

Progress in the Synthesis and Catalytic Properties of Molybdenum Carbide Materials

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Abstract: Molybdenum carbide is a new type of material with excellent physical and chemical properties due to the intercalation structure formed by the insertion of carbon atoms, which not only has the properties of a functional material, but also has excellent catalytic properties in the fields of hydrogenation and hydrogen production reactions. This paper reviews the properties and synthesis methods of molybdenum carbide, systematically introduces the advantages and disadvantages of different methods, and finally summarizes the applications of molybdenum carbide in catalytic hydrogenation, catalytic hydrogen production and photoelectric catalysis, and analyzes the current challenges and future directions of molybdenum carbide materials.

Keywords: Molybdenum carbide, Preparation method, Catalytic hydrogenation, Electrocatalysis.

1. Introduction

Transition metal carbides, such as molybdenum carbide, tungsten carbide and iron carbide, are a class of interstitial compounds formed by carbon atoms embedded in the transition metal lattice, whose structure is characterized by the radius of the carbon atoms being much smaller than that of the transition metal atoms, resulting in distortion and expansion of the lattice[1]. Transition metal carbides have unique physical and chemical properties, exhibiting characteristics of both ionic and covalent bonding, as well as metallic bonding and magnetic properties. Molybdenum carbide, as a representative of group IV-VI B metal carbides, is considered a very promising alternative to precious metal catalysts and has a wide range of applications in catalysis. Molybdenum carbide is known as a "platinum-like catalyst" due to the insertion of carbon atoms that modify the d-band properties of the parent metal, and is a new material that has been studied in recent years [2-4]. In addition, due to the special physicochemical properties and surface structure of carbides (e.g. molybdenum carbide), there is a very strong interaction between them as carriers and the active metal, which affects the geometry, particle size, and electronic state

of the dispersed metal to achieve efficient catalytic performance [5-7]. Therefore, the design and synthesis of carbide and metal/carbide interfacial catalytic materials using carbide (e.g. molybdenum carbide) as the active component or carrier has gradually become a hot research topic for scholars at home and abroad [8,9].

2. Properties of Molybdenum Carbide Materials

The spatial structure of transition metal carbides mainly depends on the valence electron number of the transition metal and the filling method of carbon atoms. In general, the insertion of carbon atoms makes the spacing between the parent metal atoms larger, resulting in a change in the structure of the carbide formed. The spatial structure of transition metal carbides can be divided into three types: face-centered-cubic (fcc), hexagonal close-packed (hcp) and simple hexagonal stacking (hex) [10] (Figure 1). For molybdenum carbide, the different order of atomic arrangement leads to the existence of four lattice structures, α - MoC_{1-x} with face-centered cubic structure, β - Mo_2C with hexagonal close-packed structure and γ - MoC and η - MoC with simple hexagonal stacking.

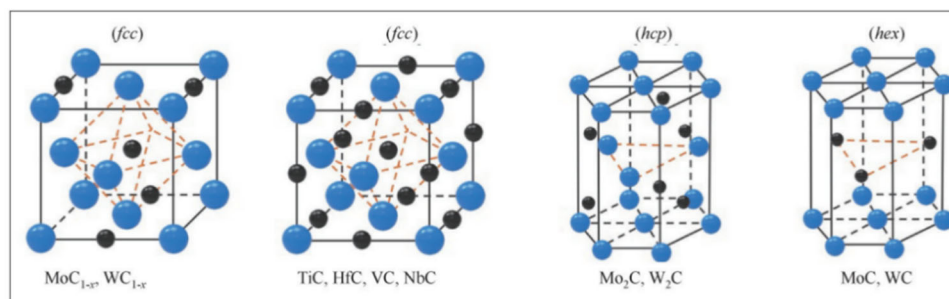


Figure 1. Four common crystal structures of transition metal carbides[11]

The spatial structure of molybdenum carbide is mainly influenced by geometric and electronic factors, and the geometric influence depends mainly on the Hägg rule, i.e., the structure of the interstitial phase depends on the ratio of the

radii of metal and nonmetal atoms $R = R_x/R_m$, and when the value of R is less than 0.59, the three structures described above are formed; while when the value of R is greater than 0.59, the more complex spatial structure of metal carbides

with more complex spatial structure^[12]. And the influence of electronic factors on the spatial structure of carbides is mainly based on the Engel-Brewer theory of metals, where the average number of s and p orbitals of metal atoms determines the lattice structure of metals^[13]. Metallic molybdenum has a body-centered cubic structure with an outermost electron configuration of $4d^55s^1$, where the 4d and 5s orbitals can undergo s-d hybridization, forming eight equivalent s-d hybrid orbitals that are arranged along eight octahedral voids in the body-centered cubic lattice. When nonmetallic carbon enters these gaps, they form covalent bonds with molybdenum atoms and allow the electron number to increase. The non-metallic carbon has the possibility of sp^2 hybridization or sp^3 hybridization, where an unpaired electron remains in the p orbital in the case of sp^2 hybridization and not in the case of sp^3 hybridization. Therefore, in this case, if the nonmetallic carbon enters the octahedral gap as sp^2 hybridization, it interacts with the electron in the s-d hybrid orbital and leads to an increase in charge density, while if the nonmetallic carbon enters the octahedral gap as sp^3 hybridization, it does not affect the s-d hybrid orbital. At high temperatures ($\sim 1000^\circ\text{C}$), due to factors such as thermal vibrational and entropic effects, non-metallic carbon tends to enter the octahedral gap as sp^2 hybridization and causes an increase in the charge density in the s-d hybrid orbitals. This leads to distortion and deformation of the molybdenum lattice and a change from a body-centered cubic structure to a hexagonal dense stacked structure or a face-centered cubic structure. In contrast, at low temperatures ($\sim 500^\circ\text{C}$), due to factors such as diminished thermal vibrational effects and the energy minimum principle, nonmetallic carbon prefers to enter the trigonal gap as sp^3 hybridization and does not affect the charge density in the s-d hybrid orbitals, which causes the molybdenum lattice to remain stable and maintain the body-centered cubic structure.^[14] The insertion of carbon atoms in molybdenum carbide leads to a d-band broadening of the metal Mo atoms, with the spacing changing from 0.27 nm to 0.30 nm, resulting in an increase in the density of states to the Fermi energy level and a change in the electronic structure properties, giving molybdenum carbide Pt-like metal properties (Figure 2), which is known as a "quasi-Platinum catalyst".

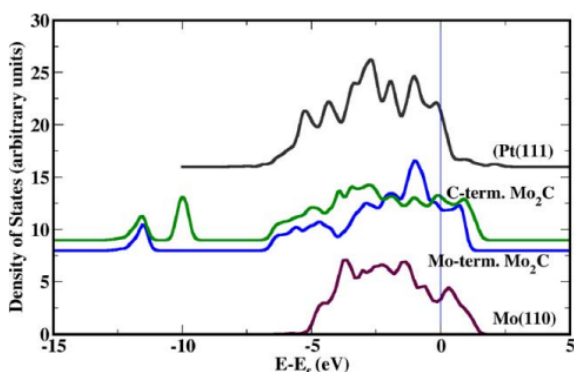


Figure 2. Comparison of d-band structures on the surfaces of Pt(111), β - Mo_2C and Mo(110)[15]

3. Synthesis of Molybdenum Carbide Material

Molybdenum carbide is a non-naturally occurring compound that requires more stringent conditions and higher temperatures than conventional synthesis methods, so the

preparation of molybdenum carbide needs to be improved and optimized. The properties of molybdenum carbide prepared by different methods vary somewhat, mainly in terms of crystalline phase, surface topography and size, so it is important to investigate the controllable preparation of molybdenum carbide. In recent years, the synthesis of molybdenum carbide has been investigated by changing the conditions of precursors and carbonization conditions.

3.1. Programmed warming reduction method

The method is also known as the gas-phase solid-phase method, named after the use of a carbon source in the gas phase and a molybdenum source in the solid phase, which mainly includes the carbon-containing gas CO and hydrocarbon gases CH_4 , C_2H_6 , C_3H_8 , etc., mixed with hydrogen as the reducing agent, while the molybdenum source is mainly molybdenum oxide and molybdenum metal salts, etc. Levy first reported the preparation of molybdenum carbide using carbon-containing alkanes as a carbon source in 1980 and named it as programmed temperature reduction method.^[16] In the programmed warming reduction method, the pyrolysis of the carbon-containing gas produces polymerized carbon, which contaminates the carbide surface and blocks the active sites and pores.^[17] In contrast, through hydrogen reduction, the polymerized carbon can be converted to gaseous hydrocarbons, which helps to remove the polymerized carbon contamination from the surface. Roohi et al. successfully prepared nanostructured Mo_2C by the TPR method using methane as the carbon source MoO_3 as the molybdenum source. It was investigated how the carburizer content, heating rate and final temperature affect the amount of carbon deposited, surface area and shape. However, the obtained Mo_2C samples showed low surface area ($25 \text{ m}^2/\text{g}$) and highly agglomerated nanoparticles, which is unfavorable for use as a catalyst.^[18] Harry Bitter et al. synthesized cubic phase α - $\text{MoC}_{1-x}/\text{NCF}$ using the TPre method. When the Mo loading was increased from 7.5 wt% to 20 wt%, hexagonal crystalline phase β - $\text{Mo}_2\text{C}/\text{NCF}$. This implies that the ratio of the molybdenum and carbon sources has a direct effect on the crystalline shape. The surface area ($130 \text{ m}^2/\text{g}$) and intrinsic activity of the two samples were approximately similar. However, the specific surface area of the prepared samples is lower than that of the carrier material NCF.^[19] TPre method is highly representative as a commonly used method for the preparation of molybdenum carbide, but its harsh preparation conditions, which require the use of large amounts of flammable gas at high temperatures, as well as the relatively high price of hydrogen-alkane mixtures, make this type of method expensive for the production of molybdenum carbide and difficult for mass production.

3.2. Carbothermal hydrogen reduction method

The carbothermal hydrogen reduction method, a modification of the TPre method, uses solid carbon sources such as activated carbon, carbon nanotubes, carbon black, and graphene instead of gaseous carbon sources, avoiding the use of flammable hydrocarbon gases and greatly reducing safety hazards. The method starts with the dispersion of molybdate solution on treated carbon carriers using impregnation method, and the loaded molybdenum carbide catalysts are prepared by drying treatment followed by programmed warming pyrolysis in the atmosphere of hydrogen. Meng et al. used SLF (carbon material made from sodium lignosulfonate), multi-walled carbon nanotubes (MWNCTs), cellulose (CEL),

and $g\text{-C}_3\text{N}_4$ as carbon sources. Loaded molybdenum carbide was successfully synthesized using the CHRe method.[20] With this method, the carrier can provide the carbon source while retaining the skeleton and porous structure of the solid carbon carrier to disperse the molybdenum source, or new structures can be generated that can have an impact on the adsorption and catalytic properties of molybdenum carbide. However, such methods can still produce polymerized carbon to cover the molybdenum carbide surface if too much carbon carrier is used.

3.3. Microwave pyrolysis method

By improving the carbothermal hydrogen reduction method, which no longer uses programmed heating such as a tubular heating furnace, a method using microwave heating was developed, called microwave pyrolysis. It takes advantage of the efficient heating and selective heating of microwaves, which can promote the in-situ decomposition of ammonium molybdate at a lower temperature and in a shorter time, thus achieving the reaction between molybdenum powder and carbon source to form molybdenum carbide particles. Vallance et al. used microwave pyrolysis to prepare pure phase tungsten carbide in a very short time, and the crystalline phase of WC can be regulated by adjusting the time of microwave pyrolysis, such as $\beta\text{-W}_2\text{C}$ can be produced by pyrolysis for 20 s and WC can be produced by pyrolysis for 40 s.[21] Huang et al. Prepared carbon-loaded molybdenum carbide particles ultra-fast using microwave pyrolysis with ammonium molybdate impregnated carbon carrier, and the prepared molybdenum carbide particles had small size and were uniformly dispersed on the carbon carrier.[22] The microwave pyrolysis method reduces the preparation time considerably compared to the conventional programmed heating method and avoids sintering of the molybdenum carbide particles in the high temperature environment for a long period of time, thus providing the advantage of small particle size. However, the method requires the use of a solid carbon source, which functions both as a carrier for absorbing microwaves and as a carbon source. In addition, the main disadvantage of microwave pyrolysis methods is that they are extremely expensive and difficult to apply on a large scale, so microwave pyrolysis methods have not been able to replace conventional preparation methods.

3.4. Single-source precursor method

Molybdenum carbide has been prepared by Giordano and Antonietti using urea as the carbon source. The reaction of MoCl_5 and ethanol, to which urea is added as a polymerizing agent, forms a glass-like substance that can be used as a precursor for subsequent transformations, a method known as the "urea glass" or "solution" method. This method allows the structure of the molybdenum carbide to be controlled, resulting in a small particle size (15-30 nm) and a high specific surface area ($22 \text{ m}^2/\text{g}$).[23,24] The advantage of the single-source precursor method is that molybdenum and carbon can be linked by chemical bonding in the precursor state, resulting in more uniform particles and less surface carbon deposition during the carbonization process. At the same time, the interaction of molybdenum and carbon groups can reduce the temperature of intramolecular redox and thus the carbonization reduction temperature[25], making it possible to prepare molybdenum carbide at low temperatures.

3.5. Chemical vapor deposition method

Chemical vapor deposition (CVD) is a technique that uses a gaseous precursor to chemically react on a solid surface, thereby forming a thin film or coating on that surface. CVD can be used to prepare a variety of materials, including metals, semiconductors, ceramics and polymers, and is one of the most effective methods for preparing molybdenum carbide films or nanostructures. The principle is as follows: First, suitable gaseous precursors, such as metal organic compounds (MOCVD), halides (HVPE), hydrides (HPCVD), etc., are selected, as well as carrier and reaction gases, such as hydrogen, noble gases, methane, etc. Then, in a heated reaction chamber, the precursors are mixed with the carrier gas and delivered to the solid substrate. At or near the substrate surface, the precursors decompose or react with the reaction gas to produce molybdenum carbide and deposit it on the substrate, while releasing by-products. Finally, the desired molybdenum carbide films or nanostructures are obtained under controlled parameters of temperature, pressure, flow rate and time. Fan et al. prepared molybdenum carbide-graphene nanoribbons ($\text{Mo}_2\text{C-GNR}$) by CVD method. They prepared molybdenum carbide by depositing a layer of metallic Mo ($\sim 75 \text{ nm}$) on graphene nanoribbons under atomic hydrogen treatment at 850°C . [26] Zhao et al. used a microwave plasma chemical vapor deposition (MPCVD) apparatus to synthesize two-dimensional (2D) $\alpha\text{-MoC}_{1-x}$. The system consisted of four main components: microwave generation and transmission module, vacuum system, quartz reaction chamber, and carrier gas system.[27] The main advantage of the chemical vapor deposition method is that it provides high purity products with good structural consistency; however, the chemical vapor deposition method requires a high vacuum environment, which is more expensive and not conducive to scalability.

3.6. Biomass carbonization method

In recent years, researchers have gradually shifted their research from traditional solid-phase carbon sources such as activated carbon and carbon nanotubes to biomass carbon sources. Biomass, being the most abundant resource on earth, is diverse, green, renewable and inexpensive. Abuliti et al. studied the catalytic steam reforming of biomass tar by preparing a biomass carbon loaded molybdenum carbide ($\text{Mo}_2\text{C/BC}$) catalyst from Japanese cedar and showed good catalytic activity, obtaining the highest H_2 yield at a Mo loading of 20 wt%, which was about 5 times higher than that of non-catalytic experiments. It was about 5 times higher than the non-catalytic experiments.[28] Yu et al. used pine wood as carbon source and carrier for the catalytic pyrolysis of rhombohedral Mo_2C under hydrogen atmosphere for the catalytic pyrolysis of lignin, which achieved lignin cracking gas phase bond breaking and deoxygenation at atmospheric pressure with a yield of 13.26 wt% of monocyclic aromatic hydrocarbons, including 74% of side chain aromatic hydrocarbons. The side chain aliphatic hydrocarbons of lignin were effectively retained and the hydrogen consumption was low, and the experiments showed that the catalyst could be targeted to break the C-O bonds of lignin and its derivatives.[29] Mu et al. prepared $\text{Mo}_2\text{C/C}$ nanoparticles using ammonium molybdate and corn stover as raw materials and calcined at 900°C for 4 h using a high temperature reduction-carbonation process with a specific surface area of $259 \text{ m}^2/\text{g}$ and a particle size of the $\text{Mo}_2\text{C/C}$ composites were synthesized as shown in Figure 3.[30] The biomass

carbonization method can prepare molybdenum carbide powder with high purity, high crystallinity, uniform distribution and excellent morphology at a lower temperature,

which effectively improves the performance and stability of molybdenum carbide, and can be used for large-scale preparation at low cost.



Figure 3. Schematic diagram of the preparation of biomass-based $\text{Mo}_2\text{C}/\text{C}$ nanoparticles

4. Catalytic Applications of Molybdenum Carbide Materials

4.1. Catalytic hydrogenation reaction

Molybdenum carbide materials have a wide range of applications in catalytic hydrogenation, showing great potential especially for hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation, and hydrodearomatization. Lewandowski M et al. used block $\beta\text{-Mo}_2\text{C}$ to catalyze the hydrodenitrogenation of indole. Under the reaction conditions of hydrogen/oil volume ratio of 600, temperature of 340°C , and hydrogen pressure of 6 MPa, $\beta\text{-Mo}_2\text{C}$ exhibited extremely high catalytic activity. The conversion of indole was close to 100% and the selectivity of aromatic products (benzene, toluene and ethylbenzene) reached about 47%. [31] Qiu et al. investigated the effect of $\beta\text{-Mo}_2\text{C}$ catalyst in the quinoline hydrodenitrogenation reaction and found that the catalyst had high catalytic activity and selectivity. Under the reaction conditions of 340°C and 4 MPa of H_2 pressure, quinoline could be completely converted and denitrogenated while the product contained 37% aromatic compounds, which was a significant improvement in performance compared to the conventional hydrodenitrogenation catalysts. [32] Yue et al. successfully prepared a new mesoporous alumina-supported molybdenum carbide by the same one-step hydrolysis followed by carbonization with a mixture of CH_4 and H_2 ($\text{Mo}_2\text{C}/\gamma\text{-MA}$), and exhibited high catalytic activity and stability in thiophene hydrodesulfurization (HDS). With 1 wt% of thiophene (3810 ppm S), $\text{Mo}_2\text{C}/\gamma\text{-MA}$ exhibited 92% conversion of thiophene, which is higher than $\text{MoS}_2/\gamma\text{-MA}$ (85%) and other molybdenum carbides supported on commercial alumina and $\gamma\text{-MA}$ prepared by impregnation, and the catalyst has well stability. [33] Yang et al. synthesized a series of palladium-loaded tetragonal phase molybdenum carbide mesoporous composite catalysts for the HDO of the biomass model molecule anisole. showed that the Pd site on $\alpha\text{-MoC}$ could increase the reaction TOF from 0.00666 to 0.115 h^{-1} and reduce the activation energy barrier from 74.5 kJ/mol to 48.2 kJ/mol, both of which were superior to the original carbide catalysts in this work and in the literature. The benzene selectivity of all catalysts was as high as 94%. [34] Chen et al. synthesized $\beta\text{-Mo}_2\text{C}$ and $\alpha\text{-MoC}_{1-x}$ in flakes by a self-assembled synthetic route using molybdenum-dopamine as a precursor. $\beta\text{-Mo}_2\text{C}$ exhibited 99.9% conversion and 95.2% benzene selectivity in the hydrodeoxygenation of diphenyl

ethers (HDO) reaction, whereas $\alpha\text{-MoC}_{1-x}$ exhibited only 74.6% conversion, 84.8% benzene selectivity and 12.7% phenol containing O product under the same conditions. 84.8% benzene selectivity and 12.7% phenol of O-containing products under the same conditions. The results suggest that $\beta\text{-Mo}_2\text{C}$ and $\alpha\text{-MoC}_{1-x}$ are promising catalysts for lignin activation. [35] Rocha et al. prepared molybdenum carbide catalysts supported on ultra-stable Y-type zeolites by adsorption of molybdenum hexacarbonyl vapor and wet spot impregnation with ammonium heptamolybdate solution, carburized at 923 K under 20% methane hydrogen mixture, which exhibited excellent hydrodearomatization performance and stability. [36]

4.2. Catalytic hydrogen production reaction

Molybdenum carbide catalysts for catalytic hydrogen production reactions mainly include methane dry reforming (DRM), methanol steam reforming (SRM) and water gas shift (WGS) reactions. Methane dry reforming reaction is the process of synthesizing CO and H_2 using the reaction of CO_2 and CH_4 , which is superior to Fischer-Tropsch synthesis for industrial applications, and molybdenum carbide catalysts with excellent potential play a great role in the reaction. Cheng et al. prepared Co and Ni loaded molybdenum carbide catalysts, respectively. It was found that $\text{Co}_{0.4}\text{Mo}_{1.6}$ exhibited DRM reaction activity due to Mo_2C at a Co/Mo ratio of 0.4, and the Ni-loaded molybdenum carbide catalysts had the best activity when the Ni/Mo ratio was 0.2. Methanol steam reforming reaction is considered to be the most effective hydrogen production reaction and has also shown excellent results in many scholars' studies. [37] Ma et al. prepared molybdenum carbide nanowires with high specific surface area, which showed excellent activity in methanol steam reforming reaction [38], while Ma et al. modified molybdenum carbide by Pt, Fe, Ni, Co and other metals, and the modified catalyst activity had The catalyst activity was significantly improved and the methanol conversion was up to 100% on Pt-modified catalysts with good stability. CO generated from hydrocarbon steam reforming and coal and biomass gasification can prepare hydrogen by water gas shift reaction (WGS), usually $\text{CuO-ZnO-Al}_2\text{O}_3$ are commercially available low temperature WGS catalysts, however, molybdenum carbide shows more excellent results in this reaction. [39] Sun et al. synthesized $\text{MoC}/\gamma\text{-Al}_2\text{O}_3$ catalyst by reverse microemulsion method and thermochemical treatment. Their high surface area ($190\text{ m}^2/\text{g}$) MoC

nanoparticle size was about 2 nm. the catalyst showed 100% selectivity for CO generation and near equilibrium CO₂ conversion (54-58% at 600°C) and high hydrogen yield at both 500-600°C. The stability of the catalysts was evaluated for 100 h at 600°C and 60000 mL/(g h), indicating that the MoC/ γ -Al₂O₃ catalysts based on reverse microemulsions have excellent stability.[40]

4.3. Photocatalytic and electrocatalytic reactions

In addition to the traditional field of thermal catalysis, molybdenum carbide has also achieved large research results in the field of photocatalysis and electrocatalysis. Liu et al. prepared Mo₂C nanoparticles with a particle size of only 5 nm and grew them uniformly in situ on reduced graphene oxide (rGO) to form graphene-modified Mo₂C (rGO-Mo₂C) nanoparticles, and finally coupled the two to form an efficient TiO₂/rGO-Mo₂C photocatalyst. The maximum hydrogen production activity of TiO₂/rGO-Mo₂C reached 880 $\mu\text{mol h}^{-1} \text{g}^{-1}$ (AQE = 2.64%), which was 5.5 and 88 times higher than that of TiO₂/rGO and TiO₂, respectively.[41] Dantas et al. investigated the effect of Mo₂C and co-doped Mo₂C under tungsten light irradiation by varying the solution pH on the photodegradation behavior of Maxilon Blue GRL 300 basic dyes. X-ray diffraction, scanning electron microscopy coupled with EDS were used to determine Mo₂C as the lowest value that helps to promote the activation of the material. The results showed that the reaction yield of molybdenum carbide samples in acidic medium was high, up to 90.5% at the final concentration of Maxilon Blue GRL 300 dye solution.[42] Yin et al. synthesized pure phase α -MoC_{1-x} with a tetragonal phase structure and demonstrated that its β -Mo₂C with a hexagonal phase structure was more active for H₂ evolution. To further improve the electrocatalytic activity, porous α -MoC_{1-x} nanorods were synthesized by controlling the carburization of MoO₃ nanorod precursors. Benefiting from their more exposed active sites and promoted mass and charge transfer, α -MoC_{1-x} nanorods exhibited significant HER performance under both acidic and basic conditions.[43] Zhang et al. prepared a nitrogen-doped carbon framework using corn kernel popcorn, impregnated Ru and Mo salts on the carbon material, and obtained porous and high specific surface area Mo₂C@Ru catalysts by pyrolysis. The catalysts had a specific surface area of up to 1079.9 m²/g and exhibited good electrochemical properties, which required only a very low overpotential of 24.6 mV to achieve a current density of 10 mA/cm². [44]

5. Conclusion

The discovery and preparation of molybdenum carbide is considered a milestone in the field of transition metal materials catalysts, which have been successfully applied in hydrogenation, dehydrogenation, water gas conversion, medical materials, superconductivity, etc. Especially, catalytic hydrogenation and hydrogen production applications have been widely studied, and molybdenum carbide and its related composite catalysts have become the electrocatalysts loved by many researchers. This paper firstly introduces the typical structure of molybdenum carbide, including the arrangement order of its atoms and the interconversion of different crystalline phases, and also elaborates the influence of geometric and electronic factors on the formation of different spatial structures of

molybdenum carbide; secondly, it introduces the current synthesis methods of molybdenum carbide and analyzes the advantages and disadvantages of different methods; finally, it introduces the molybdenum carbide in the fields of catalytic hydrogenation, catalytic hydrogen production, photocatalysis and electrocatalysis. Finally, the research progress of molybdenum carbide in catalytic hydrogenation, catalytic hydrogen production, photocatalysis and electrocatalysis is presented. Molybdenum carbide is considered to be a very promising alternative to precious metal catalysts. At present, different methods for the preparation of molybdenum carbide still have some drawbacks, so the development of new methods for the preparation of molybdenum carbide is of great significance to promote the application of molybdenum carbide in catalysis as well as other fields.

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