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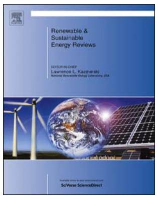

Molybdenum carbide as alternative catalyst for hydrogen production – A review

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ABSTRACT

Hydrogen energy has become an important research area worldwide for environmental-friendly and sustainable energy development. A large number of studies can be found in the literature regarding the development of novel functional catalysts for hydrogen production from various reactions such as hydrocarbon reforming, water gas shift reaction, and water decomposition reaction. Due to the unique surface and electronic properties of molybdenum carbide, it has been attracted more and more attentions as a potential catalyst. This article reviews the latest research progress on the molybdenum carbide catalyst for hydrogen production. Two main parts are included in this review: preparation of molybdenum carbide and application of it in hydrogen production technology. In the first part, various molybdenum carbide preparation methods and the strategies to modify the physicochemical properties of molybdenum carbide are described. It is concluded that solid-solid reaction method could provide high surface area and the synthesis process is relatively easy and safe. Furthermore, the addition of second metal could increase molybdenum carbide surface area and adjust catalyst surface electronic condition. In the second part, the applications of molybdenum carbide based catalysts for various reactions for hydrogen production are described. The catalytic activity, stability, and deactivation and reaction mechanism over molybdenum carbide catalyst are critically reviewed and discussed. It indicates that molybdenum carbide should be an alternative catalyst with high efficiency for hydrogen production.

1. Introduction

Energy is a necessity in our daily society and industrial life. In the past few decades, the world energy needs are fulfilled by fossil fuels, such as crude oil, nature gas, and coal. However, with the increase of population and development of technology, fossil fuel cannot satisfy people's need as the primary energy source in the future due to the shortage of energy resources and a series of environment problems. Statistical Review of World Energy 2014 reported that the world primary energy consumption in 2014 is about 3 times increase compared with that in 1965, which indicates that energy demand has been increased sharply [1]. On the other hand, based on the Earth System Research Laboratory data about CO_2 concentration in atmosphere collected at Mauna Loa Observatory, the CO_2 concentration in atmosphere was continuously increasing from 320 ppm to about 400 ppm in the years from 1965 to 2014 [2]. As mentioned above, one can see that the CO_2 concentration in atmosphere was continuously increasing along with the increase of energy demand. This is due to CO_2 is released to atmosphere during the utilization of fossil fuels. It is commonly known that CO_2 is one main gas which causes the greenhouse effect together with other gases, such as methane, NO_x, and CFC.

Nowadays, alternative environment-friendly energies are gaining more and more attention in the worldwide. Recently, many new technologies have been developed to effectively utilize the alternative energy sources, such as solar energy, wind energy, biomass, hydraulic, geothermal energy, and hydrogen energy [3–10]. Among these new energy sources, hydrogen energy gains more attention due to its advantages. For instances, (i) it has a high specific energy on a mass basis. The energy content of 9.5 kg hydrogen is equivalent with that of 25 kg of gasoline [11]. (ii) It can be produced by several ways, such as steam reforming of hydrocarbons, dry reforming of methane, gasification of biomass, and electrolysis of water, nuclear, solar and wind [12–15]. (iii) It is easy to be transported as natural gas. (iv) It only contains H atom, therefore, neither toxic nor greenhouse gas is released to the atmosphere when it is combusted. (v) It can be utilized for many purposes, eg., automobile and cell phone fuels, and electricity generation via fuel cell technology [16].

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Table 1
The cost of hydrogen produced from various source [18].

Hydrogen source	Process	Year	Hydrogen cost ($/kg)
Natural gas	Steam methane reforming	2006	3.01
Coal	Gasification	2005	1.34–0.86
Nuclear	Electrolysis	2006	4.15–7
Nuclear	Sulfur-iodine thermochemical	2006	2.01–1.75
Solar energy	Photovoltaic electrolysis	2010	5.78–23.27
Solar energy	Stirling-dish electrolysis	2010	10.49
Solar energy	Sulphuric acid/hybrid thermochemical	2007	2.80
Wind energy	Electrolysis	2006	2.27–6.03
Biomass	Gasification	2005	1.77
Biomass	Pyrolysis	1995	1.06–1.86

As above mentioned, many technologies are available for the production of hydrogen from conventional (fossil) and alternative energy such as biomass and solar energy. The economic analysis is always accompanying with the science and industrial technology. Methane is the main composition of natural gas. The cost of production of hydrogen from methane is highly sensitive to the cost of natural gas. Based on the Gray and Tomlinson analysis [17], the hydrogen production cost from methane is in the range of 2.55–2.33 $/kg, which is flexible with the natural gas price [18]. Coal is another largest energy reserves in the world. A study in the U.S. DOE national energy technology lab indicates that the hydrogen production from coal with a yield of 255,400 kg/day has a cost of 1.5 $/kg. The cost of hydrogen production from different sources is listed in Table 1 [18]. The results of economic analysis indicate that the most economical source of hydrogen is coal, with an estimated cost of 0.86–1.34 $/kg.

Hydrogen is a main chemical in our daily life and chemical industry. It has many applications in chemical industries. For example, hydrogen can be used in ammonia synthesis, petrochemical industry, electronic industry, nuclear reactor and power generation system. Recently, proton exchange membrane fuel cell (PEMFCs) has attracted considerable attention due to its high power density, low reaction temperature, low local emissions, quiet operation, fast start-up and shutdown, and in-situ power generation [19]. In PEMFC system, Pt electrode acts as catalyst for adsorption and dissociation hydrogen molecule. However, the Pt electrode is easily poisoned by CO in H_2 rich feed gas. CO molecule can be adsorbed on Pt active site strongly which will block the active site, causing the fuel cell voltage and current density to be decreased sharply. When the concentration of CO in H_2 feed gas exceeds 10 ppm, it irreversibly poisons the Pt-based anode electro-catalyst [20,21].

Traditional process options for hydrogen production choose gaseous, liquid and solid carbohydrate as feedstock. The process of hydrogen production includes steam reforming [22], dry reforming [23], partial oxidation reforming [24], auto-thermal reforming [25], oxidative reforming [26], carbon gasification [27–29], hydrocarbon decomposition [30], and water gas shift reaction [31]. Most of those reaction pathways need catalysts. The gaseous feedstock mainly includes methane; liquid feedstock includes methanol, ethanol, and gasoline; and solid feedstock includes coal, petroleum coke, and solid biomass. Some reactions are summarized in the following (Eqs. (1)–(9)):

Steam reforming:

$$CH_3OH+H_2O\rightarrow CO_2+3H_2 \quad (1)$$

$$CH_3CH_2OH+3H_2O\rightarrow 2CO_2+6H_2 \quad (2)$$

Dry reforming:

$$CH_4+CO_2\rightarrow 2CO+2H_2 \quad (3)$$

Autothermal reforming:

$$CH_3OH+(1-x)\ H_2O+0{\cdot}5x\ O_2\rightarrow CO_2+(3-x)\ H_2 \quad (4)$$

$$3CH_4+4H_2O+O_2\rightarrow 3\ CO_2+10H_2 \quad (5)$$

Oxidative reforming:

$$CH_4+1/2\ O_2\rightarrow CO_2+2H_2 \quad (6)$$

Carbon gasification:

$$C+H_2O\rightarrow CO+H_2 \quad (7)$$

Hydrocarbon decomposition:

$$CH_3OH\rightarrow CO+2H_2 \quad (8)$$

Water gas shift reaction:

$$CO+H_2O\rightarrow CO_2+H_2 \quad (9)$$

As mentioned above, hydrogen can be produced by traditional catalytic or pyrolysis process. Recently, some new technologies are developed for hydrogen production. It is known that water (H_2O) is abundant on the earth, and hydrogen can be produced directly from water by electrolysis process or photo-catalytic splitting process [32–35]. Both technologies have same reaction equation (Eq. (10)):

$$H_2O\rightarrow 1/2\ O_2+H_2 \quad (10)$$

Various catalysts have been developed for hydrogen production. Recently, Agrell et al. [36] reported that ZrO_2 promoted Cu/ZnO catalyst activity for steam reforming of methanol. They found that $Cu/ZrO_2/ZnO$ showed the turnover frequency (TOF) two or three times higher than ZrO_2-free catalyst (Cu/ZnO). They also found that compared with Cu/ZnO catalyst, catalysts contained ZrO_2 showed highly resistant to redox cycles and exhibited high stability. The XPS and TPR results indicate that high activity of ZrO_2-containing catalyst is due to the well-dispersed Cu particles which is promoted by the addition of ZrO_2. Flytzani-Stephanopoulos et al. [31] reported that isolated gold atoms on TiO_2 catalyst can be synthesized by combination of gold deposition method with UV irradiation method. The isolated gold atom catalysts show excellent catalytic activity for water gas shift reaction. Despite that coke is easily formed on the Ni-based catalysts and results in the deactivation of catalysts in the hydrocarbon reforming process, such catalysts have been extensively studied in the reforming process for the hydrogen production. Especially, Navarro et al. [37] supported Ni as well as Pt on the Ce-La-modified Al_2O_3 for the oxidative reforming of hexadecane and found that Ni-based catalysts showed higher catalytic activity with higher H_2 selectivity even than Pt-based catalysts. Biswas and Kunzru [38] supported Ni on CeO_2/ZrO_2 for ethanol reforming and found that 30% $Ni/Ce_{0.74}Zr_{0.26}O_2$ showed a high catalytic activity at 600 °C. Li and Chen [39–41] reported the sandwich structure catalyst ($CoO_x/MgO/Ta_3N_5$) for water oxidation under visible light irradiation. They found that the catalyst with sandwich structure ($CoO_x/MgO/Ta_3N_5$) showed very high water oxidation activity, and oxygen evolution rate of the resulting $CoO_x/MgO/Ta_3N_5$ photo-catalyst is 23 times than of the pristine Ta_3N_5 sample. This is the highest achievement (11.3%) for the apparent quantum efficiency under 500–600 nm illumination. The construction of p-n junctions with built-in electric field effect between two photocatalytic semiconductors is an efficient strategy to separate photo-generated carriers and enhance the photocatalytic activity. Yu and Zhang [42] reported that inserting a layer of zero-bandgap graphene at the interface between p-type NiO and n-type TiO_2 can further enhance the separation of photo-generated carriers by building double-shelled $NiO/rGO/TiO_2$ heterostructured coaxial nano-cables, which is proved to possess a remarkable high photocatalytic activity for water splitting. The characterization indicated that the high photocatalytic activity is due to that zero-bandgap rGO can increase the barrier height by lowering the Fermi level of the