MoO_4$) is heated in He-diluted H_2 to 650 °C, and then converted to the carbide by further heating at 1000 °C under CO/CO_2 gas with a carbon activity of 0.011 [6,11,12]. Numerous methods exist for preparing molybdenum carbides. Molybdenum carbide preparation is possible from heating oxide precursors, e.g., MoO_3, in ethylene glycol or peroxide solutions [13] and also via nitride precursors [14]. The β-Mo_2C and η-Mo_2C phases have been prepared under a

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* Corresponding author.
E-mail address: Arnold.Stux@nrl.navy.mil (A.M. Stux).

[1] Present address: Pierre and Marie Curie University, Paris, France.

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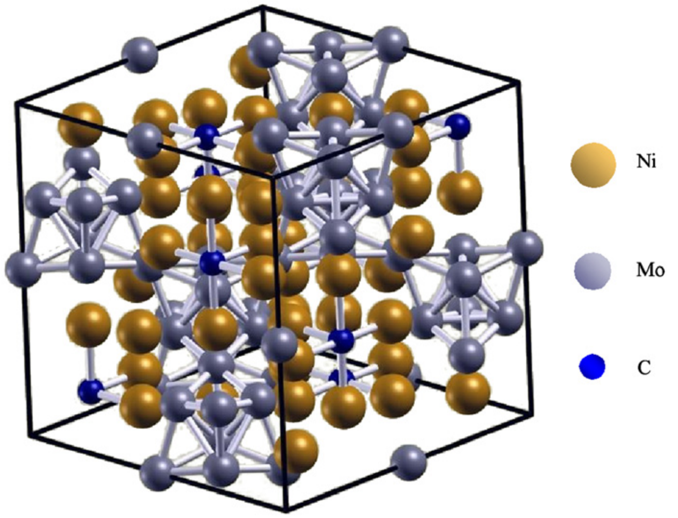

Fig. 1. Ball and stick representation of the η-Ni_6Mo_6C crystal structure.

propane/H_2 mixture at 650 °C, with the β-Mo_2C phase forming with post-treatment of H_2 [15]. Carbon-supported β-Mo_2C has been synthesized by heating ammonium heptamolybdate ($Mo_7O_{24}(NH_4)_6 \cdot 4H_2O$) mixed with an active carbon under H_2 whereby the carbon serves as a source of methane [16]. Recently, Yu et al. have described a Pechini-based process to make nanocrystalline TiC that is embedded in a mesoporous carbon composite [17]. Like the Mo_2C in Ref. [16], the TiC is formed *in situ* by a carbothermal reduction process within the carbon matrix.

We present herein the Pechini process as a new, one-step synthesis of η-Ni_6Mo_6C and β-Mo_2C, by using metal acetates, citric acid, ethylene glycol and H_2, and no solid carbon as a carbon source. This sol–gel method offers the abilities to control surface and bulk properties, to cast the material in any shape, and to form coatings, which provide advantages over other traditional processing routes. In the Pechini process [18], polybasic chelates are formed between α-hydroxyl carboxylic acids, containing at least one hydroxyl group, and metal cations. The chelates undergo polyesterification on heating with the polyfunctional alcohol (ethylene glycol) to form a large metal–organic complex. Further heating produces a viscous resin, then a rigid transparent glassy gel, and finally a fine oxide powder. Citrate gel precursors offer chemical uniformity and control of the composition [19]. Coordination of the metals in the metal–organic complexes remains unchanged on polymerization and molecular level mixing is retained at the resin stage.

We develop this Pechini process for carbide formation by observing the thermal events that occur upon heating the precursors in the presence of H_2. The resulting materials, made under pure H_2, are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), elemental analysis, and the Brunauer-Emmett-Teller (BET) method for surface area measurements. The materials are compared with our η-Ni_6Mo_6C made at 1000 °C under CO/CO_2 mixtures.

2. Experimental section

2.1. Materials and synthesis

β-Mo_2C was synthesized by the Pechini process from commercially available molybdenum (II) acetate dimer ($Mo_2(OCOCH_3)_4$, Aldrich). An aqueous solution was prepared by dissolving the Mo-acetate dimer into 50 mL H_2O to form a ~1 mM solution. Ethylene glycol ($HOCH_2CH_2OH$) and citric acid ($HOC(COOH)(CH_2COOH)_2$) were added in a 1:1:1 M ratio to the Mo-acetate dimer solution. This solution was heated to 85 °C in a beaker with vigorous

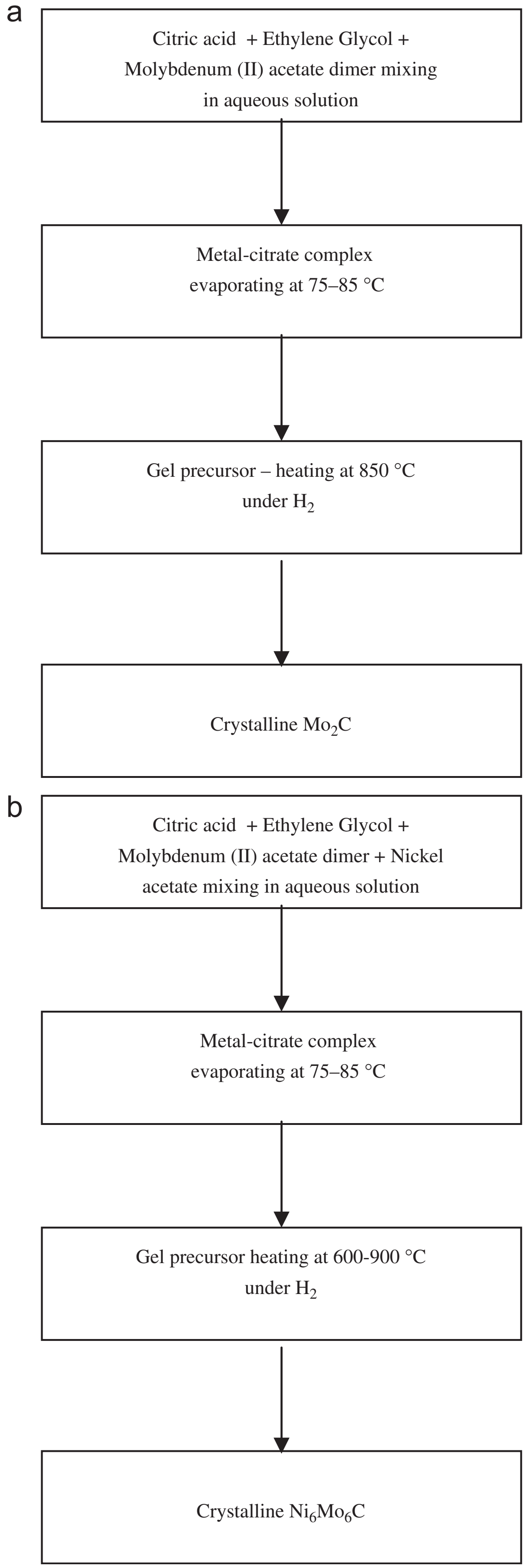

Fig. 2. Schematic diagram of the synthetic process of (A) β-Mo_2C and (B) η-Ni_6Mo_6C by the Pechini process.

stirring on a hotplate. The light green aqueous solution became brown and then reddish brown. Within a few hours of heating and stirring, the solution became redder and then reverted back to light green. The solution was evaporated on the hotplate for over a few hours at 75 °C until there was only ~10 mL left. The resulting viscous green solution was pipetted into an alumina crucible and heated in a tube furnace (alumina tube, i.d. = 2.0 cm) at a ramp rate of 2 °C min^{-1} under 9 mL min^{-1} flowing H_2. The temperature of the samples was held at 850 °C (1023 K) for 14 h and then cooled at 5 °C min^{-1}. The H_2 flow was turned off when the samples cooled down to less than 100 °C, when it was opened to the atmosphere. The H_2 was 99.95% pure with less than 0.001% hydrocarbons. The synthetic process for Mo_2C is shown schematically in Fig. 2A.

η-Ni_6Mo_6C was synthesized by the Pechini process using Mo-acetate dimer and nickel(II) acetate ($Ni(OCOCH_3)_2 \cdot xH_2O$, Alfa Aesar). The Mo- and Ni-acetates were dissolved in a 1:1 M ratio of Mo and Ni to form a 250 mL (40 mM) aqueous solution. Ethylene glycol and citric acid (1:1 M ratio) were added to form a 3:2 M ratio of ethylene glycol to nickel. The solution was heated to 85 °C in a beaker with vigorous stirring on a hotplate and was evaporated on the hotplate for over a few hours at 75 °C until the contents were viscous. The resulting reddish brown viscous solution was pipetted into an alumina crucible and heated in a tube furnace with a ramp rate of 2 °C min^{-1} to 600–900 °C (873–1173 K) for 12–14 h under 9 mL min^{-1} flowing H_2 and cooled down at 5 °C min^{-1}. The H_2 flow was turned off when the samples cooled down to less than 100 °C, when it was opened to the atmosphere. The synthesis is shown schematically in Fig. 2B.

Standards of η-Ni_6Mo_6C were also prepared by gas-phase carburization using a method adapted from the patent literature [11]. Nickel $Ni(en)_3MoO_4$ was placed in a tube furnace (alumina tube, i.d. = 3.81 cm) under a combination of flowing H_2 and Ar at 24.3 mL min^{-1} each (2.1 cm min^{-1} linear flow rate) and heated at 15 °C min^{-1} to 650 °C (923 K), where the temperature was held for 30 min. The gas was switched to pure Ar at 50 mL min^{-1} (4.3 cm min^{-1} linear flow rate) and heated to 1000 °C (1273 K) at 15 °C min^{-1}, at which point the gases were switched to a mixture of Ar, CO, and CO_2 at 61 and 20 mL min^{-1}, respectively, to impose a carbon activity 0.011. The reaction was run for 3 h, after which the reactor was allowed to cool to ambient temperature under flowing Ar at 61 mL min^{-1}.

2.2. *Characterization*

The materials were characterized for structure, porosity, and composition. Differential thermal analysis (DTA, Rheometric Scientific, Inc., STA1500) was carried out using a mixture of Ar and 5% H_2 (MG Industries, analyzed to 99.95% purity). XRD measurements were made both with and without an internal Si standard (Cu$K\alpha$ radiation: 40 kV, 40 mA; 1.2° 2θ min^{-1} step size; Bruker D8 Advance). The lattice parameters of the η-Ni_6Mo_6C were determined from their d-spacings, as obtained from Bruker's EVA program, and using a least-squares analysis program for lattice parameter refinement, UnitCell for OSX (v0.3) [20]. The lattice parameters were corrected to those of an internal silicon standard, which was refined from the d-spacings of the measured data using UnitCell, and then corrected to the NIST standard value for Si ($a = 5.43104$ Å). The correction percentage for the measured vs. standard Si value was used to adjust the refined lattice parameter of the cubic η-Ni_6Mo_6C.

The XRD patterns were also used to determine domain sizes, through analysis of the most intense diffraction peak with the Scherrer equation (e.g., the scattering angle at 43.5° 2θ for the η-Ni_6Mo_6C). The particle morphology of both materials was also characterized with SEM (Leo Supra 55) with 1 and 2 kV voltage operating conditions and an in-lens detector.

Surface areas were determined by nitrogen physisorption using a Micromeritics ASAP2010 Accelerated Surface Area and Porosimetry Analyzer. The sample was degassed at 150 °C for at least 12 h prior to characterization. Specific surface areas were determined using the multipoint BET method.

Elemental analyses were performed by Desert Analytics, Inc., Tucson, AZ.

3. Results

Table 1 summarizes the appearance and crystal phases of the materials made from the Mo-acetate and Ni-Mo-acetates at various temperatures. The compound synthesized from Mo-acetate using ethylene glycol, citric acid, and heating under H_2 (process in Fig. 2A) matches well to JCPDS pattern no. 72-1683 for the hexagonal β-phase of Mo_2C, as shown in Fig. 3.

The compounds synthesized from Ni- and Mo-acetate mixtures with ethylene glycol and citric acid (process in Fig. 2B) at 800 and 900 °C under H_2 have XRD patterns that match to the JCPDS pattern 80-0337 of the η-12 phase for Ni_6Mo_6C (Fig. 3). Their lattice parameters were 10.85 ± 0.01 and 10.860 ± 0.009 Å for materials heated to 800 and 900 °C, respectively, in good agreement with that of Newsam et al. [12] (10.8932 Å). The materials heated to 800 °C were dull-colored flakes and those heated at 900 °C were shiny flakes. Both samples exhibit additional small scattering angle peaks at ca. 45° and 59° 2θ, which are assigned to Ni_3C, and are most prevalent in the sample heated at 900 °C. The suggested presence of Ni_3C in this sample and lack of Mo_2C or Mo impurities implies the volatilization of traces of Mo. The XRD data for the sample heated at 900 °C suggest the presence of Ni peaks at 77.5° and 94.4° 2θ. There are also NiC impurities because of peaks at 51.8°, 75.4°, and 92.4° 2θ. The coexistence of either Ni, NiC, or Ni_3C is likely a result of a slight excess of Ni-acetate that was added to compensate for commercial $Ni(CH_3COO)_2 \cdot xH_2O$ being a hydrate. Analysis of the XRD peak widths indicate that the η-Ni_6Mo_6C heated at 800 and 900 °C and the Mo_2C formed at 700 °C all have crystal domain

Table 1
Results from different heat treatments of Pechini precursors plus η-Ni_6Mo_6C made by carbothermal reduction

Metal acetate precursor(s)	Heating conditions	Phase(s) present by XRD	Appearance
(a)			
Mo (II) acetate dimer	850 °C, H_2, 12 h	β-Mo_2C	Dull metal
(b)			
Ni(II) acetate, Mo (II) acetate dimer	900 °C, H_2, 12 h	η-Ni_6Mo_6C+Ni_3C+trace NiC+Ni	Shiny
Ni(II) acetate, Mo (II) acetate dimer	800 °C, H_2, 12 h	η-Ni_6Mo_6C+trace Ni_3C	Discolored shiny
Ni(II) acetate, Mo (II) acetate dimer	700 °C, H_2, 12 h	β-Mo_2C+trace η-Ni_6Mo_6C+Ni_3C	Dull metal
Ni(II) acetate,Mo (II) acetate dimer	600 °C, H_2, 12 h	β-Mo_2C	Dull metal
Tri(ethylene diamine) nickel molybdate	1000 °C, CO/CO_2	η-Ni_6Mo_6C	Shiny

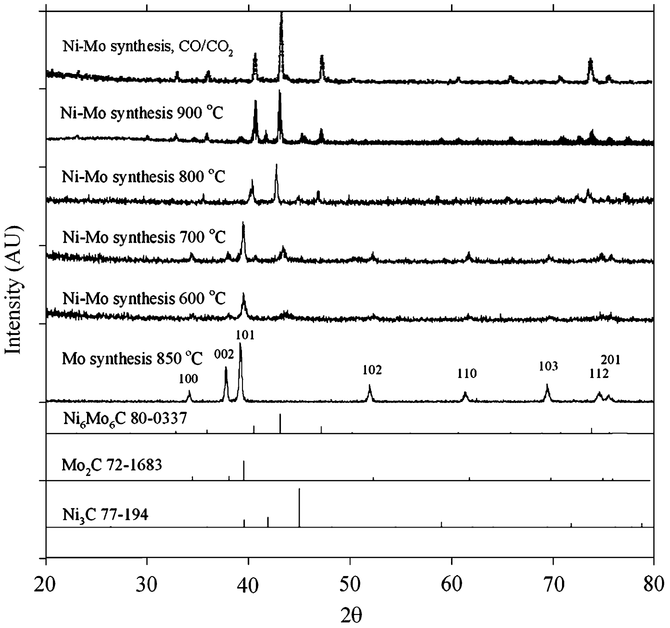

Fig. 3. XRD patterns of compounds made from Mo-acetate and mixtures of Ni- and Mo-acetates.

sizes of 30 nm; the Ni_3C impurities in the 900 °C-treated sample are about 15 nm in diameter. The samples derived from Ni- and Mo-acetates and heated at 600 and 700 °C for 12 h under H_2 are dull colored and predominantly have a distorted β-Mo_2C structure. There is a trace of Ni_3C even as low as 700 °C as indicated by a small peak at 45° 2θ. This small presence of Ni_3C likely coexists with β-Mo_2C and η-Ni_6Mo_6C to maintain the stoichiometric ratio.

Fig. 4 displays the DTA of both Mo-acetate and mixed Mo- and Ni-acetates under 2.5% H_2 in Ar. In the thermogram of the Mo-acetate precursor above 250 °C, there is only one endotherm at ~600 °C, while there are three for the Mo- and Ni-acetate precursor mixture. The thermogram for the mixed Mo- and Ni-acetate exhibits a small endotherm at 380 °C, a slightly larger one at 475 °C, and a sharp one at 730 °C. The endotherm at 730 °C can be attributed to formation of η-Ni_6Mo_6C, while those at lower temperatures are attributed to the formation of β-Mo_2C and Ni_3C. The thermal analysis is consistent with the observation of Ni_3C impurities by XRD for the samples heated at 700 °C and above. The reduction and formation of η-Ni_6Mo_6C above 730 °C and β-Mo_2C below 730 °C are in agreement with the XRD results in Table 1.

The morphology of the β-Mo_2C formed by heating Mo-acetate with the Pechini precursors at 850 °C under H_2 is shown in Fig. 5. This compound has a low surface area (non-porous but granular)

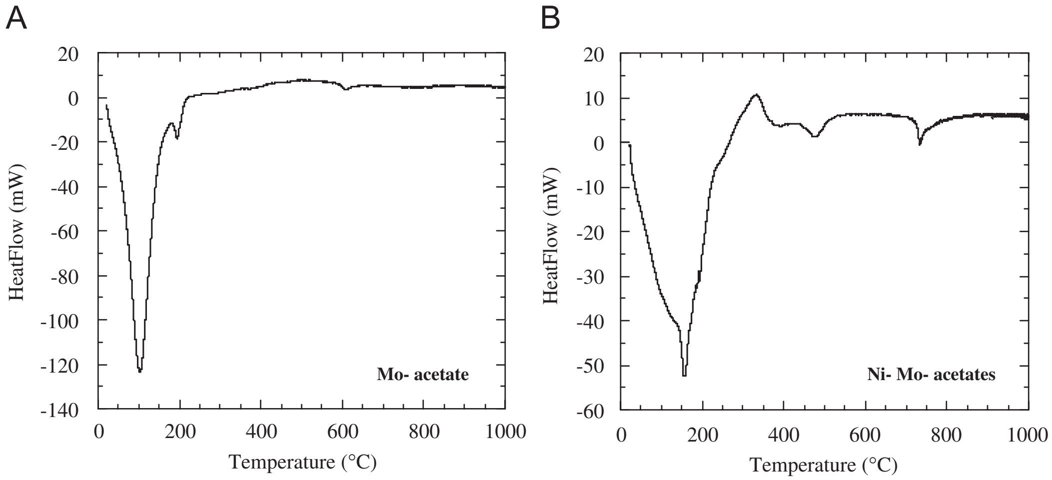

Fig. 4. Differential thermal analysis of the metal acetate precursors with ethylene glycol and citric acid under 2 °C min^{-1} 2.5% H_2/Ar flow for the (A) Mo compound and (B) Ni–Mo compound.

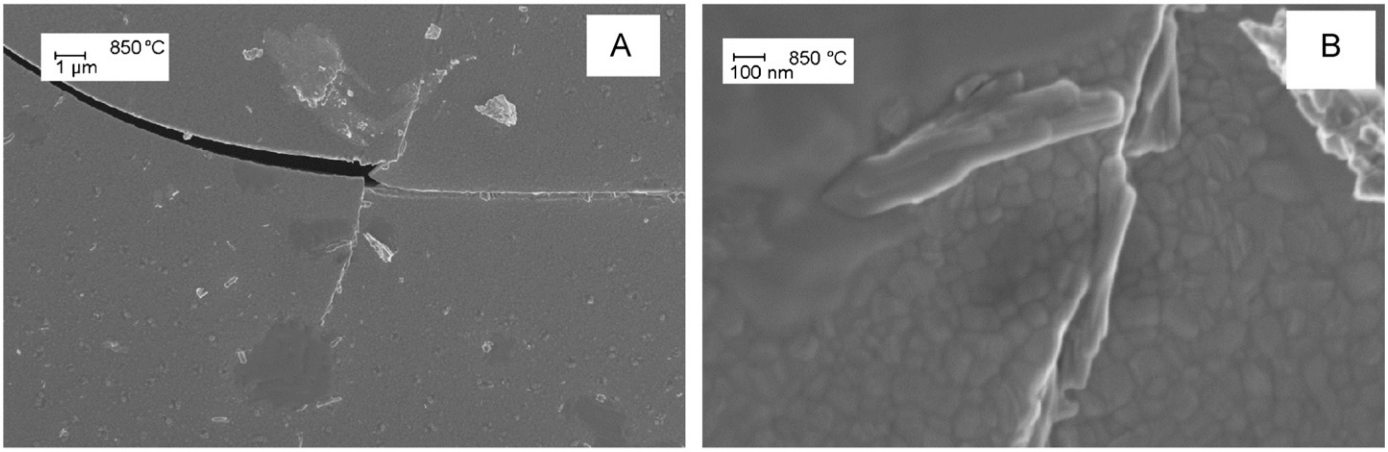

Fig. 5. SEM image of Mo-acetate gel heated under H_2 at 850 °C magnified at (A) 5000 × and (B) 50,000 ×.

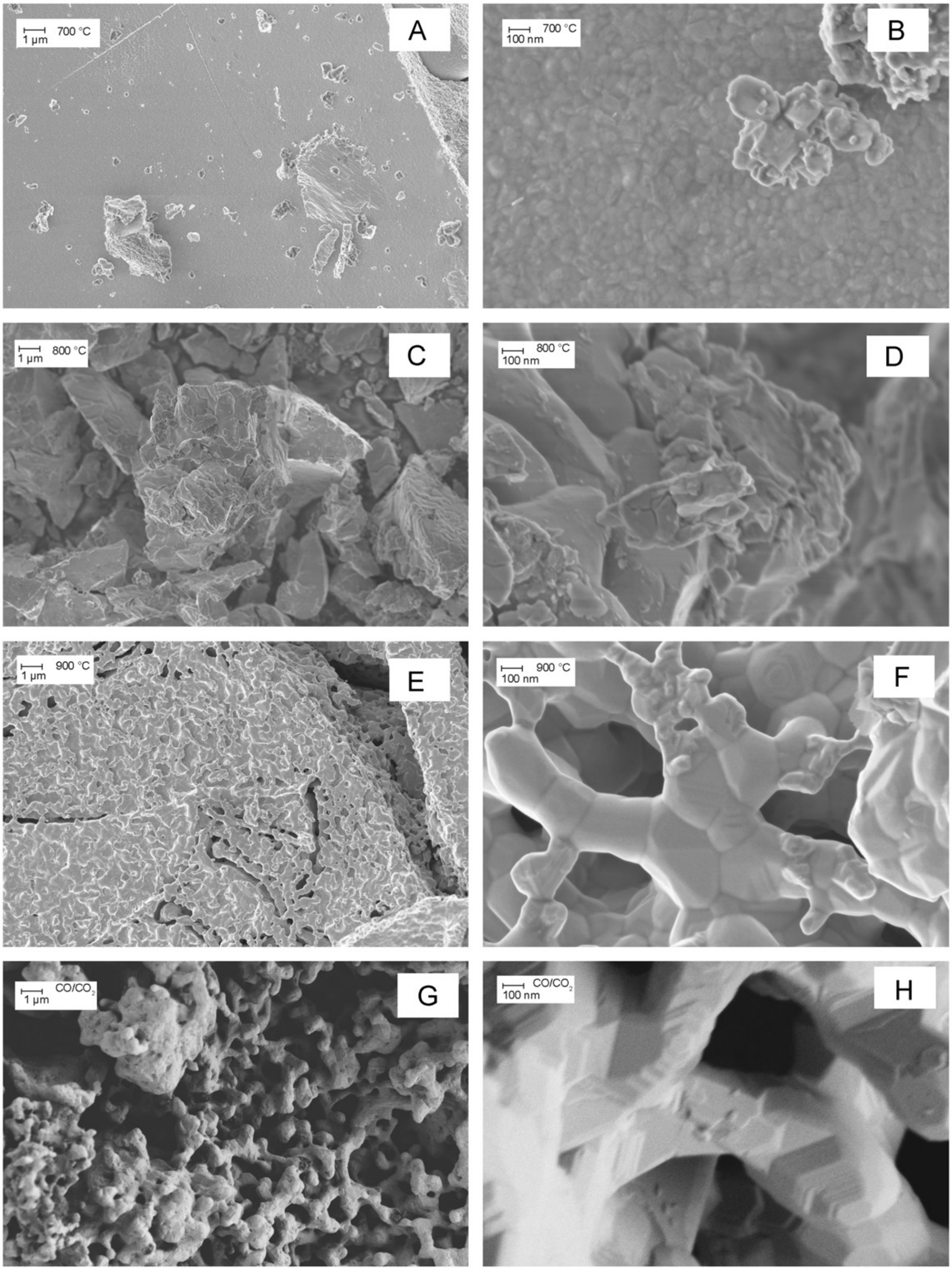

Fig. 6. SEM images of compounds made from Ni- and Mo- organics and the Pechini and CO/CO_2 processes at 5000 × and 50,000 × : (A,B) from the Pechini process at 700 °C; (C,D) Pechini process at 800 °C; (E,F) Pechini process at 900 °C; and (G,H) CO/CO_2 process at 1000 °C.

with some micrometer- and submicrometer-sized particles and a flake-like habit.

The SEM images of the various compounds made from Ni- and Mo-acetate precursors are shown in Fig. 6. The η-Ni_6Mo_6C phases that formed at 800 and 900 °C have more porosity than the predominantly Mo_2C phases that formed at lower temperatures from similar starting resins. The β-Mo_2C (with traces of η-Ni_6Mo_6C) formed by heating the Ni- and Mo-acetate mixture under H_2 at 700 °C (Figs. 6A and B) appears almost identical to that in the pure Mo-compound, shown in Fig. 5, with low surface area (non-porous but granular) and micrometer- and submicrometer-sized particles. The same Ni- and Mo-acetates heated to 800 °C (η-Ni_6Mo_6C with a trace of Ni_3C) have ~10 μm domains with some nanoparticles and porosity in some regions (Figs. 6C and D). The compound made at 900 °C under H_2, (η-Ni_6Mo_6C with a small amount of Ni_3C) is highly porous (Figs. 6E and F). As in Table 2, the η-Ni_6Mo_6C prepared at 800 °C has a surface area of 95.5 $m^2\,g^{-1}$ while the sample prepared at 900 °C has less than

Table 2
Surface area properties and percent elements present of different heat treatments of Pechini precursors of η-Ni_6Mo_6C, Ni(II) acetate+Mo (II) acetate dimer with ethylene glycol and citric acid

Treatment (°C)	Surface area ($m^2 g^{-1}$)[a]	C (1350 °C)[b]	H	Mo[c]	Ni[c]
900	4.5	2.2	<0.06	66.6	31.1
800	95.5	13.0	0.28	26.6	60.1

[a] Surface areas were determined from BET.
[b] Carbon content for the heat-treated samples was measured at 1350 °C.
[c] The analytical error was ±5% for metals.

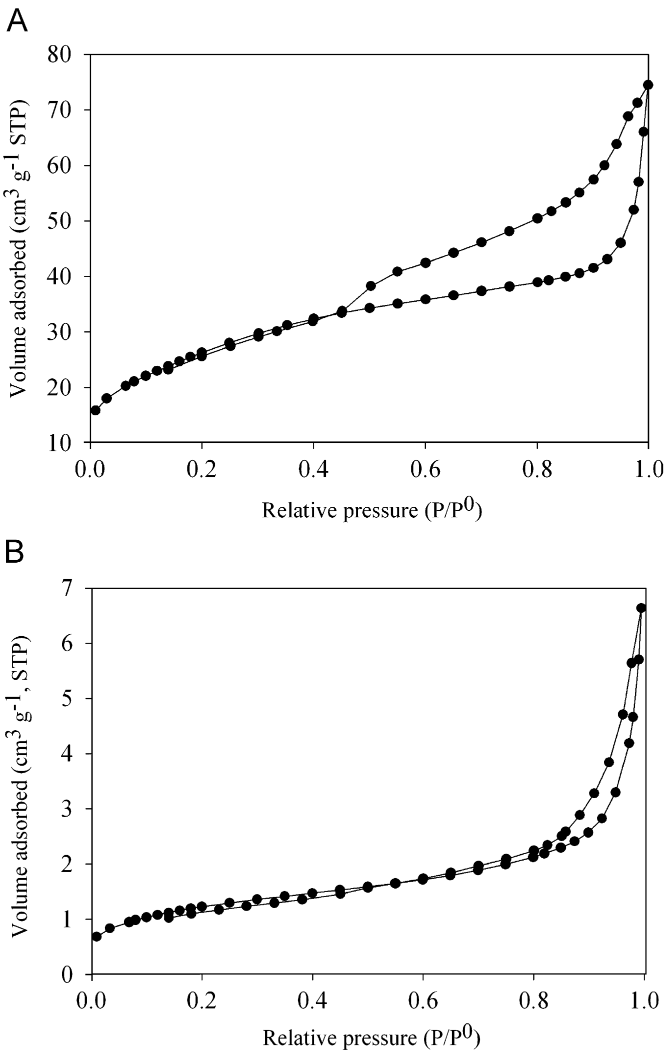

Fig. 7. N_2-sorption isotherms for the prepared η-Ni_6Mo_6C samples via the Pechini process with different heat treatments of (A) 800 °C and (B) 900 °C.

10 $m^2 g^{-1}$. The drastic decrease in surface area can be attributed to the sintering of η-Ni_6Mo_6C. The uptake of N_2 from the adsorption isotherm is greater for the 800 °C-heated than the 900 °C-heated sample as in Fig. 7. The isotherms indicate greater mesoporosity for the 800 °C-heated sample. The median pore volume of the 800 and 900 °C-heated samples for pores over 5 nm is 0.05 and 0.002 $cm^3 g^{-1}$, respectively. The broad pore size distribution is similarly shaped for both materials with a larger pore volume for the 800 °C-heated sample.

Elemental analysis in Table 2 for the 900 °C-heated sample shows a slight excess of carbon in the powder compared with the theoretical values of 1.27% C, 37.5% Ni, and 61.2% Mo. The Ni content is lower than the expected value implying excess Mo, yet no Mo was observed by XRD. The elemental analysis for the 800 °C-heated sample indicated a large excess of Ni and carbon which may be attributed to Ni_3C impurities. There is little excess of Ni and C present in the 900 °C-heated sample where there should be excess Ni and C based on the presence of Ni_3C and Ni impurities shown by XRD. The higher carbon content in the 800 °C-heated sample when compared with theoretical values suggests that a large amount of carbon is adsorbed on the surface and may partially account for the higher surface area. The slightly higher carbon content of the 900 °C-heated sample vs the theoretical values indicates that less carbon is adsorbed on its surface.

4. Discussion

The results herein demonstrate that metal carbides can form when heating acetate gels under only H_2. Heating Mo-acetate with citric acid and ethylene glycol under H_2 creates β-Mo_2C. A reaction of Ni- and Mo-acetates with citric acid and ethylene glycol under similar conditions forms η-Ni_6Mo_6C at ~800 °C. The endotherm at 730 °C for the as-prepared Ni–Mo acetate gel mixture likely corresponds to a reaction with H_2.

At 900 °C, the as-prepared Ni–Mo acetate gel mixture forms η-Ni_6Mo_6C with traces of Ni_3C, NiC, and Ni, suggesting that the Ni_3C was partially converted to Ni and NiC at 900 °C. The presence of some Ni in the 900 °C-treated sample is consistent with the decomposition of Ni_3C nanoparticles to Ni at 900 °C under H_2 [21]. The Ni_3C and other impurities coexisting with the predominant η-Ni_6Mo_6C are present as nanograins, as indicated by XRD.

The reaction of Ni- and Mo-acetates predominantly forms η-Ni_6Mo_6C at 800 and 900 °C but mostly β-Mo_2C at 600 and 700 °C. No other phases beyond β-Mo_2C, Ni_3C, NiC, η-Ni_6Mo_6C, and Ni are observed in any of the samples prepared with Ni- and Mo-acetates. If the endotherm corresponding to β-Mo_2C formation from the Ni–Mo acetate gel mixture is at 475 °C, then it is at a lower temperature than the endotherm at 600 °C for β-Mo_2C formation using only the Mo-acetate. Formation of the β-Mo_2C phase at this lower temperature in the presence of Ni-acetate suggests that Ni^{2+} ions promote the formation of β-Mo_2C.

The surface area and porosity is clearly dependent on the reaction temperature. The β-Mo_2C phases resulting from the 600 to 700 °C heat treatments are non-porous with some granularity. Larger pores formed in the η-Ni_6Mo_6C at 900 °C than at 800 °C, according to SEM, but the 800 °C-treated sample has a larger surface area from its micro and mesopores. When heated to 900 °C, these micro and mesopores collapse to give a lower surface area, less than 10 $m^2 g^{-1}$. The decrease in surface area with the 900 °C heat treatment is a result of sintering the η-Ni_6Mo_6C phase. The type of emitted gases may play a role in the initial formation of pores during decomposition of organics, but the pore size at high temperature is mostly because of the sintering process. The precise identity of the gases has not been determined, but previous work on carbon-supported Mo_2C suggests that a combination of CO, CO_2, H_2O, and CH_4 is evolved [16]. The morphology of initial pores is expected to affect the pore size at higher temperatures. Tailoring the surface of these materials was not addressed in this study because it is dependent on the final application.

The high specific surface area of the η-Ni_6Mo_6C sample at 800 °C shows that the Ni–Mo system has promise in the field of catalysis. The sorption and surface area measurements complement the pore size obtained by SEM. Based on our comparison of synthesis methods, the CO/CO_2 mixture is not the best process for carbide synthesis, and too high a reaction temperature leads to a decreased specific surface area.

The carbon source for the carbides is presumed to be from the precursors. The H_2 gas for the experiment is pure enough that it cannot be a significant source of the carbon. While the differences in compositions between the bulk and surface may be unclear, we can assume, based on the elemental analysis and surface area results, that at least as much carbon is present closer to the surface as is in the bulk. The higher carbon content for both 800 and 900 °C heat treatments of η-Ni_6Mo_6C when compared with theoretical values implies excess carbon adsorbed to the surface. Each of the carbon sources in the Pechini process, acetate, ethylene glycol and citric acid, may play a role in forming carbides. In the metal acetates before dissolution, the carbon that is bonded to the oxygen in the acetate moiety is in close proximity to the metal center. After dissolution of all reactants, the citric acid forms a chelation complex with the ethylene glycol and the metal acetates, keeping the metal atoms separated. For the formation of η-Ni_6Mo_6C, we expect an almost 20:1 M equivalent of carbon to Mo to form carbon byproducts based on reaction (1), but some of the excess carbon may remain in solid form and adsorb to the surface.

$$\begin{aligned}&Mo_2(OCOCH_3)_4 + 2Ni(OCOCH_3)_2 + 3HOCH_2CH_2OH\\&\quad + 3HOC(COOH)(CH_2COOH)_2 \rightarrow\\&\;1/3\ \eta\text{-}Ni_6Mo_6C_{(s)} + 39\ 2/3\ \text{gaseous carbon products}\end{aligned} \tag{1}$$

As the organic complex is heated, the organics are presumed to decompose to CO_2, CO, CH_4, and H_2O in the presence of H_2 to create a reducing, carburizing environment. Based on expected Pechini chemistry, water is initially removed by heating to form a viscous gel, Mo and Ni are chelated and polyesterification takes place to form a network. Under the flow of H_2, this network is decomposed and the carbon byproducts, CO, CO_2, and CH_4 are presumed to form. In the sample treated at 900 °C, presence of Ni and NiC, ostensibly from decomposition of Ni_3C, may involve some decomposition to elemental C. If this is the case, carbon forming from Ni_3C decomposition cannot be a carbon source to form CH_4 because η-Ni_6Mo_6C is formed at a lower temperature than the formation of Ni_3C and/or its decomposition. If any CH_4 forms, it could be from decomposition of acetates or of the polymer network.

Analogous to the reactions with Ni-acetate, for the formation of β-Mo_2C without Ni-acetate as a precursor, we expect reaction (2) to occur where a lower molar equivalent of carbon to Mo forms carbon byproducts.

$$\begin{aligned}&Mo_2(OCOCH_3)_4 + 3HOCH_2CH_2OH\\&\quad + 3HOC(COOH)(CH_2COOH)_2 \rightarrow\\&\;\beta\text{-}Mo_2C_{(s)} + 31\ \text{gaseous carbon products}\end{aligned} \tag{2}$$

We present a low-temperature route that provides intimate mixing for starting compounds and demonstrate this method with the production of the less widely studied η-Ni_6Mo_6C in parallel with the more commonly studied Mo_2C. We have demonstrated an alternate method of the formation of carbides in the absence of a hard carbon source or fixed carbon activity. In agreement with other results [13,14,16,21,22], we show that the synthetic processes can have a large effect on the surface areas and bulk properties. The catalytic activity of materials prepared by an optimized process based on the one presented here can be the subject of a future investigation.

5. Conclusions

Bulk *fcc* η-Ni_6Mo_6C and *hcp* β-Mo_2C were synthesized in a one-step Pechini process by heating metal acetate citrate gels with ethylene glycol under only H_2. The synthesis of η-Ni_6Mo_6C and its surface area are sensitive to temperature, with β-Mo_2C favored at temperatures of 600 and 700 °C and η-Ni_6Mo_6C at 800 and 900 °C. The impurities in η-Ni_6Mo_6C formed at 900 °C were found to be Ni, Ni_3C, and NiC. In the other process presented here using Ni- and Mo-organics under CO/CO_2, the carbon source is fixed at 0.011 by the gaseous mixture. That we could form the carbides without a fixed carbon source suggests stability of the η-Ni_6Mo_6C and β-Mo_2C carbides over a wide range of carbon activities and continued opportunity for the fabrication of high surface area carbide catalysts using “green” chemistry with few hydrocarbons. This method shows promise in forming fibers or films.

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References

[1] L.K. Storms, The Refractory Carbides, Academic Press, NY, London, 1967.
[2] S.T. Oyama, Catal. Today 15 (1992) 179–200.
[3] J.H. Sinfelt, D.J.C. Yates, Nat. Phys. Sci. 229 (1971) 27–28.
[4] R.L. Levy, M. Boudart, Science 181 (1973) 547–549.
[5] J.S. Choi, G. Bugli, G. Djega-Mariadassou, J. Catal. 193 (2000) 238–247.
[6] J.J. Pietron, C. Laberty, K.E. Swider-Lyons, ECS Trans. 3 (1) (2006) 471–477.
[7] M. Nagai, M. Yoshida, H. Tominaga, Electrochim. Acta 52 (2007) 5430–5436.
[8] R.R. Chianelli, G. Berhault, Catal. Today 53 (1999) 357–366.
[9] M. Johannes, A. Kokalj, Comput. Mater. Sci. 28 (2003) 155–168.
[10] T.H. Nguyen, T.V. Nguyen, Y.J. Lee, T. Safinski, A.A. Adesina, Mater. Res. Bull. 40 (2005) 149–157.
[11] E.L. Kugler, L.E. McCandlish, A.J. Jacobson, R.R. Chianelli, US Patent No. 5,071,813, December 10, 1991.
[12] J.M. Newsam, A.J. Jacobson, L.E. McCandlish, R.S. Polizzotti, J. Solid State Chem. 75 (1998) 296–304.
[13] H. Preiss, B. Meyer, C. Olschewski, J. Mater. Sci. 33 (1998) 713–722.
[14] L. Volpe, M. Boudart, J. Solid State Chem. 59 (1985) 348–355.
[15] X.-H. Wang, H.-L. Hao, M.-H. Zhang, W. Li, K.-Y. Tao, J. Solid State Chem. 179 (2006) 538–543.
[16] D. Mordenti, D. Brodzki, G. Djega-Mariadassou, J. Solid State Chem. 141 (1998) 114–120.
[17] T. Yu, Y. Deng, L. Wang, R. Liu, L. Zhang, B. Tu, D. Zhao, Adv. Mater. 19 (17) (2007) 2301–2306.
[18] P.A. Lessing, Ceram. Bull. 68 (5) (1989) 1002–1007.
[19] D. Segal, J. Mater. Chem. 7 (8) (1997) 1297–1305.
[20] T.J.B. Holland, S.A.T. Redfern, Mineral. Mag. 61 (1997) 65–77.
[21] Y.G. Leng, H.Y. Saho, Y.T. Wang, J. Nanosci. Nanotechnol. 6 (1) (2006) 221–226.
[22] J.A. Nelson, M.J. Wagner, Chem. Mater. 14 (2002) 1639–1642.