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A novel route to nanosized molybdenum boride and carbide and/or metallic molybdenum by thermo-synthesis method from MoO_3, KBH_4, and CCl_4

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Abstract

Nanosized molybdenum boride and carbide were synthesized from MoO_3, KBH_4, and CCl_4 by thermo-synthesis method at lower temperature. The relative content of Mo, Mo_2C, and molybdenum boride in the product was decided by the molar ratio between MoO_3, KBH_4, and CCl_4. Increasing the molar ratio of CCl_4 to MoO_3 was favorable to the production of Mo_2C. Increasing the molar ratio of KBH_4 to MoO_3 was favorable to the production of molybdenum boride. By carefully adjusting the reaction conditions and annealing in Ar at 900°C, a single phase of MoB could be obtained.

Keywords: Molybdenum boride; Molybdenum carbide; Thermo-synthesis

1. Introduction

Molybdenum boride and carbide have long since attracted considerable interest for technological application (e.g., as hard coatings, in machine tools, high-performance gear parts, golf shoe spikes, and snow tires) because of their high melting point, chemical stability, extremely high hardness, high strength, and excellent resistance against mechanic and corrosive wear [1–3]. In addition, molybdenum carbide showed catalytic properties similar to those of noble metals, which led to an explosion of interest in the use of molybdenum carbide as catalysts for a wide range of reactions, especially over the past decade. They have been shown to be particularly active for hydrogenation [4], dehydrogenation [5–8], the Fischer–Tropsch reaction [9], hydrocarbon isomerization [10], and the oxyforming of methane [11].

Some of the methods developed for synthesized molybdenum carbide include the temperature-programmed method developed by Boudart and co-workers [12], pyrolysis of metal precursors [13], solution reactions [14], and photochemically promoted formation of carbide from metallic molybdenum and graphite [15].

Several methods have been developed for synthesis of molybdenum boride: solid-state reaction [16,17], mechanochemical synthesis [18,19], electrochemical synthesis [20–22], and multiphase diffusive reaction [23]. Usually, a much higher temperature condition (above 900°C) was required by almost all of the above-mentioned methods. Moreover, the obtained molybdenum borides usually are not nanosized powder. Therefore, it is of interest and significance to develop a new method of preparation of molybdenum boride at lower temperature.

In this work, we present a novel route to the synthesis of nanosized molybdenum boride and carbide by the thermo-synthesis method at a lower temperature (300°C). To our best knowledge, there have been no reports about this new reaction of MoO_3, KBH_4, and CCl_4.

2. Experimental

Preparation: A mixture of MoO_3 and KBH_4 was mixed, and comminuted in mortar according to a proper molar ratio of MoO_3 to KBH_4. A certain mount of CCl_4

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was added to the mixture of MoO_3 and KBH_4, and then, the mixture of MoO_3, KBH_4, and CCl_4 was transferred into a 1 L autoclave. The autoclave was purged by Ar. The autoclave was heated from room temperature to 300°C, and kept at 300°C for 4 h. In the process of elevation of the temperature, the pressure in the autoclave was observed. From the rate of change of pressure in the autoclave, we could know whether the reaction between MoO_3, KBH_4, and CCl_4 proceeds slowly or quickly as a lot of gases such as H_2 and/or HCl are produced when the reactants begin to react with each other. After the reaction, the gases were let out, and the autoclave was cooled to room temperature. The product mixture was passivated by allowing a mixture of 1% O_2/N_2 to diffuse into the autoclave at a flow rate of 100 mL/min for 2 h to prevent the product from violently oxidizing if exposed to air immediately following the reaction. The final product is obtained by dissolving the above-mentioned mixture in distilled water, thoroughly washing, filtering, exchanging with acetone for several times, and drying at room temperature.

Characterization of catalysts: The composition of as-synthesized samples was determined according to the procedure as follows. The content of C was measured on Perkin-Elmer 240; the content of Mo and B was determined by using induced coupled plasma (ICP) on TJA1100. BET surface area of sample was measured on a MICROMERITICS ASPAP-2000 adsorption analyzer using nitrogen as adsorbate. Powder X-ray diffraction analysis was performed with Ni-filtered Cu$K\alpha$ radiation with Shimadzu XD-3A X-ray diffractometer. The working voltage of 35 kV and the electronic current of 25 mA were employed. The morphology of the as-synthesized samples was observed by transmission electron microscopy on JEM-100CX.

3. Results and discussion

The detailed preparation conditions and properties are presented in Table 1. It can be seen that when the molar ratio of KBH_4 to MoO_3 is 2:1, boron is not detected in sample 1 and the content of C and Mo in sample 1 is 1.43%, 98.57%. When the molar ratio of KBH_4 to MoO_3 is 3:1, boron is detected in sample 2, and the contents of C, B, Mo in sample 2 were 5.16%, 3.89%, and 90.95%. With further elevation of the molar ratio of KBH_4 to MoO_3, the content of C in the sample decreases gradually, and the content of B increases. When the molar ratio of KBH_4 to MoO_3 is 4:1, the product contains larger content of boron (7.43%) and smaller content of carbon (1.65%). As the molar ratio of KBH_4 to MoO_3 reaches 6:1, the content of B in sample 8 increases to 10.53%, and C could not be detected. As the molar ratio of MoO_3 to KBH_4 is 5:1, the elevation of the molar ratio of CCl_4 to KBH_4 from 0.52 to 1.27 leads to the increasing of the content of C from 1.24% to 1.48% and the decreasing of the content of B from 10.50% to 8.32% in the product.

Fig. 1 presents the patterns of XRD of as-synthesized samples prepared under the condition of different molar ratio of KBH_4 to MoO_3. It can be seen that the product is a mixture of Mo_2C and Mo when the molar ratio of KBH_4 to MoO_3 is 2:1. When the molar ratio of KBH_4 to MoO_3 increases to 3:1, molybdenum boride (MoB) with tetragonal crystalline structure appears in the product and the product is a mixture of Mo_2C, Mo_2B, and MoB. When the molar ratio of KBH_4 to MoO_3 is 3.5:1, the phase of Mo_2B disappears, and the product comprises of Mo_2C and MoB. With the elevation of the molar ratio of KBH_4 to MoO_3, the content of Mo_2C decreases gradually. As the molar ratio of KBH_4 to MoO_3 is 4:1, the phase of MoB_2 appears, and the product mainly comprises of MoB with a small amount of Mo, Mo_2C, and MoB_2. As the molar ratio of KBH_4 to MoO_3 reaches 5:1, the product is composed of Mo, MoB, and MoB_2 with only a small amount of Mo_2C. Meanwhile, it can also be seen that the as-synthesized sample is poorly crystalline when the molar ratio of KBH_4 to MoO_3 is above 4:1.

In order to further determine the phase composition of the as-synthesized samples prepared under the

Table 1
The properties of the products synthesized under the different conditions

No.	Molar ratio		Content (wt%)			Average crystal size by XRD (nm)					Surface area ($m^2 g^{-1}$)
	KBH_4 and MoO_3	CCl_4 and KBH_4	Mo	B	C	Mo	MoB_2	Mo_2C	MoB_2	Mo_2B	
1	2	1.43	98.57	0	1.43	111.7	111.3				1.6
2	3	1.43	90.95	5.16	3.89		87.9	58.1		129.1	7.8
3	3.5	0.52	91.44	5.84	2.72		45.1	19.4			29.1
4	4	0.52	90.31	8.04	1.65	12	27.4	15.9	12.4		35.1
5	5	1.27	90.20	8.32	1.48	15.2	43.8	15.3	14.9		17.4
6	5	0.52	88.26	10.50	1.24	25	43.8	8	12.1		33.1
7	5	0	97.46	2.56	0	9.7					37.1
8	6	0.52	89.46	10.54	0	12.4	9.8	10.7			27.6

The average crystal sizes of Mo, Mo_2C, MoB, MoB_2, and Mo_2B are determined from the broadening of corresponding X-ray spectral peaks (at 40.5°, 39.5°, 42.5°, 45.3°, and 40.99°, respectively) by Scherrer formula: $L = 0.89\lambda/\beta \cos\theta$.

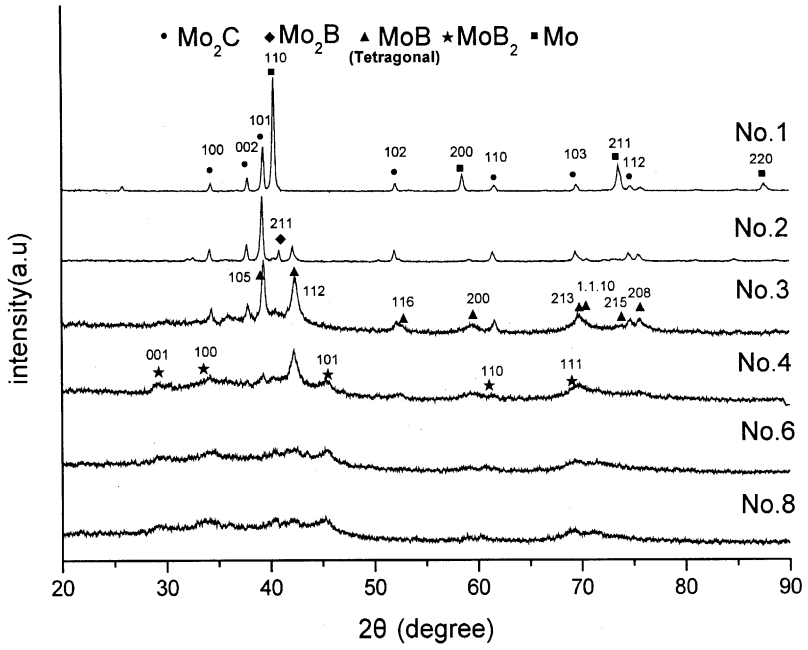

Fig. 1. The patterns of XRD of as-synthesized samples prepared under the condition of different molar ratio of KBH_4 to MoO_3.

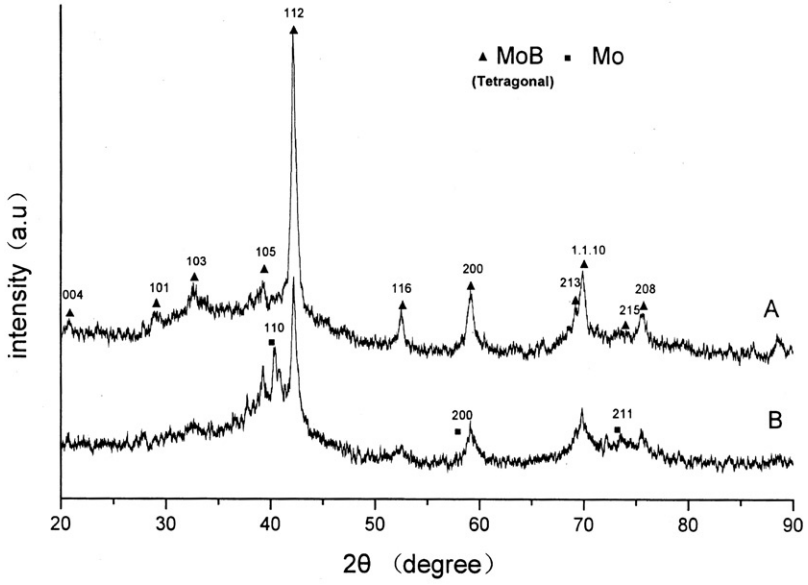

Fig. 2. The patterns of XRD of the samples annealed for 2 h at 900°C: (A) annealing sample 8 at 900°C; (B) annealing sample 6 at 900°C.

condition of higher molar ratio of KBH_4 to MoO_3, samples 6 and 8 are annealed at 900°C for 2 h under the atmosphere of Ar. Fig. 2 shows the patterns of XRD of the annealed samples. Compared with the pattern of sample 6, the phase of MoB_2 disappears, and the content of Mo decreases, and the content of MoB increases after annealing, which is indicative of the reaction between MoB_2 and Mo at 900°C:

$$Mo + MoB_2 \rightarrow MoB.$$

By annealing sample 8 at 900°C for 2 h under the atmosphere of Ar, a single phase of tetragonal MoB is obtained with disappearance of the phase of Mo and MoB_2, which shows that content of MoB_2 in sample 8 is equal to Mo.

Fig. 3 presents the patterns of XRD of as-synthesized samples prepared under the condition of different molar ratio of CCl_4 and KBH_4, and the same molar ratio of KBH_4 to MoO_3. It can be seen that molybdenum metal is obtained in the absence of CCl_4. Although there is 2.14% of B in this molybdenum metal product, no

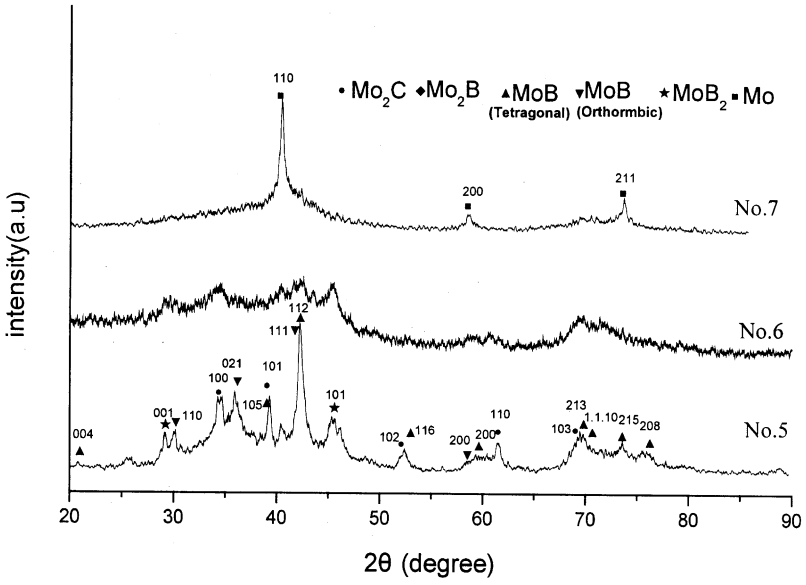

Fig. 3. The patterns of XRD of the samples prepared under the condition of different molar ratio of CCl_4 to KBH_4.

crystalline molybdenum boride and boron are detected by XRD. In the presence of CCl_4, a mixture of molybdenum carbide and boride is obtained. With the elevation of the content of CCl_4 in the reactants, the final product gets a better crystalline structure with increased content of Mo_2C and decreased content of molybdenum boride. For example, when the molar ratio of CCl_4 to KBH_4 was 0.52, the product has a poor crystalline structure with a small amount of Mo_2C. With the elevation of the molar ratio of CCl_4 to KBH_4 from 0.52 to 1.27, the product has a better crystalline structure with higher content of Mo_2C. Meanwhile, a new phase of orthorhombic MoB (β-MoB) appears in the product (sample 5). When the molar ratio of KBH_4 to MoO_3 is 2, a mixture of Mo_2C and Mo is obtained from the reaction between CCl_4, KBH_4 and MoO_3. When the molar ratio of KBH_4 to MoO_3 is 3 or above 3, the reaction between CCl_4, KBH_4, and MoO_3 leads to a mixture of Mo_2C, molybdenum boride (MoB or Mo_2B), and/or metallic Mo. However, whatever the molar ratio of KBH_4 to MoO_3 is 2, 3, 4, 5 or 6, the change of the composition of the as-synthesized product with the variation of the molar ratio of CCl_4 to KBH_4 has similar tendency to one of the products prepared at the molar ratio of KBH_4 to MoO_3 equal to 5: the higher the content of the molar ratio of CCl_4 to KBH_4, the higher the content of Mo_2C in the as-synthesized product.

When the molar ratio of KBH_4 to MoO_3 is 2, the product with a surface area of only $1.6\,m^2\,g^{-1}$ has an average crystal size of more than 100 nm. As the molar ratio of KBH_4 to MoO_3 reached 3, the nanosized product with an average particle size of 87.9 nm (Mo_2C), 58.1 nm (MoB), and 129.1 nm (Mo_2B) is obtained. The surface area increases to $7.8\,m^2\,g^{-1}$. With the elevation of the molar ratio of KBH_4 to MoO_3, the surface area of the product increases, and the average crystal size decreases. However, when the molar ratio of KBH_4 to MoO_3 is more than 4:1, a little change of the surface area and average crystal size of product is observed. Fig. 4 shows the morphology of as-synthesized samples. As can be seen from Fig. 4, the particles produced under the condition of molar ratio of KBH_4 to MoO_3 of more than 3:1 are well dispersed, especially for samples 3 and 4. The particle sizes of sample 3 which mainly range from 20 to 40 nm are obviously larger than one of the samples produced under the condition of molar ratio of KBH_4 to MoO_3 of more than 4:1. There are much more particles with less than 20 nm observed in samples 4, 6, and 8 than in sample 3. Compared with the morphology of the product synthesized at a higher molar ratio of CCl_4 to KBH_4 (sample 5), the product produced at a lower molar ratio of CCl_4 to KBH_4 (sample 6) has smaller particle size ranging from 5 to 30 nm. The particle sizes are in agreement with the average crystal sizes estimated by XRD. The more widely ranged distribution of particle size is attributed to the different average crystal sizes of several matters in the product.

As pure molybdenum boride or carbide has been applied in technological fields (e.g., as hard coatings, in machine tools, high-performance gear parts, golf shoe spikes, and snow tires) [1–3], the as-synthesized mixture of nanosized molybdenum boride and carbide could also find application in these fields. The presence of metallic molybdenum in some of molybdenum boride and carbide could overcome the brittleness of these composite ceramic materials, and make them more ductile and more easily being processed because metals such as Cr, Ni, Mo, and Fe, etc. as an adhesive usually have to be added into metal boride or its composite to make them more easy to process [24]. The application of

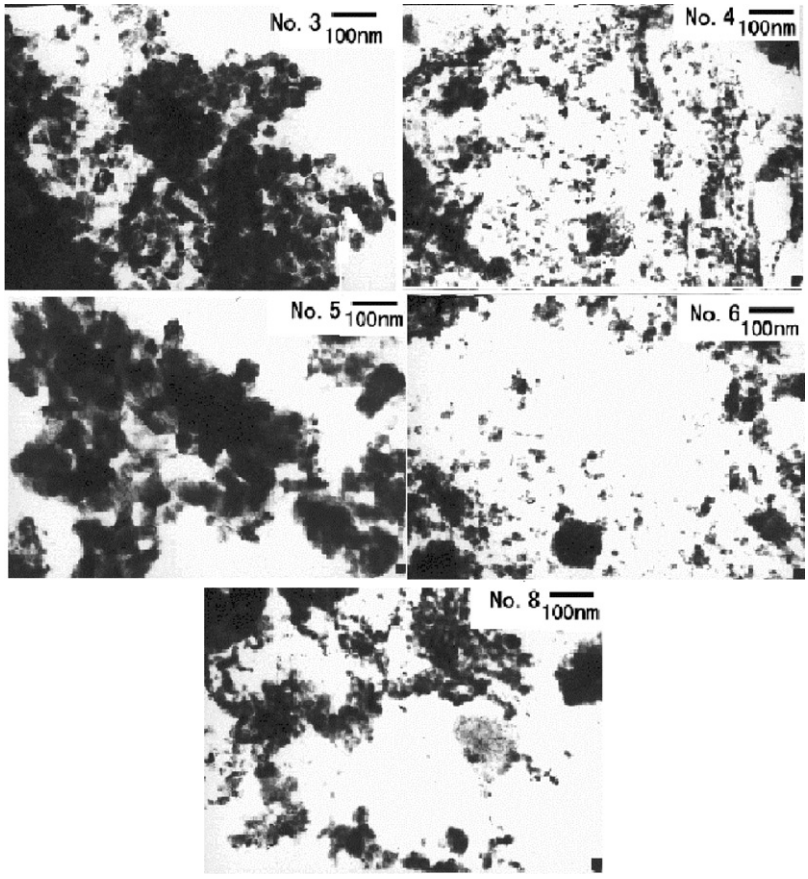

Fig. 4. The morphology of as-synthesized samples.

as-synthesized samples in catalytic selective hydrogenation of alkadiene to alkene is in progress.

In order to determine the mechanism of the above-mentioned reactions, the effluents produced by reaction of MoO_3, KBH_4, and CCl_4 are analyzed by absorbing the effluent with distilled water. It is proved that the effluents produced by the reaction of MoO_3, KBH_4, and CCl_4 are composed of HCl and H_2, and the effluent produced by the reaction of MoO_3 and KBH_4 only comprises of H_2. Fig. 5 presents the pattern of XRD of the mixture of sample produced by the reaction of MoO_3, KBH_4, and CCl_4 with 1:3.5:1.82 of the molar ratio between MoO_3, KBH_4, and CCl_4. It can be seen that the mixture contained KCl apart from molybdenum carbide and boride. KCl was formed in all the above-mentioned reactions of MoO_3, KBH_4, and CCl_4. In all the mentioned reactions of MoO_3, KBH_4, and CCl_4, a black fluffy solid matter attached to the stirrer of autoclave was obtained except for the metallic molybdenum, molybdenum carbide and/or boride. The results of chemical analysis show that this black solid is composed of B and C of which the content depends on reaction condition, e.g., the molar ratio between MoO_3, KBH_4, and CCl_4. The result of XRD shows that this black matter is amorphous. Our experiment exhibits that a black fluffy solid matter composed of B and C could be also produced in the reaction of KBH_4 and CCl_4 at 300°C even in the absence of MoO_3; the effluents produced by this reaction are proved to be H_2 and HCl. The result of XRD exhibits that KCl is produced in this reaction.

From the above observation, it is reasonably inferred that the mechanisms of the above-mentioned reactions are as follows:

$$KBH_4 + MoO_3 \rightarrow KBO_2 + Mo + H_2, \quad (1)$$

$$MoO_3 + KBH_4 + CCl_4 \rightarrow HCl + KCl + Mo_2C + CBy + H_2, \quad (2)$$

$$MoO_3 + KBH_4 + CCl_4 \rightarrow HCl + KCl + MoBx + CBy + H_2, \quad (3)$$

$$KBH_4 + CCl_4 \rightarrow HCl + KCl + CBy + H_2 \quad (4)$$

$$KBO_2 + HCl \rightarrow KCl + HBO_2. \quad (5)$$

It is discovered by our experiment that the reaction between KBH_4 and MoO_3 (1) proceeds slowly in the absence of CCl_4; the reaction between KBH_4 and CCl_4 (4) also proceeds slowly in the absence of MoO_3, and no

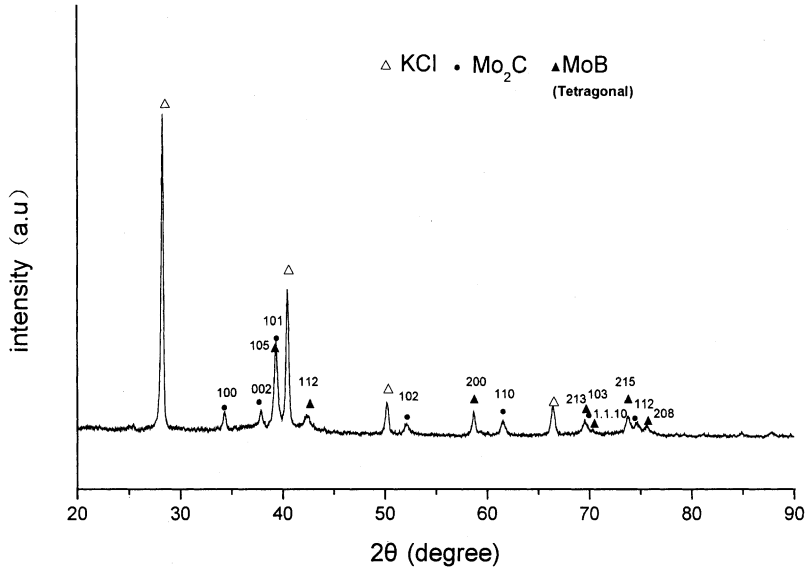

Fig. 5. The pattern of XRD of the mixture of sample produced by the reaction of MoO_3, KBH_4, and CCl_4 with 1:3.5:1.82 as the molar ratio between MoO_3, KBH_4, and CCl_4.

reaction is observed between MoO_3 and CCl_4 under our experimental condition. But reactions (2) and (3) proceed very rapidly so long as the temperature is above 260°C or so. From these observations, it is concluded that there is a cooperating role among KBH_4, MoO_3 and CCl_4 that could accelerate the reactions.

From the above mechanisms, it can be concluded that relative contents of Mo, Mo_2C, and molybdenum boride in the product is decided by the competitive rate of reactions (1)–(3). To decrease the molar ratio of KBH_4 to MoO_3 and increase the molar ratio of CCl_4 to KBH_4 is favorable to reaction (2) as it may lead to more CCl_4 molecules attacking the transient Mo species produced by the reaction between KBH_4 and MoO_3 to form molybdenum carbide. Increasing the molar ratio of KBH_4 to MoO_3 is favorable to reaction (3) because it leads to more KBH_4 molecules attacking the transient Mo species to form molybdenum boride. Under the condition of lower molar ratio of KBH_4 to MoO_3, e.g., 2:1, the final product is composed of Mo and Mo_2C without molybdenum boride, which indicates that reactions (1) and (2) proceed more easily than reaction (3). With the elevation of molar ratio of KBH_4 to MoO_3, reaction (3) is accelerated, and moves towards the left. The more the molar ratio of KBH_4 to MoO_3 is, the higher the content of molybdenum boride in the product.

Under the condition of higher more ratios of KBH_4 and MoO_3, there are more KBH_4 molecules around MoO_3, which prevent the produced nuclei of Mo, Mo_2C, and molybdenum boride from aggregating to form the products with larger crystal sizes.

4. Conclusion

Molybdenum carbide and boride are synthesized from MoO_3, KBH_4, and CCl_4 by the thermo-synthesis method at lower temperature. The relative contents of Mo, Mo_2C, and molybdenum boride in the product are decided by the molar ratio between MoO_3, KBH_4, and CCl_4. Increasing the molar ratio of CCl_4 to MoO_3 is favorable to the production of Mo_2C. Increasing the molar ratio of KBH_4 to MoO_3 is favorable to the production of molybdenum boride. There is a cooperating role among KBH_4, MoO_3, and CCl_4 that could accelerate the reaction of formation of molybdenum carbide and boride.

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