



Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: http://www.tandfonline.com/loi/gpss20

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To cite this article: Liang Gao, Yan Shi, Zhiwei Yao, Haifeng Gao, Yue Sun, Feixue liang & Baojiang Jiang (2017): Phenolic resin as a carbon source for the synthesis of monometallic Mo and bimetallic CoMo carbides via carbothermal reduction route, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: <u>10.1080/10426507.2017.1418740</u>

To link to this article: <u>https://doi.org/10.1080/10426507.2017.1418740</u>



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Accepted author version posted online: 19 Dec 2017. Published online: 29 Dec 2017.

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Phenolic resin as a carbon source for the synthesis of monometallic Mo and bimetallic CoMo carbides via carbothermal reduction route

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ABSTRACT

It was the first time that phenolic resin (PR) was used as a carbon source for the synthesis of nanostructured monometallic Mo and bimetallic CoMo carbides via carbothermal reduction route. The results showed that phase-pure β -Mo₂C can be formed under an Ar atmosphere at 900°C or a H₂ atmosphere above 700°C. However, almost pure CoMo carbides (Co₃Mo₃C and Co₆Mo₆C) can be obtained only under a H₂ atmosphere at a low temperature of 630°C for 24 and 48 h, respectively. The role of PR in the preparation process has been investigated and a detailed formation mechanism was proposed based on the experimental results.

GRAPHICAL ABSTRACT



ARTICLE HISTORY

Received 29 May 2017 Accepted 14 December 2017

Taylor & Francis

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KEYWORDS

Phenolic resin; nanostructured carbides; carbothermal reduction; monometallic Mo carbide; bimetallic CoMo carbide

Introduction

Carbon and phosphorus were one of the most common Group 14 and Group 15 elements. The chemistry of carbon and phosphorus was very important in the field of catalysis. Both carbon and phosphorus atoms can be inserted into transition metal lattices to form metal carbides and phosphides, and they were known as transition metal interstitial compounds. Transition metal carbides show unique catalytic performances similar to phosphides, and thus they have attracted considerable attention in recent years.^[1] Various kinds of transition metal carbides such as monometallic Mo₂C, WC, Fe₂C and Co₂C, and bimetallic Co₃Mo₃C/Co₆Mo₆C, Ni₂Mo₃C and Fe₃Mo₃C have been prepared and used as catalysts in various reactions, including hydrogenation and hydrotreating, ^[2] hydrogen evolution reaction,^[3] Fischer-Tropsch synthesis,^[4,5] N₂H₄ decomposition,^[6] CH₄ decomposition,^[7] water-gas shift

reaction^[8] and dry reforming of methane.^[9,10] Among these carbides, Mo₂C and Co₃Mo₃C/Co₆Mo₆C have been studied extensively in recent years.^[11,12] Monometallic Mo₂C was most commonly synthesized by temperature programmed reduction (TPR) of MoO₃ precursor under mixtures of hydrocarbons (such as CH₄, C₂H₆, C₃H₈ and C₄H₁₀) and hydrogen.^[13-15] Unfortunately, the CoMo oxide precursor was carburized to unstoichiometric CoMoC_x carbide and CoMoC_xO_y oxycarbide rather than Co₃Mo₃C/Co₆Mo₆C in the TPR process mentioned above. ^[7–16] Thus, this simple TPR method was limited to the synthesis of monometallic carbide. In recent decades, Co₃Mo₃C/Co₆Mo₆C can be synthesized using more involved or complex procedures, including nitridation of CoMo oxide by ammonia, followed by carburization of the nitride precursor, ^[17,18] successive nitridation and carburization reactions via decomposition of Co,Mo-hexamethylenetetramine

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(HMT) complex,^[12] and carburization of an oxidic precursor followed by heating in hydrogen.^[19] On the other hand, a facile carbothermal reduction route was developed for the preparation of bimetallic CoMo carbides.^[20,21] Liang et al. prepared Co₃Mo₃C carbide using activated carbon as a carbon source via this route.^[20] In addition, Regmi and Leonard reported that dispersed Co₃Mo₃C and Co₆Mo₆C particles were obtained using decolorizing carbon as a carbon source during the carbothermal reduction process.^[21] To our knowledge, there are no reports on the carbothermal reduction route to the synthesis of CoMo carbides other than the two cases mentioned above. Nevertheless, up to now the carbon source was limited to the type of solid carbon. Therefore, it was still worthwhile to explore novel carbon sources to prepare bimetallic carbides with modified microstructures.

In the present study, it was the first time that phenolic resin (PR) was used in the carbothermal reduction method for the preparation of carbides, and nanosized monometallic Mo_2C , bimetallic Co_3Mo_3C and Co_6Mo_6C carbides were successfully synthesized. It was found that the as-prepared bimetallic CoMo carbides showed much smaller sizes than those submicrometersized bimetallic CoMo carbides prepared using decolorizing carbon as carbon source mentioned above.^[21] Techniques of XRD, TEM and TG-MS were adopted for the investigation of solid and gas products, and to give insights into the formation mechanism of these carbides during carbothermal reduction.

Results and discussion

Microstructural characterization

Figure 1 shows the XRD pattern of the phenolic resin used in the study, and the result indicated that the raw resin was completely amorphous, which was similar to the result of previous study.^[22] Carburization of Mo- and CoMo-containing resin precursors was studied as a function of treatment conditions in the temperature range 500–900°C. Figure 2 shows the XRD patterns of the samples prepared from Mo-containing resin precursor under Ar or H₂ at different temperatures. It can be seen that the Mo-Ar-700-1 demonstrated the main diffraction peaks at 2 θ of 26.0, 37.0, 53.5, 60.2 and 66.6° for MoO₂ (JCPDS 78–1069) when the Mo-containing resin precursor was heated at 700°C in Ar flow. With increase of the temperature to 800°C, the peaks for



Figure 1. XRD pattern of the phenolic resin used in the study.



Figure 2. XRD patterns of the samples prepared from Mo-containing resin precursor at different temperatures in Ar (a) or H_2 (b).

MoO₂ became very weak but β -Mo₂C phase (JCPDS 35–0787) was observed, with the main peaks at 2θ of 34.4, 38.0, 39.4, 52.1, 61.5 and 69.6°, corresponding respectively to (100), (002), (101), (102), (110) and (103) planes. With a further increase of the temperature to 900°C, the MoO₂ phase disappeared completely, and the β -Mo₂C was obtained as a single phase. As for the products obtained in H₂ gas, the MoO₂ phase was minor and poorly crystalline β -Mo₂C can be observed even at 600°C. The pure β -Mo₂C phase can be obtained when the temperature increased up to above 700°C. The results indicated that H₂ atmosphere facilitated the carburization of MoO₂.^[23]

Figure 3 shows the XRD patterns of the samples prepared from CoMo-containing resin precursor under Ar or H₂ at different temperatures. In the case of CoMo sample treated under an Ar atmosphere (see Figure 3a), at 500°C some main diffraction peaks at 2θ of 19.1, 23.3, 25.5, 26.5 and 27.3° ascribed to CoMoO₄ phase (JCPDS 21–0868) and a weak peak at 2θ of 37.0° due to Co₃O₄ phase (JCPDS 65-3103) were detected besides some weak peaks assigned to the MoO₂ phase. The results were in agreement with the results reported in the literature.^[20] For the sample reduced at 630°C or 650°C, the peaks due to CoMoO₄ and Co₃O₄ phases disappeared, and new $Co_2Mo_3O_8$ (main diffraction peaks at $2\theta = 17.9$, 25.3, 32.5, 36.0, 37.1 and 45.5°, JCPDS 71-1423) and Co phases (main diffraction peaks at $2\theta = 44.2$, 51.5 and 75.9°, JCPDS 15–0806) were observed. The results indicated that the CoMoO₄ and Co₃O₄ phases were reduced by carbon to form Co₂Mo₃O₈ and Co phases, as suggested before.^[24] When the temperature





Figure 3. XRD patterns of the samples prepared from CoMo-containing resin precursor at different temperatures in Ar (a) or H_2 (b).

increased up to 700°C, there were new diffraction peaks at 2θ of 35.3, 39.9, 42.4, 46.4 and 72.4°, which was assigned to Co₃Mo₃C carbide (JCPDS 65-7128). It was clear that the CoMo bimetallic carbide was obtained from Co₂Mo₃O₈. In addition, some β -Mo₂C and Co impurities were found in the material. With a further increase of the temperature to 800°C, the diffraction peaks for Co₃Mo₃C became weaker but those for β -Mo₂C and Co became much sharper, indicating that phase separation occurred in the Co₃Mo₃C carbide at a higher temperature. The result was similar to the observation in previous study.^[20] It was therefore reasonable to deduce that the β -Mo₂C and Co impurities were obtained via two pathways of (i) the carbothermal reduction of MoO₂, CoMoO₄ and Co₃O₄ phases at lower temperatures and (ii) the decomposition of Co₃Mo₃C phase at higher temperatures. In the case of CoMo sample treated under H₂ atmosphere (see Figure 3b), the resulting materials were similar to those described above. However, H2 atmosphere promoted the formation, growth and decomposition of Co₃Mo₃C. It was found that the Co₂Mo₃O₈ began to be converted into Co₃Mo₃C phase even at 600°C. The complete transformation of the CoMo oxide occurred at 630°C, and at this temperature a very small amount of β -Mo₂C and Co impurities were found in the Co₃Mo₃C product. With the increase in temperature, the Co₃Mo₃C crystallites grew, at the same time they began to decompose with temperature. The Co₃Mo₃C phase was almost



Figure 4. XRD patterns of the samples prepared from CoMo-containing resin precursor under H_2 at 630°C with different calcination times.

completely decomposed to β -Mo₂C and Co at 800°C. It can be concluded from Figure 3 that a H₂ atmosphere and a low temperature of 630°C were the most appropriate conditions to prepare Co₃Mo₃C with minor impurities.

Subsequently, the influence of calcination time on the growth of Co₃Mo₃C crystallites was investigated. Figure 4 shows the XRD patterns of the samples prepared from CoMo-containing resin precursor under H₂ at 630°C with different calcination times. The results clearly showed that the Co₃Mo₃C crystallites grew with calcination time and they appeared to be of good quality at 24 h. However, the β -Mo₂C and Co impurities were always very minor and they remained unchanged in quantity with calcination time. It was interesting to note that when the calcination time was increased to 48 h, only little shifts of 2θ values can be observed for all reflection peaks in comparison with those obtained at 24 h. These reflection peaks located at $2\theta = 35.8, 40.5, 43.1, 47.1$ and 73.7° matched with the standard data of Co6Mo6C phase (JCPDS 80-0338). The result indicated that Co₃Mo₃C phase can be transformed into Co₆Mo₆C phase via long calcination time probably due to the fact that their metal atom arrangement and the type of crystal lattice (*Fd3m*) were the same as each other.^[24] Therefore, it confirmed that Co₆Mo₆C carbide had been prepared by this resin-based carbothermal reduction route.

The morphologies of as-prepared β -Mo₂C (Mo-Ar-900-1), Co₃Mo₃C (CoMo-H₂-630-24) and Co₆Mo₆C (CoMo-H₂-630-48) samples were characterized by TEM. It can be seen from TEM images (Figure 5) that the morphologies of these samples were composed of dispersed nanoparticles with the sizes of <100 nm. Some particles gathered closer to each other and formed large aggregates. Note that there was a halo around the agglomerate in Figs. 5b and c, and the EDX results (Fig. S 1 Supplemental Materials) revealed that only carbon could be detected in this microregion. Therefore, this halo might be a carbon platelet originated from the carburization of resin. The result agreed with our previous study in which resin-based carbothermal reduction route can produce carbon plateletwrapped particles.^[22] According to the XRD data (Figs. 2 and 4), the crystal sizes of β -Mo₂C, Co₃Mo₃C and Co₆Mo₆C samples estimated by the Scherrer method were 30, 53 and 54 nm, respectively. These values were in the size range observed by TEM. Note that the as-prepared bimetallic CoMo carbides



Figure 5. Low and high resolution TEM images of (a) Mo-Ar-900-1, (b) CoMo- H_2 -630-24 and (c) CoMo- H_2 -630-48 samples.

showed much smaller sizes than those submicrometer-sized bimetallic CoMo carbides prepared using decolorizing carbon as a carbon source.^[21] Additionally, the HRTEM images clearly showed that the measured spacings between lattice fringes of 0.228, 0.213 and 0.209 nm can be found, and they were consistent with the d-spacings of the (101) plane of β -Mo₂C, the (511) plane of Co₃Mo₃C and the (511) plane of Co₆Mo₆C, respectively.^[25] For catalysis, one of the main characteristics was the specific surface area. The specific surface areas of the Mo-Ar-900-1, CoMo-H₂-630-24 and CoMo-H₂-630-48 samples measured by surface area analyzer were 387.5, 405.4 and 400.2 m² g⁻¹, respectively.

Formation mechanism

The carburization processes of the Mo- and CoMo-containing resin precursors were followed by TG-MS in Ar to investigate the formation mechanism of monometallic and bimetallic carbides. As suggested by previous studies,^[26,27] when the resins were carburized in inert atmosphere or vacuum, the volatile products should be mainly composed of H₂O, CH₄, H₂ and



Figure 6. TG-MS profiles of (a) PR, (b) Mo- and (c) CoMo-containing resin precursors.

C₂H₂, with a comparatively low level of benzene and toluene. In this work, only the results for masses (m/z) of 2 (H_2) , 16 (CH₄), 18 (H₂O), 28 (C₂H₂ or CO) and 44 (CO₂) were shown for understanding the formation mechanism, as the masses of 78 (C_6H_6) and 91 (C_7H_8) were almost featureless or provided little additional information. Figure 6 shows the TG-MS profiles of PR and Mo- and CoMo-containing resin precursors, and the corresponding results are listed in Table 1. It can be seen that the carburization process of PR involved two temperature regions: low-temperature (≤440°C) and high-temperature (>440°C) stages (see Figure 6a). In the low-temperature range a successive sharp weight loss (40.16%) was observed on the TG profile, which should be due to the dehydration reactions of resin,^[27] because a large quantity of H_2 (m/z = 2) and H_2O (m/z = 18) gases were detected by MS. The TG profile showed a sharp weight loss (20.21%) in the high-temperature range,

	Weight loss (%)		Assig	Assignment	
Sample	≤440°C	>440°C	≤440°C	>440°C	
PR	40.16	20.21	Resin dehydration	Resin carburization	
Mo precursor	25.89	26.87	Resin dehydration and MoO ₂ formation	Resin carburization and Mo ₂ C formation	
CoMo precursor	22.58	26.36	Resin dehydration and CoMoO _x formation	Resin carburization and CoMoC _x formation	

Table 1. The TG-MS results for PR, Mo- and CoMo-containing resin precursors.

which was probably due to the carburization of resin to produce carbon.^[27] A large quantity of multi-component gases were detected by MS and the simultaneous signals of m/z = 2, 16, 18and 28 corresponded to H₂, CH₄, H₂O and C₂H₄, respectively. In comparison to the PR, the TG-MS profiles of Mo- and CoMocontaining resin precursors showed several different features in both the low- and the high-temperature stages. On the one hand, we observed that in the low-temperature regions (see Figs. 6b and c), the difficulty in the dehydration of resin ranked in the order of CoMo-containing resin $(215^{\circ}C) < Mo$ -containing resin $(360^{\circ}C) < PR (400^{\circ}C)$. The results indicated that Mo and Co metal species (especially for Co) can facilitate the dehydration of resin. And the weight losses of Mo and CoMo precursors (25.89 and 22.58%) were less than that of PR (see Table 1), which suggested the formation of MoO_x and CoMoO_x.^[27] On the other hand, in the high-temperature ranges (Figs. 6b and c), the TG curves showed another strong weight losses around 830 and 790°C for Mo and CoMo precursors, respectively, but the weight losses (26.87 and 26.36%) were more than that of PR (see Table 1). In addition, MS curves showed that a large amount of CO was evolved, accompanied with a small amount of CO_2 . The facts indicated that the high-temperature carburization stages of Mo- and CoMo-containing resin precursors involved strong redox reactions, leading to the formation of carbides. It was therefore reasonable to conclude that the solid product (i.e. carbon) from thermal carburization of resin should serve as a reducing agent in these redox reactions. In addition, there was a consumption of the H₂ generated at about 600°C during carburization processes, which contributed more or less to the reduction of oxide precursors. It was obvious from Figs. 6b and c that the final carbide products were formed at 830 and 790°C for Mo- and CoMo-containing resin precursors, respectively. The results also indicated that the addition of Co to resin precursor facilitated the formation of carbide, which was in accord with the XRD analyses (Figs. 2 and 3).

The formation processes of carbides under H₂ atmosphere via carbothermal reduction method were proposed as following.^[20] Reduction of metal oxides by hydrogen; reaction between partially reduced oxides and surface carbon atoms of carbon materials under the hydrogen atmosphere. The processes were similar to those under Ar mentioned above. However, it can be seen from Figs. 2 and 3 that H₂ atmosphere facilitated the formation of carbides at lower temperatures than Ar atmosphere.

Experimental

Sample preparation

The raw resin used was a phenolic resin (PR, $[C_6H_6O\cdot CH_2O]_x$, purchased from Wuxi Xinyehao Chemical Co. Ltd.) and the major indexes and properties were listed in Table 2. Firstly, the

raw resin was dried at 110°C for 12 h, and then ground to a fine powder. After that, the resin powder was incipient-wetness impregnated by an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O, or an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O and Co(NO₃)₂·6H₂O mixture (1:1 Mo:Co ratio) with a 30 wt% Mo loading. The slurries were evaporated at 110°C for 12 h to obtain Mo- and CoMo-containing resin precursors. Finally, about 1.0 g of the dried resin precursor was packed in the middle of a 4.2 cm ID, quartz tubular reactor. The quartz reactor was heated with a tubular electric resistance furnace equipped with a temperature controller (purchased from Xiamen Yudian Automation Technology Co. Ltd.) and the temperature was measured with a thermocouple placed adjacent to the sample inside the reactor. The carrier gas (Ar or H₂) was controlled using mass flow controllers (purchased from Beijing Sevenstar Electronics Co. Ltd.) and was introduced at a flow rate of 50 mL min⁻¹. The precursor was heated from room temperature (RT) to a given value at a rate of 10°C min⁻¹ and maintained at this temperature for different times from 1 to 48 h, followed by cooling to RT under Ar or H₂ flow, and then passivated in a 1% O₂/Ar flow for 2 h. A series of products were obtained from heating at 500, 600, 630, 650, 700, 800 and 900°C, designated as Mo-Ar/H₂-T-t and CoMo-Ar/H2-T-t for Mo and CoMo samples, respectively (T = 500, 600, 630, 650, 700, 800 and 900, t = 1, 6, 12, 24)or 48).

Sample characterizations

X-ray diffraction (XRD) measurements were carried out using Cu K α source with a X'Pert Pro MPD diffractometer. BET surface area and pore structure of the sample were measured through nitrogen adsorption at liquid-nitrogen temperature (77 K) by a surface area analyzer (NOVA4200). The morphologies and microstructure of the products were characterized by transmission electron microscopy (TEM, Philips Tecnal 10) equipped with an EDX system. Thermogravimetrymass spectrometry (TG-MS) experiments were performed using thermoanalyzer STA 449 F5 Jupiter coupled with quadrupolar mass-spectrometer QMS 403 D Aeolos. The samples were heated in a stream of pure Ar gas at a rate of 10°C

Index/Property	Value
Softening point ^a (°C)	100
Polymerization rate ^a (s)	130-180
Free phenol ^a (%)	6
Fugitive constituent ^a (%)	1
BET surface area ^b (m ² g ^{-1})	5.7
Average pore diameter ^b (nm)	7.21
Total pore volume ^b (cm $^{-3}$ g $^{-1}$)	0.01

^aProvided by the company.

^bObtained by BET surface area measurement.

min⁻¹ from 50 to 1000°C. The traces of masses (m/z) with the increase of temperature were recorded as follows: m/z = 2, m/z = 16, m/z = 18, m/z = 28, m/z = 40, m/z = 44, m/z = 78 and m/z = 91.

Conclusions

In summary, a phenolic resin (PR) was reported firstly as a carbon source for the synthesis of nanostructured monometallic Mo and bimetallic CoMo carbides via carbothermal reduction route. The results showed that phase-pure β -Mo₂C can be formed under an Ar atmosphere at 900°C or a H₂ atmosphere above 700°C. However, almost pure CoMo carbides (Co₃Mo₃C and Co₆Mo₆C) can be obtained only under a H₂ atmosphere at a low temperature of 630°C for 24 and 48 h, respectively. The carburization processes of the Mo- and CoMocontaining resin precursors involved two temperature regions: low-temperature (\leq 440°C) and high-temperature (>440°C) stages. The formation of Mo and CoMo carbides was observed at the high-temperature ranges, in which oxide precursors were reduced by the carburization products (C and H₂) to yield carbides, with the release of CO_x and H₂O. Additionally, the replacement of Ar atmosphere with H₂ atmosphere facilitated the formation of carbides in the carbothermal reduction route.

Acknowledgements

The work was supported by the National Natural Science Foundation of China (No. 21276253) and by talent scientific research fund of LSHU (No. 2013XJJ-018).

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