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The graphene-meso-macroporous SiO₂ supported Pt–Ni alloy nanocatalyst for preferential oxidation of CO in H₂-rich gases

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ABSTRACT

In this work, nanoparticles of Pt–Ni alloy were supported on a new kind of composite which composed of graphene sheets and meso-macroporous SiO₂, and the composite supported Pt–Ni catalyst was applied to the preferential oxidation of CO (CO-PROX) in H₂-rich gases. The bimetallic Pt–Ni alloy catalyst was characterized by using techniques of SEM, TEM, XRD, TPR, CO chemisorptions and XPS. The catalyst showed excellent catalytic performance for CO-PROX with high activity at low temperature, high selectivity and very good stability, which was attributed to the following characters of the catalyst: Pt–Ni nanoparticles were in alloy state and highly dispersed, Pt–Ni nanoparticles were preferentially loaded on the surface of graphene sheets, and the meso-macroporosity of the composite markedly improved the mass transferring ability. This is a case study, and this kind of catalysts can be extended to other gas–solid catalytic reactions.

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Introduction

Hydrogen which is the fuel for fuel cells and acts as a highly efficient and environmentally clean energy carrier is generally produced from various hydrocarbons via the steam reforming and the water-gas shift (WGS) reactions. Due to thermodynamic limitation of WGS reaction, small amounts of unconverted CO is remained in the H₂-rich gases, which is required to be purified to less than 10 ppm, in order to prevent poisoning the platinum anode of fuel cells [1]. There are

several methods for removal of CO from H₂-rich gases, including physically cryogenic separation, pressure swing adsorption, selective diffusion of hydrogen, preferential oxidation (PROX) of carbon monoxide and CO methanation, and among those, the PROX is regarded as the most effective way [2].

The catalysts reported for CO-PROX include base metal oxide catalysts, such as CuO–CeO₂ [3] and cobalt oxide based catalysts [4], and noble metal catalysts, mainly Pt, Ru, Rh, Ir [5] and Au [6]. The Pt-based catalyst is the most promising one, which exhibits high activity and selectivity, while

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improvement on its low temperature activity is needed. Recently, the interest in PROX catalysts has concentrated on Pt-based bimetallic catalysts which show much better activity, selectivity and stability than its counterpart mono-Pt-based catalysts. For the Pt-based bimetallic catalysts, another metal reported mainly includes Co [7], Ni [8], Fe [9] and Ru [10]. For example, Li et al. [11] reported that Pt–Co intermetallic compounds were much active and selective for CO-PROX, and Chin et al. [12] found that SiO₂ supported Pt–Ru catalysts exhibited high catalytic activity and stability for low temperature CO oxidation.

In recent years, nano carbon materials, namely activated carbon, graphitic nanofibers, carbon nanotubes (CNTs) and graphene, as catalyst support have been attracted great attention [13]. Among the nano carbon materials, graphene with two dimensional (2D) structure is of particular interest recently. For example, Truong-Huu et al. [14] has prepared palladium nanocatalyst which was dispersed on a few-layer graphene surface and applied it to liquid-phase selective hydrogenation of C=C bond. The high hydrogenation activity was attributed to the dispersed 2D morphology of the graphene in liquid phase with high external surface area as well as full surface accessibility and edge reactivity. However, to the best of our knowledge, only two reports can be found on using graphene sheet (GS) as the catalyst support for gas–solid catalytic reaction, which are Pt–Ni/GS [15] and Pd/GS [16] for CO oxidation. Both of the two catalysts showed relatively poor catalytic performance, possibly due to two limitations. The first, fixed bed reactor which is the generally used reactor for gas–solid catalytic reaction requires the catalyst being in a macrostructure, such as particulate or monolith in the size of millimeter or centimeter level. However, graphene sheets are in thickness of several nanometers and in width of microns, thus when reactant gases pass through the stacked GS, the pressure drop is too high. The second, for the catalysts of nano metal particles supported on GS, the metal nanoparticles are generally in the size of several nanometers, which will be enveloped by the GS with width of microns, hence, the metal nanoparticles can hardly contact with the reactant due to the blockage of the GS.

The way for overcoming the two limitations is to make GS in a particulate shape or in the form of monolith. Preparing GS with macrostructure is of great significance and is a focus for GS application [17]. For example, Kim [18] et al. had prepared several-layer graphite oxide (GO) membranes by spin-casting of a GO solution on the polyethersulfone membrane surface. It exhibited desired gas separation ability for carbon dioxide/nitrogen, and the selective gas diffusion can be achieved by controlling gas flow channels and pores via different stacking methods. Marcus [19] et al. developed a three-dimensional (3D) graphene assembly with properties similar to those of individual GS, and used it as a promising graphene-based electrode.

However, the reported GS macrostructures can't be used as catalyst supports, due to their poor mechanical strength. Only a few reports can be found on GS macrostructure as catalyst support. Nguyen-Phan et al. [20] prepared the 3D wormhole-like mesoporous TiO₂/GS layered composites. The growth of mesostructured graphene layers lead to a significant enhancement in mesoporosity, and the composites were

applied to removal of dye components from wastewater via photocatalysis. Kamat et al. [21] used graphene supported with Pt nanoparticles as fuel cell electrodes in liquid hydrazine, and showed very good performance. Both of them are solid–liquid phase reactions, and in liquid phase GS can be spread out, thus the surface is contactable.

Meso-macroporous oxide which acts as a new frontier for hierarchically-porous materials is of great value. The meso-macroporous oxide support, such as SiO₂ and Al₂O₃ [5], possesses a multi-level porous structure. The macro-pores can ensure the rapid transport of reactant gases with low pressure drop and the mesopores can provide high surface area. Besides, the meso-macroporous oxide can be made in macrostructure, including particulate and monolith. Hence, the composites of GS-meso-macroporous oxides with macrostructure should be a much promising catalyst support for gas solid reactions, which can overcome the problem of the mass transfer limitation in nano metal/GS catalysts, and possess the special properties of both GS and the meso-macroporous oxides.

In this work, Pt–Ni bimetallic nanoparticles were supported on GS-meso-macroporous SiO₂ composite by using a simple co-impregnation method. The catalytic performance for CO-PROX and the nano bimetallic structure of the catalyst were investigated. This is a case study on GS-meso-macroporous oxide as catalyst support for gas solid reactions, and can be extended to other reactions.

Experimental method

Preparation of Pt–Ni/graphene-meso-macroporous SiO₂ composite

The graphite oxide (GO) was synthesized from oxidation of flake graphite according to the Hummers method [23]. The meso-macroporous SiO₂ was prepared by using macroporous polystyrene (PS) as the template for the macropores and using A tri-block copolymer poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) as template for the mesopores. The composite of GS-meso-macroporous SiO₂ was prepared by a simple sol–gel method, and details were stated in our previous work [24]. The PS foams which were used as macroporous template were obtained from polymerization of styrene in highly concentrated water-in-oil (W/O) emulsions, and the details were stated in Ref. [25]. Briefly, the monolithic GS-meso-macroporous SiO₂ composite was prepared by impregnating PS foam with the mixed sol of silicon oxide hydrosol and GO. The PS templates were impregnated into the hydrosol under vacuum condition until no air bubble escaped from the PS template. The impregnated samples were dried at 60 °C for 24 h. This impregnation process was repeated for several times. The dried samples were calcined in N₂ at 600 °C for 4 h to remove P123 and PS template, at the same time the GO could be thermally exfoliated. The thus prepared GS-meso-macroporous SiO₂ composite was signed as GMMSiO₂.

GMMSiO₂ supported bimetallic Pt–Ni catalysts were prepared as follows. The GMMSiO₂ monoliths were crushed into 40–60 mesh particles, maintaining the meso-macroporous structure after the crush. The particles of the GMMSiO₂ were

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