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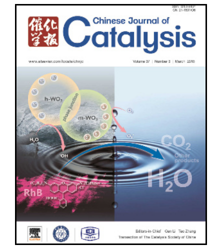

Review

Plasma methods for preparing green catalysts: Current status and perspective

Changjun Liu *, Minyue Li, Jiaqi Wang, Xintong Zhou, Qiuting Guo, Jinmao Yan, Yingzhi Li

Collaborative Innovation Center of Chemical Science and Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

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Most current catalyst preparation methods cause pollution to air, water and land with the use of hazardous chemicals, lengthy operation time, high energy input and excessive water usage. The development of green catalyst preparation is necessary to prevent and eliminate waste from each step of the catalyst preparation. We summarize recent progress in the application of cold plasmas for green catalyst preparation. Cold plasma preparation can reduce the catalyst size, improve the dispersion and enhance catalyst-support interaction with the use of less or no hazardous chemicals. These improvements also lead to the enhancement of catalyst activity and stability. An alternative room temperature electron reduction with a non-hydrogen plasma as an electron source was developed for the reduction of noble metal ions in which no hazardous chemical reducing agent or hydrogen was needed. This creates many opportunities for the development of supported catalysts with heat sensitive substrates, including metal organic frameworks (MOFs), covalent organic framework (COFs), high surface area carbon, peptide, DNA, proteins and others. A novel floating metal catalyst on a water (or solution) surface has been established. Template removal using low temperature cold plasmas also leads to the formation of high surface area porous materials with characteristics that are normally only obtainable with high temperature calcination, but sintering can be avoided. Micro combustion has been developed for the removal of carbon template using cold plasma. This is promising for preparing many structured oxides in a simple way with no use of auxiliary chemicals. Many opportunities exist for the use of cold plasmas to make multi-metallic oxides. Some future development ideas are addressed.

1. Introduction

Catalysis is extensively applied in the chemical industries. A catalyst is involved in the production of most of the important chemicals. With depleting petroleum resources, the development of renewable energy and increasing concern about the environment, catalysts will play an even more important role in the future. The use of a catalyst is in the list of the twelve principles of green chemistry [1,2].

Catalysis now has a core comprising the sciences of chemistry, chemical engineering, and materials science. The world market for many catalysts is blooming, and there are significantly increasing publications on their catalysts. Two kinds of catalysts are applied at present: heterogeneous and homogeneous catalysts. A heterogeneous catalyst means that the catalyst is spreaded or dispersed in a different phase, which is normally on a porous solid substrate or a porous solid support material with a high surface area. Alumina, silicon dioxide, tita-

* Corresponding author. Tel: +86-22-27406490; E-mail: coronacj@tju.edu.cn
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nium dioxide, activated carbon, zirconia, micro- and mesoporous materials, polymer porous materials and others have been used as the substrate. High activity and excellent long term stability with high selectivity are needed for a good heterogeneous catalyst. Catalytic reactions can be affected by many factors including size [3–5], phase structure [6,7], shape [7], catalyst-support interaction [3,6], interface [8–10], surface properties [11–15], reaction condition, feedstock and others. In many cases, it is not easy to reach the goal of high activity, high selectivity and excellent stability. Great efforts have been made towards the understanding of the fundamental issues of catalysis and also towards the development of new catalysts and novel catalyst preparation technology that give controllable size and structure in order to achieve the optimum catalytic properties.

One of the challenges in the field of catalysis is its increasing pollution to air, water and land and the high consumption of materials and energy during the preparation of a heterogeneous catalyst. Although the use of a catalyst is one of the green chemistry principles, the catalyst preparation is not really green. Fig. 1 shows the procedure of the preparation and application of a heterogeneous catalyst. Each step can cause pollution or excessive consumption of materials and energy. A hazardous chemical or hydrogen is required for the reduction of the catalyst. Also, present catalyst preparation is time consuming. A quick preparation is desired. Catalyst preparation in a green way is necessary. The objectives of green catalyst preparation should follow the 12 principles of green chemistry: (1) prevent waste; (2) the reactions used must meet the requirement of atom economy as much as possible; (3) less hazardous catalyst preparation; (4) design benign catalyst or catalyst precursor; (5) use of benign solvents and auxiliaries; (6) design energy efficient catalyst preparation; (7) use of renewable feedstocks as much as possible; (8) reduce derivatives, which would become necessary with the development of organic porous materials; (9) consider the applications of the catalyst prepared; (10) design catalyst that can be easily re-generated when deactivated; (11) develop inherently benign catalyst preparation to prevent accidents; (12) develop real time analytic technology or *in situ* characterization for catalyst preparation. Some of these objectives are long-term ones that cannot be achieved easily. For example, most of the catalyst preparation methods now rely on a trial and error approach. It is still a challenge to design the catalyst from the beginning, although theoretical studies have made some progresses [5,15,16]. There are many works conducted to meet the objectives above. Innovation in catalyst preparation has been a hot topic for a long time. Microwave heating [17,18], use of plasmas [3,19–21], ionic liquids [22], ultrasonic treatment [23], electron beams [24], electrostatic field [25], biochemicals [26] and others have been employed and developed. Among these innovations, the use of plasmas has received remarkable attention. Patents and publications with the keywords of plasma and catalyst have recently increased significantly. In this article, we summarize the progress in the plasma methods of green catalyst preparation. Differences between plasma preparation and thermal treatment are discussed. Future development is addressed.

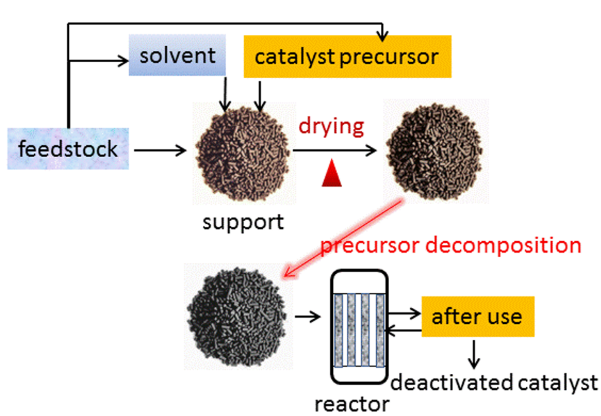

Fig. 1. Preparation and application of a heterogeneous catalyst.

2. Nucleation and crystal growth under the influence of a cold plasma

With the supply of sufficient electrical energy to a gas, the gas will be ionized and an electric gas discharge or discharge plasma will be created. Based on the energy of the discharge plasma, thermal plasma or cold plasma is generated. Thermal plasma is an equilibrium one where the bulk temperature reaches several thousands of degrees Celsius. Cold plasma is a non-equilibrium one where the bulk temperature remains as low as room temperature but the electron temperature reaches several thousands of degrees Celsius or even more [20,27]. Both thermal plasma and cold plasma have been found useful for catalyst preparation. Thermal plasma is normally applied for the preparation of oxide support materials in a rapid way with a smaller particle size compared to the use of thermal treatment [27]. The cold plasma has been more investigated for catalyst preparation because of its low temperature operation with highly energetic electrons. Based on the electrode configuration and operation condition, cold plasmas can be very different. Glow discharge and dielectric barrier discharge (DBD or silent discharge) are two conventional cold plasma phenomena that have been employed for heterogeneous catalyst preparation. Glow discharge can be easily created in a low vacuum (e.g., 100 Pa) by putting two electrodes into the gas. One electrode is connected to a high voltage generator (several hundred volts) and the other electrode is grounded. This has been extensively applied for neon lights, surface cleaning treatment and others. Based on the application, the distance between the electrodes in the glow discharge is varied, ranging from several millimeters up to several meters. DBD has been applied for the industrial production of ozone, and used in a plasma TV and others. Different from glow discharge, one or two electrodes within the DBD are attached to quartz plate(s) or the dielectric material(s) with a thickness of millimeters. The distance between the two electrodes is normally less than 10 mm depending on the operational pressure. A large distance would cause the discharge to be unstable if the pressure is around atmospheric pressure or higher. There exist many micro-discharges within the DBD under normal conditions. Once DBD is initiated at any location within the gap between the electrodes, charge accumulates on