REACTIVE & FUNCTIONAL POLYMERS

Temperature responsive copolymer as support for metal nanoparticle catalyst: A recyclable catalytic system

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ABSTRACT

A recyclable catalytic system was developed by using a temperature responsive poly(acrylamide-co-acrylonitrile) (P(AAm-co-AN)) copolymer with an upper critical solution temperature (UCST). Palladium nanoparticles (NPs) immobilized on P(AAm-co-AN) copolymer were synthesized by the chemical reduction method using NaBH$_4$. TEM characterizations showed the highly dispersed and small (~3 nm) Pd nanoparticles formed on the surface of the P(AAm-co-AN) copolymer. UV–Vis measurements indicated the increase of UCST of P(AAm-co-AN) from 30 to 35 °C after the deposition of Pd metal. P(AAm-co-AN) supported Pd catalyst showed high activity in allyl alcohol hydrogenation and facile separation and recovery via sharp solubility changes of catalyst by cooling below UCST.

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1. Introduction

Green catalysis using heterogeneous catalysts in an aqueous media has gained increasing attention in organic synthesis, because water is a clean, inexpensive and highly environmentally friendly solvent [1]. However, many reactants and reagents show poor solubility in water. The use of temperature responsive polymer with reversible conformational changes in response to external temperature as supports has been developed to devise methodologies for performing homogeneous catalytic reactions at one temperature and for facilitating the separation and recovery of catalysts via sharp solubility changes of polymers in aqueous solutions by cooling or heating [1–10]. Such polymers can create controllable hydrophobic microenvironments [1,2,11,12] and significantly improve the mass transport of the reactants/products in aqueous solutions. Moreover, the deposition of metal nanoparticles in the polymer supports induced by the conformational changes of polymer chains can be used to modulate multiple catalytic processes, including reaction rates and selectivity of products, within the constrained environment [13,14].

Generally, thermal responsive polymers are divided into two typical kinds: negative responsive type with a low critical solution temperature (LCST) aggregating upon heating and positive responsive type with an upper critical solution temperature (UCST) aggregating upon cooling [15]. Specially, the LCST types (i.e., poly(N-isopropylacrylamide), PNIPAM) with LCST at ~32 °C as catalyst reactor or support have been intensively studied [1–10,16]. In our previous work, Pd supported on PNIPAM with high activity and facile recovery via heating was prepared and used in the hydrodechlorination of 4-chlorophenol [17]. It should be pointed that a low reaction temperature below LCST is required to achieve the homogeneous reaction using PNIPAM supported catalysts. However, a relatively high temperature for many catalytic reactions is desired to obtain a high reaction rate. Thus, the UCST polymers show more potential application in catalytic reactions even they are still less studied.

Here, we tried to develop a suitable UCST responsive polymer with water soluble properties upon heating as supports for metal nanoparticles in catalytic reactions. A UCST responsive poly(acrylamide-co-acrylonitrile) (P(AAm-co-AN)) copolymer was synthesized in a simple and cost-effective way and used as a support to stabilize Pd nanoparticles. The P(AAm-co-AN) is water soluble above 30 °C through intermolecular hydrogenation bonding and can form quasi-homogeneous/semi-heterogeneous catalytic system at a high temperature. However, it will precipitate through intramolecular hydrogen bonding at room temperature and lead to a two-phase separation from reaction medium [18].

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Thus, the P(AAm-*co*-AN)-Pd catalyst showed high activity as the soluble polyvinyl pyrrolidone (PVP) supported Pd nanoparticles and facile recyclability by cooling in the hydrogenation of allyl alcohol.

2. Experimental

2.1. Materials

Polyvinyl pyrrolidone (PVP), allyl alcohol, *n*-propanol, *n*-propanal, dimethylsulfoxide (DMSO) and sodium borohydride (NaBH$_4$) were purchased from Tianjin Guangfu Technology Corporation (Tianjin, China). Palladium (II) chloride (PdCl$_2$) was obtained from KRS Fine Chemical Co. Ltd. (Tianjin, China). Azobisisbutyronitrile (AIBN, KRS) and acrylamide (AAm, Aldrich) were purified by recrystallization in ethanol and stored in refrigerator. Acrylonitrile (AN, Aldrich) was distilled before use. Poly(*N*-isopropylacrylamide) was synthesized by our previous work [17]. De-ionized (DI) water was used for all experiments.

2.2. Catalyst preparation

2.2.1. Synthesis of P(AAm-co-AN) copolymer
P(AAm-*co*-AN) copolymer was synthesized using a solution polymerization method according to reference [18]. In a typical synthesis, 0.19 g acrylonitrile was dissolved in 16.5 mL DMSO in a three necked round flask, and then 1.02 g acrylamide was added. The above solution was degassed by three freeze-thaw cycles. Then 1.5 mL separately degassed DMSO solution containing 14.7 mg AIBN was injected as the polymerization initiator. The reaction was carried out at 60 °C for 5.5 h. After the polymerization reaction, the reaction mixture was quenched to room temperature in an ice bath, and then excess methanol was added drop by drop using a pipette under vigorous stirring to precipitate the copolymer. The resulted methanol suspension was centrifuged (10 min, 5000 rpm) and the sediment was washed with fresh methanol for three times. Finally, the resulting product was dried in vacuum oven at 70 °C for 48 h.

2.2.2. Synthesis of P(AAm-co-AN)-Pd, PVP-Pd, PNIPAM-Pd and Pd/γ-Al$_2$O$_3$
The P(AAm-*co*-AN), PVP, PNIPAM and γ-Al$_2$O$_3$ supported Pd nanoparticle catalysts were prepared by the NaBH$_4$ reduction method according to the previous report [19]. In a typical experiment, 0.1 g P(AAm-*co*-AN), PVP or γ-Al$_2$O$_3$ was added into 80.0 mL DI water preheated at 45 °C under magnetic stirring. To obtain supported Pd catalysts with around 0.5 wt.% Pd, the resulted solution was mixed with 0.43 mL K$_2$PdCl$_4$ (0.0116 mol L^{-1}) solution, then 0.56 mL (25 mmol L^{-1}) of freshly prepared NaBH$_4$ aqueous solution was added dropwise under vigorous stirring. Finally, the mixture was stirred and refluxed at 45 °C for 4 h. The P(AAm-*co*-AN) or the PVP supported Palladium nanoparticles (denoted as P(AAm-*co*-An)-Pd and PVP-Pd, respectively) were obtained with a molar ratio of polymer–monomer/Pd (polymer$_{mono}$/Pd) at 305 and 200 respectively, and 0.062 mmol L^{-1} Pd metal were detected in this polymer supported Pd solution by the inductively coupled plasma atomic emission spectrometry (ICPAES) on an IRIS Intrepid spectrometer. The resulted Pd/γ-Al$_2$O$_3$ (0.5 wt.% Pd confirmed by ICPAES characterization) sediment was filtrated and washed thoroughly with DI water and then dried in the vacuum oven. For preparation of PNIPAM supported Pd nanoparticle (PNIPAM-Pd), the synthesis temperature was reduced to 25 °C because of its LCST at 32 °C.

2.3. Catalyst characterization

Molecular weight and polydispersity of P(AAm-*co*-AN) were determined by gel permeation chromatography (GPC) in dimethylsulfoxide (DMSO). Copolymerization was confirmed by Fourier transform infrared spectroscopy (FTIR) using a spectrometer of FTS6000 Varian. BRUKER AVANCE-400MHZ Magnetic Resonance Spectroscopy (NMR) was employed to further confirm the structure and organic group

interactions of the copolymer using DMSO-d_6 as solvent, tetramethylsilane (TMS) as internal standard. The UCST of P(AAm-*co*-AN) and P(AAm-*co*-AN)-Pd aqueous solutions were estimated by measuring the transmittance at 670 nm wavelength using the Shimadzu UV-1800 UV–Vis recording spectrometer and before each measurement the tested solution was equilibrated for 5 min at the corresponding temperature. The temperature corresponding to a decreasing compared with the initial transmittance is defined as UCST. Transmission electron microscopy (TEM) was performed using FEI Tecnai G2 high resolution transmission electron microscopy operated at 200 kV to characterize the morphology and size of Pd nanoparticles.

2.4. Catalytic reaction

The hydrogenation of allyl alcohol was selected as the model reaction to evaluate the catalytic performance of the catalysts. In a typical experiment, 42 mL mixtures of Pd-contained catalyst and DI water were added into a three necked round flask and stirred with 1000 rpm to avoid external diffusion using a heterogeneous catalyst. Before hydrogenation, catalysts in water were treated by H$_2$ flow (20 mL min^{-1}) for 0.5 h, and then 2.5 mL allyl alcohol aqueous solution (1 mol L^{-1}) was added for hydrogenation.

To confirm the proper catalyst amount, we chose a molar ratio of the substrate (allyl alcohol) to total Pd metal in each catalyst (substrate/Pd) between 500 and 1500 to do the experiments. The time-dependent conversion of allyl alcohol over homogeneous Pd clearly illustrates the conversion of ally alcohol increased at all reaction time. When substrate/Pd molar ratio was 1000, the hydrogenation reaction finished in 1 h, and such a molar ratio of 1000 is selected in the following reactions.

The hydrogenation products were analyzed by gas chromatography equipped with a flame ionization detector using capillary column with a stationary phase of polyethylene glycol.

2.5. Catalyst stability

After hydrogenation, the resulted mixture was cooled in an ice bath and the P(AAm-*co*-AN)-Pd catalyst precipitated from the aqueous phase. The liquid phase was removed with a syringe. Then a fresh batch of reactant was added in to start a new hydrogenation to study the recyclability of the catalyst under the same conditions.

3. Results and discussion

3.1. Catalyst characterization

GPC analysis of linear P(AAm-*co*-AN) in DMSO solvent showed the coefficient viscosity of 0.94 L/g and the viscosity average molecular weight of 44,668. A FT-IR spectrum of P(AAm-*co*-AN) was recorded to confirm the copolymerization between monomers. In Fig. 1, characteristic peaks of amide groups, carbonyl groups and nitrile groups were observed at 3100–3500 cm^{-1}, 1671 cm^{-1} and 2245 cm^{-1}, respectively. The highest absorbance peak at 2932 cm^{-1} in 2800–3000 cm^{-1} was assigned to the C—H stretching. Multiple small peaks in 1300–1460 cm^{-1} corresponded to the bending vibrations of C—H. All these characteristic peaks confirmed the formation of the P(AAm-*co*-AN) copolymer. Proton NMR spectrum of P(AAm-*co*-AN) was shown in Fig. 2. The peaks at 2.50 ppm and 3.30 ppm were attributed to solvent peaks. The chemical shifts of 1.2–2.0 ppm, 2.0–2.3 ppm, 2.7–3.0 ppm and 7.0 ppm were attributed to the proton in the groups of —CH$_2$—, —CH—CO—, —CH—CN, —NH$_2$, respectively.

To elucidate the UCST behavior, transmittance values of the polymer or catalyst solutions were measured at 670 nm using UV–Vis spectroscopy. As shown in Fig. 3, the initial transmittance values of P(AAm-*co*-AN) and P(AAM-*co*-AN)-Pd aqueous solution differ from 100% to ~94% because the loaded Pd nanoparticles block the transmission of partly visible light. Transmittance values of both solutions keep constant at a