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Preparation of Metal-Supported Nanocatalyst Using Cold Plasma

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Introduction

Supported-metal nanocatalysts have been extensively used in numerous areas. The characteristics of metals such as morphology and crystal structure are crucial to their catalytic performance. Furthermore, the metal-support interaction also significantly affects the activity. The characteristics of metals are closely related to how they are loaded on the support materials. The present state-of-the-art status of technologies is far from perfect. The performance of nanoparticles is not perfect, and the activity and durability need to be improved. The preparation generally involves the utilization of hazardous materials, which is not preferred from the point view of green chemistry. Here we summarize our recent work on the preparation of metal nanocatalysts via cold plasma

Cold plasma phenomenon

Plasma is a substance in which many of the atoms or molecules are effectively ionized. The electrons in cold plasma can reach temperatures of 10,000–100,000 K (1–10 eV), while the gas temperature can remain as low as room temperature. It is the high electron temperature that determines the unusual chemistry of cold plasmas. Plasmas are mostly created by applying direct or alternating high voltage to a gas or a gas mixture [1, 2].

The plasma utilized in our work is glow discharge plasma. It is used to treat the catalyst after metal precursor is impregnated on support materials. Specifically, the catalyst powders are placed in a quartz boat located in a discharge cell. The cell was evacuated to a pressure of 100-200 Pa. Then flowing gas such as Ar, N_2, and air is introduced to maintain the pressure and to serve as the plasma-forming gas. A DC high voltage generator was applied to the electrode to initiate the plasma. The gas temperature of glow discharge is below 100°C, so the thermal effect is negligible.

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Plasma-enhanced preparation of metal-supported nanocatalysts :

The plasma-enhanced preparation includes traditional impregnation, plasma treatment, calcination, and if necessary, hydrogen reduction. Compared with the traditional one, the only difference for this method is the inserted plasma treatment. Generally, the treatment does not influence the support materials. However, the "plasma treatment + thermal calcination" model significantly does enhance the physicochemical properties of supported metal nanopartices and thus their activity and durability.

The most evident improvement is the size of metal particles. The XRD peaks belong to the metals (or their oxides) are weakened and broadened significantly. This means the metal particles is highly dispersed with smaller grain size. TEM further gives direct observation on this phenomenon. Plasma treated metals are well distributed on the support with small and uniform size, whereas these prepared traditionally is badly dispersed with larger size and big aggregate. This characteristic is observed for all the metal tested, including Pt, Pd, Ni and Rh. Small particle means a large metal surface is available for the adsorption of reactant and more active sites for reaction. H_2 and CO chemisorptions show the metal dispersion is almost doubled with plasma treatment [3, 4].

The morphology of metal nanopartices is also greatly modified by the plasma treatment [5]. For traditionally prepared sample, the metal particle exhibits a spherical shape. However, the plasma treated particles are flattened and spread out on the support. This characteristic results in a larger contact interface and a smaller contact angle between the metal particle and the support. In this case, the metal particles are fixed on the support surface more tightly, and thus a stronger metal-support interaction exists. This is testified by H_2-TPR profiles where the reduction peak is extended to higher value for the plasma treated NiO catalyst [6].

Another amazing characteristic of the plasma treated catalyst is the novel metal-support interface structure. A high-resolution TEM observation is conducted on Pt/TiO_2 prepared by traditional and plasma methods, respectively [3, 7]. On the plasma treated sample, the Pt(111) fringes are nearly perpendicular to TiO_2(101) fringes, with a cross-angle of 80°, whereas the cross-angle is about 19° on the traditional one. The perpendicular alignment means Pt lattices have to match more TiO_2 planes, thus resulting in a close contact at the interface. Therefore an enhanced metal-support interaction is generated. This interaction is proofed by further characterizations. TEM observation shows the plasma treated Ni particles have well-defined Ni(111) fringes, indicative of uniformly crystallized particles with specific crystallographic plane [8]. On the other hand, the traditional particles appear to be a complicated combination of many crystallographic planes. CO adsorbed DRIF studies carried out over Pt/ZrO_2 and NiO/Al_2O_3 show the defect sites are decreased but more close packed plane sites are formed on the plasma treated samples [6, 9]. The interaction also affects the properties of support to some degree. The acidic sites of zeolites are redistributed and increased due to the effect of highly dispersion Pd nanoparticles [10]. And the local band structure of TiO_2 is modified by the supported Pt particles, with improved optical absorption in UV region [3].

The novel characteristics of plasma treated catalysts lead to excellent performance in many catalytic reactions. The activity of Pt/TiO_2 in the photocatalytic H_2 generation from water/methanol mixture is increased 2.29 times using plasma method [3, 4]. For the photocatalytic water splitting, the H_2 formation rate over NiO/Ta_2O_5 and NiO/ZrO_2 is increased by 1.7 and 1.5 times, respectively [5]. It is proofed that the electron transfer from the semiconductor to the metal is significantly enhanced over the plasma treated sample due to the novel metal-support interface.

Another successful example is the methane conversion. Methane combustion over plasma treated Pd/HZSM-5 reaches a 100% conversion at 450°C, but it is only 50% over the traditional catalyst [10]. Moreover, the plasma treated catalysts are very stable, whereas the traditional samples quickly deactivate. EXAFS studies confirm the plasma preparation leads to a specific tetragonal PdO species that can keep stable during reaction [11]. Similarly, plasma treated Pt particles are more resistant to sintering under the oxidizing atmosphere, exhibiting excellent stability during the partial oxidation of methane [9].

In CO_2 reforming of CH_4, plasma prepared NiO catalyst shows high catalytic activity and excellent resistance to coke formations [6, 8]. NiO/Al_2O_3 is very stable for more than 50 h at 750°C, meanwhile the traditional counterpart begins to deactivate in10 h. TEM observations show the formation of filamentous and encapsulating carbon are largely prohibited over plasma treated samples. The flattened metal particles limit the dissociation direction of CH_4. And close packed planes decrease the rate of CH_4 dissociation. Therefore, the produced carbon is removed by CO_2 more quickly, resulting in a better carbon formation–gasification balance.

Green plasma reduction of metal nanoparticles :

During the plasma treatment, the metal precursors are decomposed into oxides at room temperature, like the case of $Ni(NO_3)_2$ [5]. Some oxides, to our surprise, can be further converted into amorphous metallic clusters. XPS characterizations shows Pt^{4+}, Pd^{2+}, Ag^{+} and Au^{3+} ions are reduced into zero valance by Ar plasma [12]. EXAFS analysis on Pd/HZSM-5 also confirms the formation of Pd-Pd shell, consistent with the Pd foil [11]. The reduction is independent of plasma-forming gas. Even O_2 effectively reduces these metal ions. The highly energetic electron is believed to be responsible for the reduction. The reducibility of metal ions by non-hydrogen plasmas can be evaluated by their standard electrode potential. Those metal ions with positive standard electrode potential can be easily reduced. This plasma reduction does not require reductive agents such hydrogen, NaH_4B and H_2NNH_2, thus being more environmentally friendly. Moreover, the reduction is carried out at room temperature, avoiding any undesired thermal effect. The plasma reduction may open the door of “green” reduction of structure-sensitive nano-particles.

Some work has been done to apply the novel plasma reduction in preparing some functional nanomaterials. The hydrogen storage capacity of activated carbon at 298 K is increased almost 3-fold by doping with 3% of Pt, using a plasma reduction. With H_2 reduction, the

increase in hydrogen storage is only 54% [13]. Nano-materials within the channels of SBA-15 are also synthesized using plasma reduction. Spherical Pd and Pt nanoparticles as well as Au and Ag nanowires are obtained [14]. Their diameters can be tailored according to the pore diameter of host. It is expected the fabricated materials will be both fundamentally and technologically useful for catalytic, optical, electronic and energy-storage applications.

Conclusions

The catalyst preparation assisted with clod plasma treatment leads to a formation of special nano-structured metal cluster with novel properties, which could lead to a better low-temperature activity, an enhanced stability and a better anti-carbon deposition performance. The noble metal ions applied can be effectively reduced at room temperature during the plasma treatment, which opens the door of "green" preparation of structure sensitive metal nano-materials.

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