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New finding on Sb (2–3 nm) nanoparticles and carbon simultaneous anchored on the porous palygorskite with enhanced catalytic activity

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ABSTRACT

A series of Sb/C/palygorskite nanocomposites, Sb (2–3 nm) nanoparticles anchored inside a porous palygorskite, were successfully prepared through facile impregnation and in-situ calcination method. Catalytic performance was evaluated on the basis of the reduction reaction of 4-nitrophenol where $NaBH_4$ was used as reductant. In the synthesis process, the reduction of SbO^+ and carbonization of tartrate ions occurred simultaneously, thereby inhibiting the agglomeration of Sb particles and promoting the dispersion of 2–3 nm Sb nanoparticles on the surface and tunnel of the palygroskite. The produced nanocomposites, *x*%-Sb/C/palygorskite composites, exhibited higher turnover frequency and stability than Sb/C nanocomposites synthesized under the same condition but without palygroskite as support, which is attributed to a strong interactions between Sb nanoparticles and modified palygorskite. These interactions efficiently stabilize the Sb nanoparticles and enhance the catalytic activity and stability. What's more, the presence status of antimony in the nanocomposite is clearly explained. This research can provide a new strategy for designing functional nanocomposites that are based on natural clay mineral.

1. Introduction

Over the last decade, metal nanoparticles (NPs) have attracted extensive attention and have been applied in several fields. Accordingly, significant progress has been achieved mostly on the preparation and application of transition and precious metals, main group metals are also gaining widespread interest from researchers. For example, Sb/C [1,2] and Sb/Sb_2O_3 nanocomposites were reported as potential anode materials for high-performance lithium-ion and sodium-ion batteries [3]. Sb nanoparticles in these nanocomposites are embedded homogenously in an interconnected framework of reduced graphene nanosheets, which provides structurally stable hosts for sodium-ion intercalation and deintercalation [4]. More importantly, recent studies demonstrated that Sb nanocomposites present good catalytic performance [5,6]. For example, aromatic nitro compounds, *p*-nitrophenol (4-NP) is usually acknowledged as a hazardous organic materials owing to it easily caused person get skin cancer by immediate contact [7–12]. In the heterogenous catalytic hydrogenation, it is not only a great pregnant manufacture for converting 4-NP into *p*-aminophenol (4-AP), 4-AP often remarked as a medical synthetic intermediaters included analgetic, antipyretic, photosensitizer and dyestuff etc [13–15]; it is also widespreadly served as a model reaction for the assessment of the catalytic performance at the room temperature. Our previous research confirmed that Sb-rich Sb_2Se_3 catalysts can enhance catalytic activity for the reduction of *p*-nitrophenol (4-NP). Basing on this result, we proposed that Sb is a key factor that enhances the catalytic performance of Sb_2Se_3 catalyst [16–18]. We synthesized Sb/palygorskite composite by a hydrothermal method [19]. We found that 2–5 nm Sb NPs dispersed well on the surface of palygorskite fibers. However, partially aggregated Sb NPs with sizes smaller than 200 nm were mixed among the crystal bundles of palygorskite, thus affecting the stability of the Sb/palygorskite catalysts. This condition remains a challenge to the development of new strategies for overcoming the aggregation of Sb NPs,

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clarification of composite material structures, and improvement the catalytic properties of nanocomposites.

Given that the hydrophobicity of Sb/C nanocomposite is not conducive to catalytic reactions in an aqueous phase, introducing hydrophilic substances as carriers is necessary for the preparation of emerging Sb nanocomposites. Natural clay minerals, such as montmorillonite [20–22], kaolinite [23,24], halloysite [25–31], and sepolite [32], are currently exploited as functional substrate materials because of they are hydrophilic. Palygorskite is distinct from most minerals with hierarchical structure. It has a transitivity layer-chain structure, where Si–O tetrahedron is present on the top and bottom layers; and (Al, Mg, Fe)–O–OH octahedron, on the medium layer. The inner and outer surfaces of palygorskite either have an abundant amount of silicon hydroxyl, and thus palygorskite is often preferred as a porous support. For example, mercapto and amino-functionalized palygorskite evidently enhances the adsorption amounts and adsorbed selectivity of heavy metal ions [33]. In addition, Y_2O_3/palygorskite functional composites greatly improve the performance for the methyl blue removal [34]. The stability of palygorskite can be enhanced by assembling catalysts inside its surface and tunnel. Therefore, this approach enables the uniform distribution of antimony on palygorskite.

The preparation of antimony nanocomposites includes hydrothermal method [19], impregnation [35], electrodeposition [36,37], and chemical reduction [38,39]. Hydrothermal method was found to lead the growth and aggregation of Sb NPs. [19], while impregnation method enables the thorough mixing of an active material with the support and facilities the control of the amount of an active material. Recently, the surface coordination chemistry of metal nanomaterials is receiving considerable attention [40–42]. In the present study, we proposed a strategy of taking full advantage of the coordination compound, antimony potassium tartrate, to control the size, morphology, and composition of catalysts by means of the surface coordination interaction between the organic ligands and the surface of catalysts. Therefore, a Sb/C/palygorskite nanocomposite was designed and prepared by impregnation method in combination with in-situ calcination method in a reducing atmosphere.

The scheme (see Scheme 1) shows the flow process of Sb/C/palygorskite nanocomposite preparation. First, palygorskite is pretreated with NaCl and an acid to remove its magnesium component in order to facilitate the formation of mesoporous palygorskite fibers (Pal). Second, the modified palygorskite is thoroughly mixed with different concentrations of antimony potassium tartrate. The resulting mixture is then dried by heat treatment. During this process, the coordination compound-generated SbO^+ and tartrate ions, which are adsorbed on the surface and tunnel of the modified palygorskite, are hydrolized. Finally, the precursor is reduced by heat treatment in the reducing atmosphere. Thus, emerging hybrid composites containing Sb nanoparticles, which are highly dispersed on modified Pal fibers, are typically fabricated by simple impregnation and in-situ calcination method under argon and hydrogen atmosphere. Highly dispersed Sb nanoparticles increase the active sites in Sb/C/Pal composites, thereby enhancing the catalytic activity and stability of composites for the catalytic reduction of 4-NP. The textural characteristics, changes in the morphologies, and thermal stabilities of the nanocomposites were investigated. The influence of Sb loading content on catalytic properties was also studied. Catalytic hydrogenation mechanism was then proposed. Finally, we present for the first time an insight into Sb NPs anchored at interior and out surface of the porous palygorskite and containing reduced carbon on its surface exhibiting high catalytic activity for the reduction of *p*-nitrophenol.

2. Experimental

2.1. Materials and regents

Raw palygorskite was purchased from Xuyi, China. Sodium chloride, hydrochloric acid, antimony potassium tartrate, sodium borohydride, and 4-nitrophenol, all of analytic grade, were purchased from Sinopharm Chemical Regent Co., Ltd.. The calcination atmosphere for the reduction of SbO^+ was 90% Ar and 10% H_2.

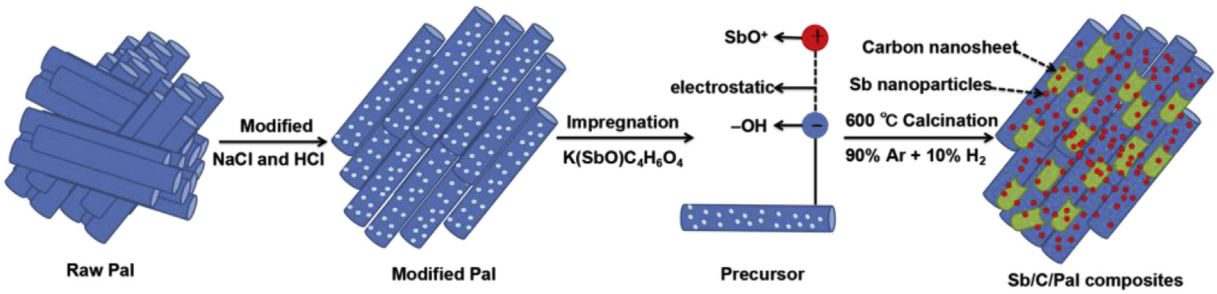
2.2. Preparation of materials

2.2.1. The modification of raw Pal clay mineral

Raw palygorskite (20 g), NaCl (29.22 g), and deionized water (500 mL) were added into a flask and then disaggregated by ultrasonic wave with 600 W power for 90 min. The mixture, named Na–Pal, was continuously stirred for 24 h, and then filtrated, and finally washed three times with deionized water. Na–Pal was then treated by HCl (1 M, 500 mL) for 1 h and then was filtrated and washed three times with deionized water. The modified Pal, was obtained after drying the Na–Pal at 80 °C for 24 h.

2.2.2. Preparation of Sb/C and X%-Sb/C/Pal catalysts

A series of Sb/C/Pal nanocomposites with different Sb contents were synthesized. Pal (0.3 g) ($K[SbO]C_4H_6O_4$ 0.1946 g) and 100 mL of deionized water were added into the flask. The catalyst in precursor powder form was obtained by continuously stirring the above solution at 80 °C for the volatilization of the solvent used. At 24 h of continuous stirring, the hydrolysis of the antimony potassium tartrate generated SbO^+ and tartrate ions, which were adsorbed on the modified palygorskite through electrostatic interaction between the SbO^+ and the rich-negative Si–OH groups. Finally, the precursor was reduced by heat treatment at 600 °C for 4 h under the following conditions: 5 °C/min of heat flow and 40 mL/min of gas flow. The catalyst was denoted as 20%-Sb/C/Pal (20% is the theoretical amount of Sb), and the preparation of the other Sb/C loadings catalysts and pure Sb/C catalysts were performed in accordance with the information mentioned above. The



Scheme 1. Schematic illustration of the preparation of the Sb/C/Pal nanocomposite.