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A recoverable sandwich phosphorotungstate stabilized palladium (0) catalyst for aerobic oxidation of alcohols in water

Lijuan Chen[a,b,*], Tao Feng[c], Pengfei Wang[c], Ziwen Chen[a], Riqing Yan[a], Bo Liao[a,b], Yujun Xiang[a]

[a] *School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, PR China*
[b] *Key Laboratory of Theoretical Chemistry and Molecular Simulation of Ministry of Education, Hunan University of Science and Technology, Xiangtan, PR China*
[c] *School of Energy Source, Hunan University of Science and Technology, Xiangtan, PR China*

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ABSTRACT

The preparation, characterization and catalytic properties of tetra metal substituted sandwich phosphorotungstate $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$($M_4P_2W_{18}$, $M^{2+} = Fe^{2+}$, Co^{2+}, Mn^{2+}, Cu^{2+}, VO^{2+}) stabilized Pd nanoparticles, which were in-situ encapsulated in mesoporous aluminum phosphate (mAPO) by a one-pot method, were demonstrated for aerobic oxidation of alcohol in water. The synthesized catalysts were characterized with N_2 adsorption, XRD, TEM, FT-IR and UV–vis. TEM analysis revealed that Pd-$M_4P_2W_{18}$/mAPO thus obtained has a mean palladium particle size of less than 5 nm. The solid Pd-$M_4P_2W_{18}$/mAPO catalysts exhibit excellent activity for aerobic oxidation of benzyl alcohols in water without any base additives. It was found the introduced $M_4P_2W_{18}$ polyoxanions encapsulated palladium nanoparticles as both stabilizing agent and promoters, leading to enhanced activity and recyclability of palladium catalyst. The recycling test of representative Pd-$(VO)_4P_2W_{18}$/mAPO for oxidation of benzyl alcohol suggested no significant decrease in activity and selectivity even after twelve times of successive reactions. This novel heterogeneous catalyst composed of polyoxometalates stabilized palladium nanocatalysts and mesoporous aluminophosphate can also be extended to the selective oxidation of various alcohols.

1. Introduction

The oxidation of alcohols is one of the most fundamental transformations of great commercial and research significance because the corresponding aldehyde/ketone products serve as important intermediates in the fine chemicals and pharmaceutical industries. The stoichiometric oxidants like $KMnO_4$ or CrO_3 are conventionally used to accomplish this transformation [1]. However, these processes usually produce large amount of toxic inorganic salts waste and the yields of the desired product aldehyde/ketone are often low. With the ever-increasing environmental concerns, the development of heterogeneous transition-metal based catalysts for aerobic oxidation of alcohols using air or oxygen as oxidant has attracted much attention [2,3]. Water is an ideal solvent for this protocol because it can avoid explosions and the hazards associated with the use of oxidisable organic solvents under oxygen pressure. Among these studies, palladium-based homogeneous or heterogeneous catalysts show promising activity in aqueous solution under mild conditions, a number of palladium-based catalysts in the form of metal complexes or nanoparticles have been investigated for this purpose [4–11]. Although the progress for palladium catalyzed aerobic oxidation of alcohols is notable, palladium catalysts often suffer from easy agglomeration and formation of palladium black that cause their deactivation in many cases. Moreover, in many aerobic alcohol oxidation systems using noble metal based catalysts, base additives are often necessitated to improve conversion of alcohol and selectivity for corresponding carbonyl product. According to literature, the base additives can facilitate the dehydrogenation of alcohol and promote to the β-H elimination of a dissociated alcohol on the Pd surface [9]. However, the alkaline environment under oxygen atmosphere is harmful to the stability

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[*] Corresponding author at: School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, PR China.
E-mail address: ljchen11@163.com (L. Chen).

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of palladium catalyst, leading to an easier deactivation of palladium catalyst due to over-oxidation and poisoning [6]. In this context, the development of palladium-based heterogeneous catalysts with improved recyclability for base-free aerobic oxidation of alcohols in water is desirable in recent years.

For supported Pd nanoparticles catalyst, the morphology and particle size control of Pd nanoparticles is an important factor affecting the recyclability of catalysts. The previous studies indicate that the catalytic activity of nano-sized metallic Pd for aerobic oxidation of alcohols is dependent on the size and morphology of the surface Pd nanoparticles, and the Pd nanoparticles with particle size of a few nanometers show the highest activity [12,13]. However, it is well known that the nanoparticles of small particle size are very mobile and thermodynamically prone to agglomerate into larger inactive particles [14]. Thus the improved recyclability of heterogeneous palladium catalysts is dependent on the better control and maintenance of the particle size of Pd nanoparticles in desired range during the catalyst preparation and the sequent catalytic reactions. The strategies preventing the growth of Pd nanoparticles that are widely used in heterogeneous palladium catalysts includes combinations with the promoter metal such as Bi, Pb or Au, surface functionalization of support in order to strengthen the bonding of Pd nanoparticles and confinement of Pd nanopartices in nano-sized channels of supports [15–22]. However, these methods often suffer from some disadvantages, for example, some promoters such as Bi and Pb are not green agents, Pd and Au needed to form a desired alloy phase to generate the enhanced activity, the procedures for surface functionalization of support and post-treatment are complicated and part of active species that located in small mesopores is difficultly contactable by substrate molecules.

Recently, one of the important applications of polyoxometalates emerged in metal clusters stabilization [23]. D'souza and coworkers reported a simple synthesis of Krebs type polyoxoanions $[(TBA)_4H_4M_4(H_2O)_{10}(XW_9O_{33})_2]$ stabilized Pd, Au and Ag metal colloidal systems, the metal particle size in these systems were well controlled in a narrow range and remained unchanged for approximately three/six months in solution media [24]. On the other hand, polyoxometalates are a kind of efficient catalyst for selective oxidation of organic chemicals, in palladium catalyzed oxidation reactions, the combinations with polyoxometalates can effectively promote to the activity of palladium catalysts [24–31]. Neumann and co-workers reported a Pd^{II}-polyoxometalate catalyst by attaching a sandwich type $[WZn_3(H_2O)_2][(ZnW_9O_{34})_2]$ polyoxoanion to a Pd^{II} center for aerobic oxidation of primary aliphatic alcohols, this group also reported a polyoxometalate appended with alkylthiol tethers $[SiW_{11}O_{40}(SiCH_2CH_2CH_2SH)_2]$ stabilized Pd nanoparticles catalysts for liquid aerobic oxydehydrogenation of vinylcyclohexene and vinylcyclohexane to styrene [29,30]. Zhang and coworkers reported the enhanced electrocatalytic properties of Pd and Pt nanoparticles/polyoxometalates/graphene tri-component nanohybrids for methanol and formic acid oxidation [31]. In these systems, the synergic catalysis of Pd species and polyoxometalates lead to improved conversion and selectivity, the promotion effect of polyoxometalates is most likely related to their electron-accepter properties and oxygen-activating capability [32].

Inspired by the above studies, here we reported a integrated catalytic system based on sandwich type polyoxometalates $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$($M_4P_2W_{18}$, $M^{2+} = Fe^{2+}$, Co^{2+}, Mn^{2+}, Cu^{2+}, VO^{2+}) and palladium nanoparticles through in situ encapsulation of pre-synthesized $M_4P_2W_{18}$ stabilized palladium nanoparticles in mesoporous aluminophosphate by a sol-gel method. The synthesized catalyst showed high catalytic performance for aerobic oxidation of alcohols in water. The catalyst also showed enhanced stability and recyclability compared with other heterogeneous palladium catalysts without modification of polyoxometalates.

2. Experimental

2.1. Chemicals and methods

Powder X-ray diffractions of samples were recorded on a Brucker AXS D8 Advance diffractometer using Cu Kα radiation. TEM images were recorded on a JEM 3010 TEM operated at 200 kV. More than 100 particles for each sample were randomly counted to determine the particle size distributions. N_2 adsorption and desorption isotherms were obtained on a micromeritics ASAP 2010 instrument at 77 K, samples were degassed at 120 °C for 5 h under high vacuum prior to measurements. Surface areas and pore distribution were calculated by BET and BJH methods, respectively. Elemental analysis of samples was performed with an inductively coupled plasma-optical emission spectrophotometer Shimadzu ICPs-7500 to determine the amount of Pd and polyoxometalates in heterogeneous catalyst. IR spectra were recorded on KBr pellets by a Nicolet Niclet 6700 spectrophotometer. UV–vis spectra of samples were obtained with Perkin-Elmer Lambda-35 spectrophotometer.

K_2PdCl_4 was used as Pd precursor. Sodium tungstate dihydrate, phosphoric acid (85%), cobalt nitrite hexahydrate, manganese acetate tetrahydrate, vanadium sulfate heptahydrate and ferrous sulfate pentahydrate were used as the sources of W, P, Co, Mn, V and Fe for the synthesis of the tetra metal substituted tungstophosphates. To prepare mesoporous aluminophosphate, aluminium isopropoxide and phosphoric acid were used as the sources of aluminum and phosphorous, respectively, and hexadecylamine (HDA) was used as template. All the chemicals were analytical grade and used as received without further treatment.

2.2. Preparation of sandwich tungstophosphates

The potassium salts of sandwich polyoxoanions $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ ($M_4P_2W_{18}$, $M^{2+} = Co^{2+}$, Fe^{2+}, Mn^{2+}, VO^{2+}) were synthesized by the reaction of $Na_9PW_9O_{34}$ with the corresponding soluble metal salts in water and precipitation with solid potassium chloride, as described by the published literature [33]. The purity of the samples was tested by IR and NMR spectroscopy.

2.3. In-situ encapsulation of $M_4P_2W_{18}$ stabilized Pd nanoparticles in mesoporous aluminophosphate

The pre-synthesized $M_4P_2W_{18}$ stabilized Pd nanoparticles was incorporated in mesoporous aluminophosphate by a hydrothermal method from a gel composition of 0.0057 K_2PdCl_4: 0.0011 $M_4P_2W_{18}$: Al_2O_3: P_2O_5: 1.2HDA: 65ethanol: 300H_2O. In a typical synthesis, $M_4P_2W_{18}$ stabilized Pd nanoparticles colloidal solution were obtained by the following procedures: the mixture of 2.5 mL of $M_4P_2W_{18}$ (10 mM) and 12.6 mL of K_2PdCl_4 (10 mM) aqueous solution was stirred for 5 min, then Pd^{II} was reduced to Pd^0 with 3 mL of freshly prepared 0.1 M $NaBH_4$ by ultrasonication for 10 min. The $M_4P_2W_{18}$ stabilized Pd nanoparticles colloidal solution was then added to the precursor solution composed of 2.24 g of aluminium isopropoxide, 1.06 g of orthophosphoric acid and 1.32 g of hexadecylamine in 11.5 g of water and 27.8 g of ethanol. The resulting gel of the above composition was stirred for 3 h at room temperature and then transferred into a Teflon lined autoclave in an oven at 120 °C for 24 h. After cooling, the solid in gray color was filtered, washed thoroughly with distilled water and dried in air. The template was removed by a combined solvent extraction and calcination method. For extraction procedures,1 g of the above dried solid was stirred in 40 mL of 0.05 M HCl/ethanol at room temperature for 15 min and washed with ethanol, the process repeated for five times. The solid product after extraction was dried at 80 °C overnight, and then calcinated at 400 °C for