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Review

Graphene supported heterogeneous catalysts: An overview



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ABSTRACT

The unique properties of two-dimensional structure, great intrinsic carrier, well developed porosity, active surface area, outstanding electronic properties and promising mechanical and thermal stability make graphene as the current support key material in the heterogeneous catalyst system. Accordingly, graphene plays a pivotal role in most heterogeneous catalysts ranging from single to bi-functional, hybrid, oxide and nano systems. This combination also inspires and widens the heterogeneous catalyst application areas, including chemical conversion, photocatalyst, electrochemical sensor, fuel cell, energy storage and others. This review highlights the advantages and limitations of carbon materials as catalyst support materials, addresses recent progress on synthesis routes with technological advances in the characterization of graphene, and follows the properties dependent of graphene as a superior catalyst support material.

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Introduction

Essential principle of catalyst support

The application of catalytic methods in organic chemistry has become one of the intensive research areas. Almost 90% of all commercially produced chemicals utilize the catalyst at some stage in the production process, including food processing, fine chemicals, bulk chemicals, energy processing and environment, which make the manufacture of catalysts alone account for over USD 10 billion in sales revenue [1–4]. In 2010, one-third of the materials gross national product in the US contained a catalytic process somewhere in the production chain [1,2,5]. Nevertheless, the currency generated due to

catalyst sales is enormously outweighed by the overall value of the generated products including, pesticides [6], polymers [7,8], antibiotics [9,10], cosmetics [11], cleaning products [12] and others. For example, procedures with the longest history are hydrogenations, which are mainly catalyzed by supported metals. Over the course of decades, various metal catalysts have been developed with the purpose of achieving high activity and selectivity. Since the metal catalyst has met a number of special requirements, in addition to ceramics (SiO₂, Al₂O₃, zeolite, etc.), the development of hybrid, oxide, bifunctional catalyst materials have also gained increased importance [18,19]. Catalytic reactions are sensitive to the catalyst's structure, surface atomic arrangement and coordination, which can be well controlled by tuning the specific composition, morphology and size of catalyst [10–14]. In

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supported catalysts, catalytically active components are bound to a(n) (inert) support with large surface area such as alumina, silica, zeolite and other materials. For stabilization of high dispersion of active components such as noble metal nanoparticles against sintering, reduction of costs and utilization of important mechanical and morphological properties of the support.

Importance of heterogeneous catalyst

Industrial catalysis are generally divided into two types, homogeneous and heterogeneous (Fig. 1). Heterogeneous catalysis is where the catalyst and the reactants are in the different physical phases, while homogeneous is where both are in the same phase [18]. In general, homogeneous catalysts exhibit excellent catalytic activities with high selectivities in particular. But, it is difficult for the homogeneous catalyst to be separated from reaction media as compared to heterogeneous catalyst [19,20]. Thus, most of the industries tend to shift towards the heterogeneous catalyst.

As heterogeneous catalysis have evolved, it has become more apparent that it has a large part to play in green chemistry and thus removing or substantially reducing pollution and undesirable by-products from both the chemical and refining processes [21–23]. In the other words, the by-products of heterogeneous catalyst reactions would not end up with harmful emissions and nasty waste materials that are dangerous and detrimental to the ecosystems and the environment [22]. However, conventional heterogeneous catalysts are suffering from relatively low activities due to the limitation of exposed active sites [24,25]. One of the promising routes to overcome is to support these catalytically active centers on porous inorganic solids such as silica, zeolite, mesoporous materials and others [18,19]. However, with these supports, inorganic materials have high sensitivity towards acid and base conditions. Owing to good stabilities in both alkaline and acid conditions, carbons as supports have attracted much attention [26–29].

Importance of heterogeneous catalyst support

In industrial chemical engineering, it is often desired that a homogeneous catalyst be heterogenized or supported on a porous material [19]. The heterogeneous catalysts are

required to be in micro or as mesoporous catalyst, which makes it more easily separated from the fluid (liquid or gaseous) products and reactants, and enable it to be packed inside a reactor vessel or tube, with fluids flowing via the packed and fixed bed. In addition, the agglomeration of heterogeneous catalyst, especially with respect to its nano-sized characteristic, is one of the main reasons to use a support material [22,30]. However, if the nano-sized heterogeneous catalyst is not strongly anchored on the surface of the support, the agglomeration can still take place [31]. However, it is necessary to strongly attach the nano-sized heterogeneous catalyst to the surface, for example, of defect sites on the surface or functional groups bonding to the surface and catalyst itself [24,32,33]. With that in mind, researchers have introduced many kinds of support catalyst materials included, zeolite, carbon, silica and others [18].

Another advantage of support catalyst is concerned with the surface area and porosity in relation to the total catalyst loading, in order to achieve high dispersion of the active site phase in the catalyst [34–36]. It seems clear that a large surface area formed by accessible pores is important for obtaining highly dispersed and active catalyst [35]. Furthermore, surface chemical properties are another carbon characteristic that has to be taken into account to explain the catalytic behavior of a carbon supported catalyst system [31]. The carbon surface contains a given number of heteroatoms (O, N, H) in the form of functional groups, similar to the way that heteroatoms appear in organic compounds, which as a consequence, can confer the carbon surface an acid–base and hydrophilic character [28–30]. Some effort has been focused on the role of surface oxygen groups in the dispersion and resistance to the sintering of carbon supported metal catalysts [37,38]. For example, high surface area of carbon black has been heated in hydrogen at the 1000 °C for removing most of Pt oxygen surface functionality before being oxidized with hydrogen peroxide solution, and it was found that more acidic groups have been consequently developed, which could decrease the hydrophobic character of the carbon support and make the Pt/C surface became more accessible to the aqueous solution [39,40]. Thus, an increment in Pt dispersion with the minimized Pt sintering process is recorded. Similar outcomes have been observed in Ru supported carbon catalyst for

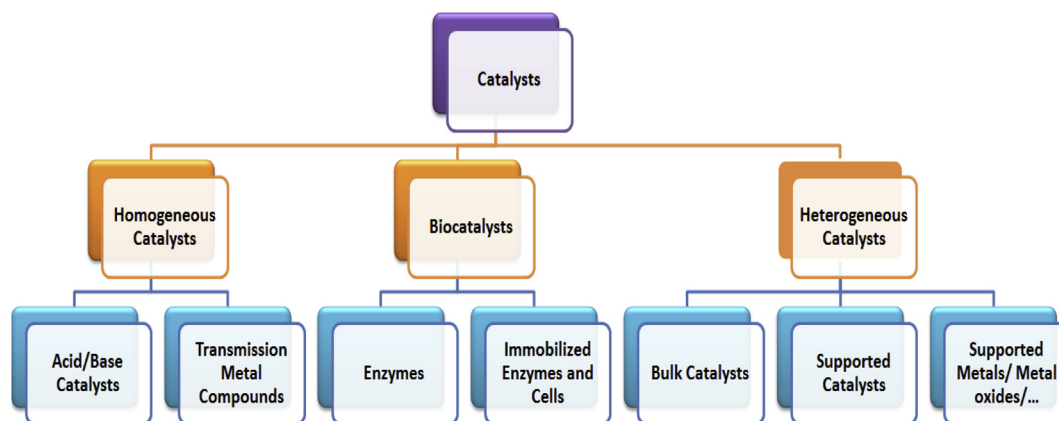


Fig. 1 – Series of catalysts based on homogeneous, bio and heterogeneous categories.

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