

Methods for the Carbon-Supported Pd-Based Bimetallic Catalysts

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Pd is the most efficient metal for this reaction due to its unique electronic structures as well as its superior ability to dissociate dihydrogen and activate acetylene, e.g., supported Pd nanoparticles can easily catalyze the reaction to achieve complete conversion of acetylene even at room temperature and normal pressure.

palladium

bimetallic

catalysts

semi-hydrogenation

acetylene

ethylene

cold plasma

1. Wet Chemistry Technique

1.1. Incipient Wetness Impregnation (IWI) Method

The IWI method is a high-productivity, cost-effective, and straightforward approach that is widely used in the preparation of industrial Pd-based bimetallic catalysts for bulk chemicals, fine chemicals, and petrochemical products ^{[1][2]}. Depending on the impregnation sequence of two metal precursor solutions, (IWI) these methods are divided into two types: sequential incipient wetness impregnation (Seq-IWI) and incipient wetness co-impregnation (Co-IWI). The IWI method typically consists of four sequential steps ^[3]. First, the mixed solution of two metal precursors (for Co-IWI) is introduced onto a support, or two different metal solutions are successively impregnated onto a support. The intermediate nanomaterial will then be dried to remove water or solvent, followed by thermal calcination to form a catalyst precursor. Finally, bimetallic catalysts with catalytic activity would be prepared by thermal reduction of the precursors. However, the IWI method-derived Pd-based bimetallic catalysts normally govern large and un-uniform nanoparticles, resulting in low metal dispersion because of the weak interaction between metal precursors and catalytic support, even after the thermal treatment processes, i.e., calcination and thermal reduction ^{[3][4][5]}. Researchers have made a lot of efforts to solve these problems by optimizing the preparation process ^[6], supporting modification ^{[1][7][8]}, as well as the introduction of emerging supports ^{[7][8]}, etc.

1.2. Precipitation Method

The precipitation method is the other most efficient and simplest way of synthesizing supported Pd-based bimetallic catalysts ^{[1][2][9][10]}. Depending on the forms of support precursors (solid substrate or metal cation) introduced into the precipitation system, the precipitation method is divided into deposition–precipitation (DP) and co-precipitation (CP). Similar to the IWI method, the DP method typically consists of four steps: metal precursor

loading on support, drying, calcination, and thermal reduction ^{[1][2]}. Nevertheless, the metal precursor loading on support for DP is carried out in the liquid phase. In more detail, the mixed solution of two metal precursors is introduced to a suspension of support nanoparticles. Next, with strong stirring, the pH of the liquid-phase mixture is adjusted by an acidic or basic reagent to make metal ion complexes deposit onto the support. The key objective of this method is to achieve simultaneous precipitation of different metals onto a support in suspension by controlling the processing conditions, including pH ^[10]. For CP, the difference from DP is that the support is also derived from its metal precursor by precipitation together with precursors of the other two target metals.

1.3. Sol-Gel Method

Typically, the sol-gel method mainly consists of four steps. First, metal and support precursors are dissolved in a solvent to form a clear and stable colloidal solution (called sol) through primary condensation. Subsequently, the colloidal particles (micelles) undergo anisotropic condensation to produce polymeric chains, resulting in the formation of a transparent gel with a three-dimensional spatial network structure. After that, the gel is dried at low temperatures under reduced pressure, followed by thermal reduction to obtain the final sample ^{[11][12]}.

1.4. One-Pot Reduction Deposition (One-Pot RD) Method

The one-pot RD method can solve the issue of the scattered particle size distribution faced by precipitation methods to a certain extent because it normally avoids the thermal treatment processing. It is a one-pot method to prepare supported Pd-based bi-metallic catalysts in the liquid phase. Just as its name implies, this method is similar to deposition-precipitation. The difference between the two is that a reducing agent (e.g., hydrogen, ascorbic acid, hydrazine, borohydrides, and polyols) is introduced in the reduction-deposition system, and as a result, metal cations with different reduction potentials can be reduced by a one-pot liquid reaction to form supported bimetallic nanoparticles directly. Commonly, after further deposition onto a support as well as drying, the resulting sample does not need high-temperature treatment. Depending on the adding sequence of support and metal precursors, the preparation process is slightly different.

1.5. Sequential Reduction-Deposition Method (S-RD)

S-RD is suitable for the deposition of a metal onto a ready-made supported parent metal in the liquid-phase environment to form bimetallic catalysts. Our group ^[13] as well as many other researchers ^{[14][15][16]} have demonstrated that a specific strong metal and support interaction (SMSI) could give a high catalytic performance for the selective semi-hydrogenation of acetylene. Noteworthy, in this method, the ready-made supported parent metal, which can be prepared by any suitable synthesis method, can also achieve SMSI. This approach can effectively adjust the loading amount of a secondary metal on to the parent metal, therefore demonstrating extraordinary potential in the synthesis of single atom alloys (SAAs). Synthesis of Single Atom Alloy and Dual Catalysts). Depending on the reduction mode of the secondary metal, the sequential reduction deposition method can be divided into electroless reduction deposition (eless-RD) ^{[1][17][18][19][20]}, galvanic replacement (GR) ^{[2][18][21][22][23][24][25][26]}, and controlled surface reactions (CSR) ^{[3][16][18][27][28]}.

Eless-RD is also called electroless plating deposition. Just in terms of the synthesis procedure, eless-RD is basically the same as one-pot RD, except that the parent substrate is ready-made supported metal particles, as well as there is only one kind of metal precursor in the liquid phase for reduction and deposition. The reduction of the secondary metal in eless-RD refers to a class of reduction that occurs with the participation of chemical reducing agents, which do not involve electrochemical mechanisms.

1.6. Photochemical Reduction (PR)

Most recently, the interest in the PR synthesis of metal nanocrystals is growing rapidly due to its simplicity, high efficiency, as well as greenness resulting from generally not using any chemical or physical additives and being normally operated at room temperature and atmospheric pressure [1][2][29][30][31][32]. The unique feature of the PR method is the exposure of metal precursor-containing solutions to visible or ultraviolet (UV) light. Photogenerated electrons are used as reductants to reduce metal cations to metal atoms. However, the preparation of palladium-based bimetallic catalysts by photochemical reduction for selective hydrogenation of acetylene is rarely reported, which might be a direction of future efforts.

1.7. Colloidal Synthesis

The boom in colloidal chemistry in the past two decades has made it possible to synthesize nanoparticles with uniform shapes, sizes, and compositions [20][33][34][35][36][37][38][39], because the metallic colloid is prepared in the presence of a chemical reducing agent (e.g., hydrogen, ascorbic acid, hydrazine, borohydrides, and polyols) and organic ligands, such as poly(vinylpyrrolidone) (PVP), cetyltrimethylammonium bromide (CTAB), poly(vinyl alcohol) (PVA), polyamidoamine (PAMAM), dodecyl mercaptan, trioctylphosphine, oil amines, oleic acid, etc. [40]. The former allows reduction to take place in the aqueous phase, so that the reduction is mild, fast, and controllable; the latter can serve as surfactants, capping ligands, and shape-directing agents to precisely control the directional growth of Pd-based bimetallic nanocrystals as well as prevent the coalescence of nanoparticles. Both the one-pot reduction deposition (colloidal one-pot RD) and the electroless reduction deposition (colloidal eless-RD), with the addition of organic ligands, are classified as colloid synthesis here [37][41].

1.8. Hydrothermal/Solvothermal Method

The synthesis of nanomaterials by the hydrothermal/solvothermal method is one of the most attractive fields in materials science to date. This method refers to the synthesis technique using the chemical reactions of substances in a saturated solution at a given temperature (100–1000 °C) and pressure (1–100 MPa). It provides a special physical and chemical environment for the reaction and crystallization of various precursors, which cannot be obtained under normal pressure conditions, so that some chemical reactions that are difficult or even impossible to occur under normal conditions can be carried out smoothly in an autoclave. By this method, it is conducive to the preparation of dispersed and crystalline powders, and the reaction is conducive to the synthesis of toxic systems in closed containers, reducing the pollution to the environment [42][43].

1.9. Surface Inorganometallic Chemistry

Lately, the Ding group ^[44] proposed a novel and general strategy for the synthesis of the supported bimetallic nanoparticles called the surface inorganometallic chemistry approach.

2. Plasma Treatment

Plasma is a partially ionized gas consisting of molecules, ions, radicals, electrons, photons, and other excited species, also known as the fourth state of matter ^[45]. About 99% of the matter in the universe exists as plasma. For instance, lightning and polar lights often seen in nature are plasma. Depending on their temperature, ionic density, and energy level, plasmas are usually classified as high-temperature (equilibrium) plasmas and low-temperature (non-equilibrium) plasmas (including thermal and non-thermal plasmas). In thermal plasmas, the gas bulk temperature can reach up to 100,000 K or more. By contrast, the bulk temperature of non-thermal plasmas can be as low as room temperature, or even below. If the gas bulk temperature is close to room temperature, a non-thermal plasma is also called cold plasma. High-temperature plasmas can be created by nuclear fusion and be a clean energy the future of humanity. On the other hand, low-temperature plasmas are important for the syntheses and processing of matters, including catalyst preparation ^{[45][46]}. Plasmas used in laboratories and industry are mostly created by applying AC or DC high voltage to a gas phase. They are normally referred to as gas discharge plasmas. The cold plasmas generated with different electrode configurations or under different operating conditions are very different. Glow discharge, dielectric barrier discharge (DBD), and radio frequency (RF) discharge are three conventional cold plasma phenomena ^{[45][47][48]}.

3. Thermal Pyrolysis

The thermal pyrolysis of precursors is another promising method for the preparation of carbon-supported Pd-based bimetallic catalysts. The catalyst precursors can include a physical mixture of metal cations, or a small molecular metal-organic complex as metal source and biomass material, or polymeric organics as the source of carbon support ^[14]; moreover, it can also be polymeric metal complex formed by the coordination of the grafting of metal ions and the polymer ^[49].

4. Vapor Deposition and Electrochemical Deposition

Although vapor deposition is a time-honored technique and can be traced back to centuries ago, it is still one of the most important methods for sample preparation in surface science and is mainly used for the preparation of bimetallic catalysts, especially single atom alloy model catalysts in catalysis area. At present, physical vapor deposition (PVD) and atomic layer deposition (ALD) are the two main types of used methods for vapor deposition.

5. Ball Milling

Ball milling is a method that has been gaining momentum recently and is suitable for the preparation of supported catalysts most recently ^{[2][50]}. A pulverisette planetary micro mill and milling equipment made of zirconia, including a

milling jar, and grinding balls of different sizes, are the key devices for this method. Using this method, several α - Al_2O_3 -supported Pd–Ag bimetallic catalysts were prepared by the Kley group [50]. Typically, the coarse metal powders (about 5 wt% of Pd and Ag) and support precursor (boehmite, γ - AlOOH) were loaded in one pot and ball-milled to obtain a concentrated batch. Thereafter, under suitable ball-milling conditions, boehmite dehydrates to form α - Al_2O_3 with a remarkably high specific surface area, concomitantly Pd–Ag alloy nanoparticles formed on the resulting HSA- α - Al_2O_3 to obtain the final catalyst. Determining the optimization of the reaction conditions is the key to success for the method. Experimental results show that catalysts prepared via ball milling possess characteristics of smaller particle size, more uniform distribution, and better stability compared to those prepared by the conventional impregnation method.

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