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Pd^0-PyPPh$_2$@porous organic polymer: Efficient heterogeneous nanoparticle catalyst for dehydrogenation of 3-methyl-2-cyclohexen-1-one without extra oxidants and hydrogen acceptors

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ABSTRACT

In this contribution, we have developed an efficient and recyclable porous organic polymer (POP) supported Pd nanoparticle catalyst (Pd°-PyPPh$_2$@POP) for dehydrogenation of 3-methyl-2-cyclohexen-1-one. This heterogeneous catalytic system represents a totally clean process without using any extra oxidant and hydrogen acceptors. The SEM-EDS mapping images of the Pd°-PyPPh$_2$@POP catalyst reveal the highly uniformly dispersed character of C, Pd, P and N elements. The coordination bonds between Pd nanoparticle and exposed P atom as well as N atom on the surface of PyPPh$_2$@POP polymer are confirmed by means of solid-state ^{31}P NMR and XPS. Importantly, both P atom and pyridyl ring on the PyPPh$_2$@POP polymer are themselves used as solid base over the Pd°-PyPPh$_2$@POP catalyst, leading to a catalytic conversion of 88.2% even without the employment of inorganic base additives (K_2CO_3). Our results have provided a strategy for designing highly active bifunctional POP supported nanoparticle catalysts.

1. Introduction

Phenols and its derivatives are important precursors and core structures of useful chemical molecules in the field of pharmaceuticals, agrochemicals and polymers et al [1,2]. The introduction of functional groups in meta-position of phenolic hydroxyl group still remains a key challenge in the preparation of these molecules due to the strong electronic directing effect of −OH group which cause *ortho-* and *para-*substituent easier [3–6]. Thus, intensive efforts have been devoted to achieve a facile route to substituted phenols. Recently, palladium-catalyzed aerobic dehydrogenation of cyclohexenes is emerging as a versatile strategy to achieve this goal. Stahl and co-workers develop an efficient Pd/Py-based homogeneous catalytic system to dehydrogenate cyclohexanone to phenols by using molecular oxygen (Scheme 1a) [7–15]. However, oxidative dehydrogenations for the synthesis of phenols are frequently hindered by over-oxidation due to the inherent nature of susceptible to oxidation of phenols [16]. In addition, the homogeneous nature of this system limits the catalyst recycling process [17,18]. To solve the catalyst recycling problem and realize the sustainable green catalysis, immobilization of metal complex onto insoluble supports, such as polymers, silica method in commercial exploitation [19–24]. Thus, Liu et al. report AC (activated carbon) supported palladium catalyst (Pd°@AC) for dehydrogenation of cyclohexanone to phenol in the context of oxidant- and hydrogen-acceptor-free conditions (Scheme 1b) [25]. Nonetheless, in such a catalytic system, large amount of additional K_2CO_3 need to be added to achieve high activities, which will cause metal contamination of the products and pollutions to the environment [26]. Porous organic polymers (POP) are one of the promising supports because of their large surface area, advanced porous structure, low skeleton density, flexible synthetic strategy, ready functionality and high stability [27–35]. Intense and continuous efforts have led to the rapid development of various POP with useful structures and properties, but there is still a persistent requirement for the design and synthesis of POP containing specific functional groups to improve their performance in heterogeneous catalysis. The incorporation of coordination groups is regarded as an efficient method to stabilize nanoparticles (NPS) [36–45]. Many monodentate and bidentate nitrogen-containing POP supported nanoparticles are employed for heterogeneous catalysis but supported nanoparticles catalyst by using POP containing both of nitrogen and phosphine

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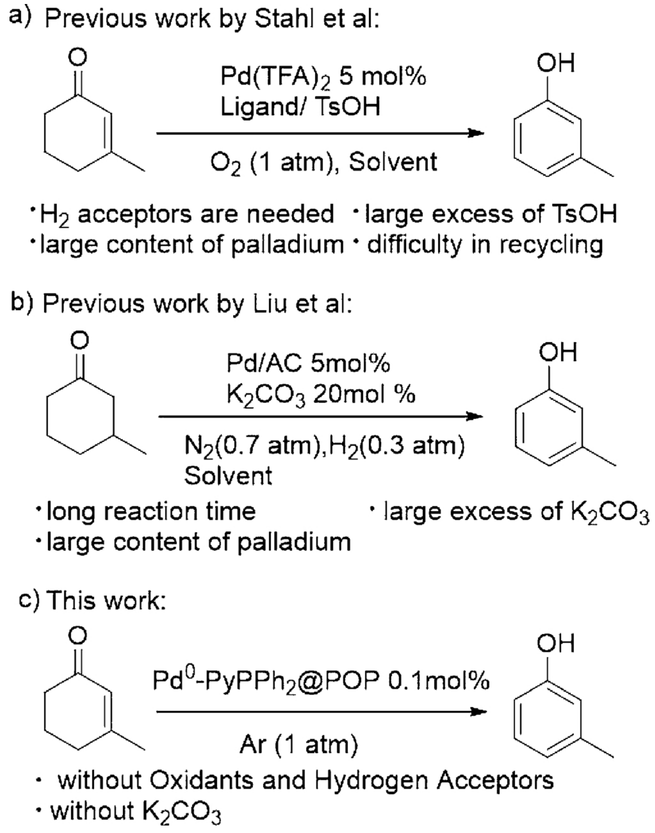
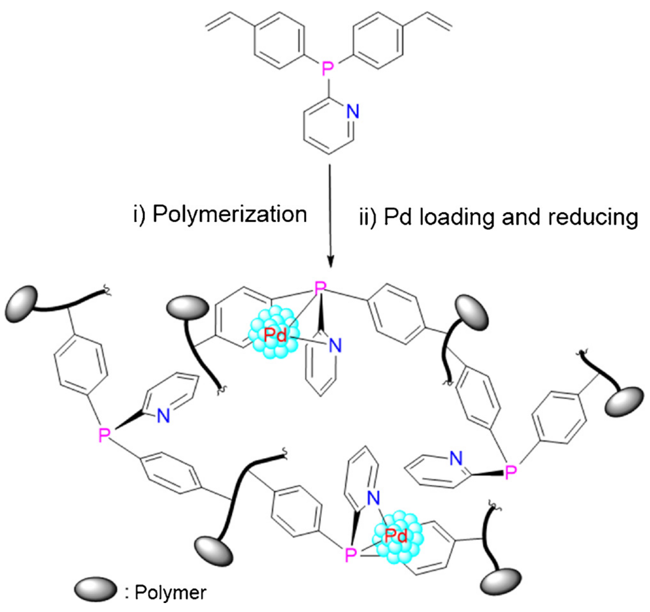


Scheme 1. Dehydrogenation of 3-methyl-2-cyclohexen-1-one or 3-methyl-cyclohexanone to 3-methyl phenol.

coordination sites has not yet been reported [46,47].

Recently, we report a novel two-fold cross-linked porous organic polymer PyPPh$_2$@POP, which is synthesized through polymerization of vinyl-functionalized diphenyl-2-pyridylphosphine (2- PyPPh$_2$ ligand) containing both P and N [48]. Herein, we report PyPPh$_2$@POP supported palladium nanoparticle catalyst (Pd°-PyPPh$_2$@POP, Scheme 2) for oxidant- and hydrogen acceptor-free dehydrogenation of 3-methyl-2-cyclohexen-1-one to 3-methyl phenol. This novel heterogeneous nanocatalyst exhibits relatively high activities even without additional K$_2$CO$_3$. From the viewpoint of efficiency and green chemical process, the heterogeneous POP supported nanocatalyst combines excellent reactivity and eliminated pollutions as well as easy product separation.



Scheme 2. Preparation of Pd°-PyPPh$_2$@POP catalyst.

2. Experimental

2.1. Chemicals

All reagents are of analytical grade and used as purchased without further purification unless otherwise stated. Tetrahydrofuran (THF) is distilled from sodium and pyridine is distilled from calcium hydride under argon.

2.2. Catalyst preparation

All operations are carried out under argon conditions. PyPPh$_2$@POP is synthesized according to our previously report (Scheme 2). The porous organic polymer support with smaller surface area which is denoted as PyPPh$_2$@POPs is synthesized by changing the amount of AIBN and solvent during the solvothermal producing process. The procedure for preparing Pd°-PyPPh$_2$@POP is as follows. In a typical run, 0.16 g PyPPh$_2$@POP is added into a solution of 0.0143 g PdCl$_2$ in 6 ml acetonitrile. After stirring 2 h at room temperature, the mixture is dried under reduced pressure at 65 °C to give a brown solid. The sample is denoted as PdCl$_2$-PyPPh$_2$@POP. And then it is reduced in a stream of H$_2$ (100 ml/min) at the temperature of 300 °C (heating rate: 9 °C /min) for 5 h. In addition, the Pd°-PyPPh$_2$@POP catalyst could also be prepared by using Pd(OAc)$_2$. The porous organic polymer supported catalyst with smaller surface area is denoted as Pd°-PyPPh$_2$@POPs. Pd°@AC and Pd°@Al$_2$O$_3$ catalysts are prepared by the same procedure.

2.3. Characterization

Nitrogen sorption isotherms are measured using an AutoSorb-1 instrument. The Pd°-PyPPh$_2$@POP catalyst is outgassed for 24 h at 120 °C before measurements. SEM and SEM-EDS mapping study is performed on a JSM-7800 F scanning electron microscope. The thermal stability of Pd°-PyPPh$_2$@POP is detected in N$_2$ flow (20 ml min^{-1}) using a Diamond TG/DTA instrument, with a heating rate of 10 ℃ min^{-1} up to 1000 °C. Solid-state ^{31}P NMR experiments are carried out on an Infinity plus 400 spectrometer operating at 161 MHz. ^{13}C MAS NMR spectra are recorded under a magic angle spinning rate of 6 KHz. XPS spectra are carried out on a ESCALAB 250Xi Alα radiation. TEM study is performed on a JEM-2100 transmission electron microscopy.

2.4. Catalytic performance testing

In a typical run, 25 ml flask is charged with 0.016 *g* Pd°-PyPPh$_2$@POP catalyst, 0.90 *g* 3-methyl-2-cyclohexen-1-one and then the reactor is sealed. After replaced 5 times with argon, the contents are heated to 140 °C and stirred for 12 h. Then the reactor is cooled to room temperature with ice-water, the liquid samples are centrifuged to isolate the catalyst. And then the solution is analysed offline by Agilent 7890 A gas chromatography with a HP-5 capillary column and FID detector using isopropanol as an internal standard. Pd°@AC and Pd°@Al$_2$O$_3$ are used in the reaction according to the same procedure described above for the Pd°-PyPPh$_2$@POP catalyst.

2.5. Hot filtration test

The reaction is carried out in the presence of the Pd°-PyPPh$_2$@POP catalyst in 1 h and at that point the solid insoluble catalyst is filtered off at the reaction temperature. The resulting liquid filtration is placed under the same conditions as the original reaction for another 1.5 h and also analysed by GC.