Preparation of microporous polymer-encapsulated Pd nanoparticles and their catalytic performance for hydrogenation and oxidation

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ABSTRACT

Palladium nanoparticles (Pd NPs) encapsulated by conjugated microporous polymers (CMPs) were prepared by the Pd-catalyzed polymerization followed by a thermal treatment with N_2 or H_2. The Pd catalysts were embedded in the porous network during polymerization and used as a precursor for the generation of Pd NPs in CMP. Although no Pd NPs were formed in the as-synthesized Pd/CMPs, Pd NPs with 1.6–3.5 nm size were formed after the thermal treatment. The obtained Pd/CMP-N_2 and -H_2 catalysts were highly selective in the hydrogenation of 4-nitrostyrene to 4-ethylnitrobenzene, whereas Pd NPs supported on carbon (Ketjen black) gave a fully reduced product, 4-ethylaniline. Substituents in CMP framework could change the catalytic activity of Pd NPs; hydroxy-substituted CMP encapsulated Pd NPs showed higher catalytic activity than Pd/CMP-H_2 for benzyl alcohol oxidation.

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1. Introduction

Nanoporous materials such as metal-organic frameworks (MOFs) are currently of great interest owing to their potential applications to gas sorption, separation, and heterogeneous catalysis. They are also expected to be efficient supports for the confinement of metal nanoparticles (NPs) with controlled size in their porous structures.[1] Recently, well-defined nanoporous organic polymers constructed by only covalent bonds have also attracted growing interest because of tunable building units and high thermal and chemical stability.[2] Several kinds of nanoporous organic polymers, such as covalent-organic frameworks (COFs),[3] covalent triazine frameworks (CTFs),[4] and conjugated microporous polymers (CMPs),[5] have been reported to be useful as metal NPs supports.

To deposit metal NPs into the porous structures, post-loading methods, in which metal precursors or metal NPs are loaded into the porous materials, are commonly used, e.g., chemical vapor deposition,[3c,6] solid grinding,[7] impregnation,[5] and sol

immobilization.[4] Cooper et al. have reported the synthesis of CMP by Pd-catalyzed Sonogashira–Hagihara coupling reaction of 1,4-dihalobenzenes with 1,3,5-triethynylbenzene.[5,8] They have also deposited Pd NPs in CMP by impregnation using $Pd(acac)_2$ as a precursor in supercritical CO_2 as a solvent, followed by thermal decomposition of Pd complex to form Pd NPs.[5] However, relatively large (5–10 nm) Pd NPs were also formed.

To stabilize metal NPs, the introduction of functional groups containing heteroatoms into their porous frameworks has often been exploited. Prati et al. demonstrated that Pd/CTF showed higher catalytic performance than Pd/C did.[4] They concluded that the incorporation of N atoms in the framework enhanced the interactions between Pd and supports, preventing the aggregation of Pd NPs during immobilization and improving catalyst durability. However, aggregation of Pd NPs on the CTF surface was observed after catalytic reactions. Thus, post-loading method cannot completely prevent the aggregation of metal NPs on the outer support surface, in particular for organic polymers without coordination sites to metal precursors.

On the other hand, Ogasawara and Kato have reported the one-pot entrapping of Pd NPs in polymer matrices by the polymerization-induced phase separation technique, in which Pd

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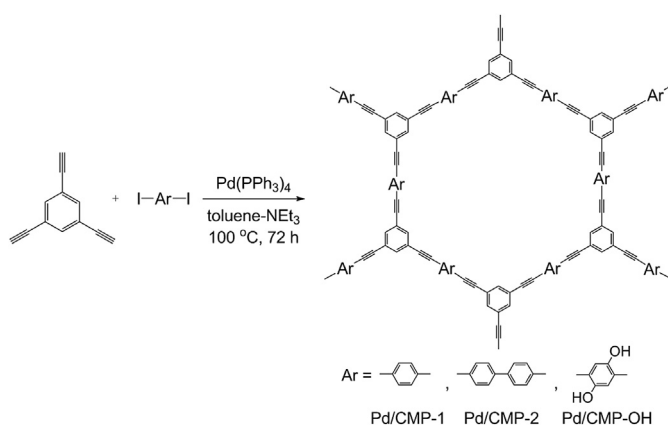
NPs formation concurrently occurs with the synthesis of polymer matrices.[9] However, Pd precursors have to be stabilized by amide-containing dendritic monomer units before the polymerization reactions. Thus, in situ loading of metal source during polymerization of monomers without coordinating groups to metal ions and size control of metal NPs confined in nanoporous polymers without coordination sites are still challenging research targets.

As mentioned above, Cooper's CMPs are prepared by Pd-catalyzed cross-coupling reaction. Their polymers inspired us to attempt that Pd catalysts, which were used for the polymerization, were exploited as the precursors for the generation of Pd NPs. In this work, we synthesized CMP-1 in the presence of Pd catalysts without Cu co-catalysts and treated in N_2 or H_2. As a result, Pd NPs were formed and highly dispersed in CMP framework even heteroatoms were not contained in the porous framework. We examined the catalytic performance of the obtained Pd/CMP-1-N_2 and -H_2 and found that they were active for selective hydrogenation of 4-nitrostyrene to 4-ethylnitrobenzene. We also studied the effect on the functional groups of CMP backbone to a Pd NPs-catalyzed reaction.

2. Results and discussion

2.1. Preparation and characterization of Pd/CMPs

CMP-1 was prepared from 1,3,5-triethynylbenzene and 1,4-diiodobenzene in a similar manner established by Cooper et al.[8a] with minor modifications in the presence of Pd(PPh$_3$)$_4$ without copper co-catalysts (Scheme 1). The as-synthesized polymer was abbreviated as Pd/CMP-1. The Pd content in Pd/CMP-1 was measured by atomic absorption spectrometry (AAS) and 0.9 wt % of Pd was contained. This was almost consistent with the reported value.[8a] It can be assumed that ca. 50% of Pd remained in the CMP network during the polymerization. The obtained Pd/CMP-1 was dried and then treated in a flow of N_2 or H_2 at 250 °C to give Pd/CMP-1-N_2 and -H_2, respectively.

backbone. For Pd/CMP-1-N_2 and -H_2, the peaks at 2195 cm^{-1} of internal alkynes remained.

The construction of arylene–ethynylene structure was also confirmed by ^{13}C CP-MAS NMR, based on the peak at 90.6 ppm, which corresponded to the internal alkyne carbons (Fig. S2). Small peaks at 78 and 82 ppm indicated the presence of terminal alkyne in the polymer backbone. The peaks at 123.9 and 131.8 ppm were ascribed to the aromatic carbons. After thermal treatment, a shoulder peak at around 137 ppm was observed, and the peak of Pd/CMP-1-H_2 was more obvious. This was probably due to the partial decomposition of the polymer network or the reduction of the internal alkyne by H_2. Taking into account the absence of alkane peaks at around 30 ppm, it could be suggested that some part of alkyne groups was not fully reduced to alkyl chains.

The N_2 adsorption isotherms of Pd/CMP-1, Pd/CMP-1-N_2, and -H_2 showed the type I isotherms by IUPAC classifications, suggesting that all the three had microporous structures (Fig. S3). The Brunauer–Emmett–Teller (BET) surface area of Pd/CMP-1 was calculated to be 744 m^2/g, which was almost consistent with the reported value (834 m^2/g),[8a] suggesting that the absence of Cu co-catalysts did not strongly affect the polymerization. The BET surface areas of Pd/CMP-1-N_2 and -H_2 decreased to 521 and 458 m^2/g, respectively. This was probably due to a partial collapse of porous structures by thermal treatment or blocking the pores by the formation of Pd NPs.

The presence and the size of Pd particles were evaluated by high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observations. For Pd/CMP-1, the formation of Pd NPs was not observed (Fig. 1a). In contrast, Pd NPs were observed as white spots and highly dispersed in Pd/CMP-1 network for both Pd/CMP-1-N_2 (Fig. 1b) and -H_2 (Fig. 1c). These results suggested that thermal treatment caused the formation of mono-dispersed Pd NPs. Large Pd NPs located outside of the porous network were not observed, indicating that Pd NPs were confined in the porous network. The mean diameters were calculated to be 1.6±0.4 and 3.5±0.8 nm for Pd/CMP-1-N_2 and Pd/CMP-1-H_2, respectively (Fig. S4). It was assumed that hydrogen treatment of Pd/
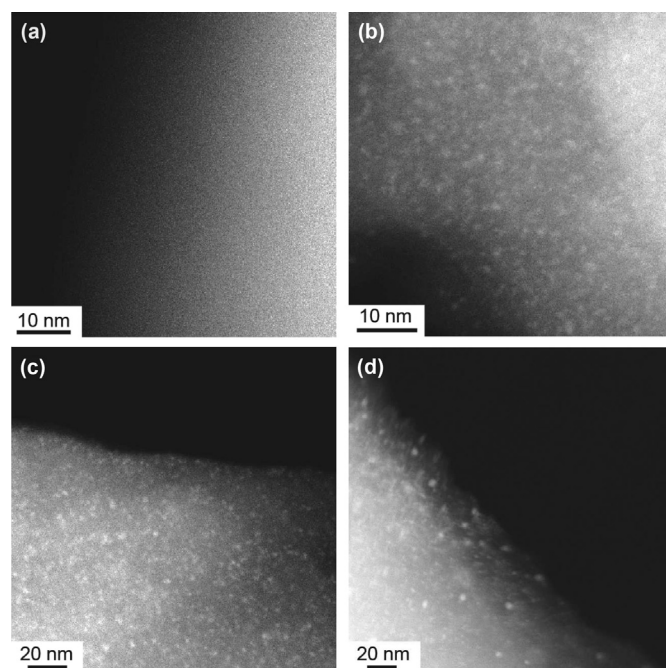
Scheme 1. Synthesis of Pd/CMPs.

Structures of Pd/CMP-1, Pd/CMP-1-N_2, and -H_2 were characterized by FT-IR, N_2 adsorption isotherms, and ^{13}C CP-MAS NMR. FT-IR spectrum of Pd/CMP-1 revealed that the disappearance of the peaks at 1068 and 3280 cm^{-1} corresponded to the C–I stretching vibrations of 1,4-diiodobenzene and to the C–H stretching vibration of terminal alkynes of 1,3,5-triethynylbenzne, respectively (Fig. S1). In addition, a new peak was observed at 2195 cm^{-1}, which corresponded to C–C stretching vibrations of the internal alkyne. These results suggested the construction of arylene–ethynylene polymer

Fig. 1. HAADF-STEM images of (a) Pd/CMP-1, (b) Pd/CMP-1-N_2, (c) Pd/CMP-1-H_2, and (d) Pd/CMP-2-H_2.