Preparation of a novel homogeneous bimetallic Rhodium/Palladium ionic catalyst and its application for the catalytic hydrogenation of nitrile butadiene rubber

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ABSTRACT

A new hybrid second-generation poly (propylene imine) dendrimer terminated by nitrogen-containing triolefinic macrocycle on the periphery (G2-M) was synthesized. The bimetallic Rhodium (III)/Palladium (II) (Rh^{3+}/Pd^{2+}) dendrimer-stabilized catalysts ($G2\text{-}M(Rh^{3+}_xPd^{2+}_{10\text{-}x})$) were prepared by a co-complexation route within G2-M and analyzed by ^1H NMR, XRD and XPS. The catalytic activity, selectivity and separation capability for the hydrogenation of nitrile-butadiene rubber (NBR) catalyzed by the $G2\text{-}M(Rh^{3+}_xPd^{2+}_{10-x})$ have been researched. As a novel catalyst system, the bimetallic ions of Rh^{3+} and Pd^{2+} have influenced on the catalytic activity for the hydrogenation of NBR, which can be related to electron-deficiency effect of Rh^{3+} resulting from the interaction of Rh^{3+} and Pd^{2+} within G2-M.

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1. Introduction

The copolymer of nitrile-butadiene rubber (NBR) has been widely applied in various fields. However, the residual unsaturated carbon-carbon bonds make NBR susceptible to degradation when exposed to oxygen, ozone, ultraviolet light, high temperature and some other extreme conditions [1,2]. Normally, this deficiency can be alleviated by selectively hydrogenating NBR to yield hydrogenated nitrile-butadiene rubber (HNBR) [3,4].

At present, the solution hydrogenation of NBR has been the main approach of preparing HNBR by using a homogeneous or heterogeneous catalyst. To contrast the difference between using the two catalysts, the former displays higher catalytic activity. Generally, the Rhodium (Rh) and Palladium (Pd) catalysts are the frequently adopted ones for the homogeneous catalytic hydrogenation of NBR [5–10]. Particularly, the Rh catalysts are the most popular homogeneous catalysts because they can provide excellent hydrogenation degree without reduction of nitrile group [11]. However, the high cost results from the high-price of Rh compared with other metals for hydrogenation, such as Pd, and the poor separation of the catalysts from substrates have been the major obstacles. The levels of the metal residues reported are about 160–800 ppm for HNBR before post treatment, which will result in high producing cost of HNBR. Moreover, the large amount of Rh residue can result in crosslinking after hydrogenation [12]. Although the ion extraction, organic extraction and chemical precipitation methods have been applied to reduce the Rh residue, the removal of Rh residue is very time-consuming and costly. Therefore, the preparation of an active bimetallic catalyst, which is consisted of Rh and Pd and can be facilely separated, will be very promising.

Dendritic polymer has a stereoregular, highly branched and well-defined structure. Therefore, the dendrimer-stabilized metallic particles can be obtained by transferring the catalytic active centers to the periphery of the functional dendrimer [13,14]. The peripherally modified dendrimer can stabilize the metallic particles, enhance the catalytic activity, and be easy to remove or recycle. The double bonds in the nitrogen-containing 15-membered triolefinic macrocyclic ligands are excellent electron donors for the transition metallic atoms, and the macrocyclic ligands have high antioxide stabilization and tend to coordinate with metallic atoms to form complexes, which are beneficial to stabilize and recover metals [15,16]. One can see that it might be applicable for the catalytic reaction of polymer substrate. However, few reports have been made on the macrocyclic complexes in a process for the catalytic hydrogenation of NBR.

In this paper, the hybrid poly (propylene imine) dendrimer (G2-M) has been obtained by modifying the surface of the second-generation PPI dendrimer with 15-membered triolefinic macrocycles. Pd^{2+} was employed to partly replace Rh^{3+} in the preparation of the novel Rh^{3+}/Pd^{2+} catalysts ($G2\text{-}M(Rh^{3+}_x Pd^{2+}_{10-x})$). Furthermore, the structure and catalytic activity of the bimetallic Rh^{3+}/Pd^{2+} catalysts were also investigated.

2. Experimental

2.1. Materials

The second-generation poly (propylene imine) dendrimer (G2-PPI) with a diaminobutane core were purchased from SyMO-Chem B. V. in Netherland. The nitrogen-containing triolefinic macrocycle (MAC) poly (propylene imine) and the dendrimer modified by MAC (G2-M) were synthesized by the pathway shown in Scheme 1 and Scheme 2, respectively. $RhCl_3.3H_2O$ (99%) and $Pd(OAc)_2$ (99%) and triphenyl phosphate (TPP, 99%) were purchased from Macklin company (China). NBR (N31, ACN: 33.5 wt%) was obtained from Shanghai Nessen International Trading Company.

The triolefinic 15-membered macrocycle **6** (MAC) has been obtained in excellent yields. For the preparation of **5** the NH_2 groups must be protected in **1** and **2** to avoid N-dialkylation in step III, and to obtain a successful reaction between **2** and the arenesulfonamide **2** (step IV).

Scheme 1. Conditions: I. (1) HSO_3Cl, 0 °C (2) $NH_3 \cdot H_2O$, 13 °C; Yield: 33.4%; II. (tert-BuOCO)$_2$O, Et$_3$N, dimethylaminopyridine (DMAP, 0.1 equiv), CH_2Cl_2; Yield: 92%; III. K_2CO_3, CH_3CN, trans-1,4-dibromo-2-butene (4 equiv), reflux; Yield: 82.1%; IV. K_2CO_3, CH_3CN, arenesulfonamide (0.5 equiv), reflux; Yield: 67.5%; V.

Trifluoroacetic anhydride (TFAA), CH_2Cl_2, room temperature; Yield: 89.3%; VI. K_2CO_3, refluxing CH_3CN, trans-1, 4-dibromo-2-butene (1 equiv); Yield: 76.5%.

Characterization data of the arenesulfonamide 3: m. p.: 102 °C; elemental analyses: found C, 39.02; H, 4.27; N, 4.96; S, 11.76. Calc. for $C_9H_{12}BrNSO_2$: C, 38.85; H, 4.32; N, 5.04; S, 11.51. MALDI-TOF MS (matrix alpha-Cyano-4-hydroxycinnamic acid): m/z Calc. for $C_9H_{12}BrNSO_2$, 278 $[M^+]$; found, 302.4 $[M^+ Na^+]$. IR (KBr) 3358, 3273, 2930, 2851, 1595, 1550, 1329, 1168, 902 cm^{-1}.^{1}H NMR (D-DMSO, 600 MHz, ppm): $\delta = 1.28$ (m, 2H), $\delta = 1.95$ (t, 2H), $\delta = 2.68$ (m, 2H), $\delta = 6.48$ (s, 2H), $\delta = 6.59$ (d, $J = 8.8$ Hz, 2H), $\delta = 6.92$ (d, $J = 8.8$ Hz, 2H).

Characterization data of the azamacrocycle 6: m. p.: 139 °C; elemental analyses: found C, 61.13; H, 7.38; N, 4.17; S, 9.27. Calc. for $C_{51}H_{74}BrN_3S_3O_6$: C, 61.20; H, 7.40; N, 4.20; S, 9.60. MALDI-TOF MS (matrix alpha-Cyano-4-hydroxycinnamic acid): m/z Calc. for $C_{51}H_{74}BrN_3S_3O_6$, 1000 $[M^+]$; found, 1024.4 $[M^+ Na^+]$. IR (KBr) 2955, 2858, 1595, 1313, 1155, 972 cm^{-1}. ^{1}HNMR (CDCl$_3$, 600 MHz, ppm): $\delta = 1.24$ (m, 36H), $\delta = 2.18$ (t, 2H), $\delta = 2.87$ (m, 4H), $\delta = 3.39$ (t, 2H), $\delta = 3.78$ (m, 12H), $\delta = 4.08$ (m, 4H), $\delta = 5.77$ (m, 6H), $\delta = 7.15$ (d, 4H), $\delta = 7.36$ (d, $J = 8.8$ Hz, 2H), $\delta = 7.74$ (d, $J = 8.8$ Hz, 2H).

2.2. Preparation of G2-M

MAC (0.48 g, 4.8×10^{-1} mmol) was reacted with G2-PPI (0.052 g, 6.7×10^{-2} mmol) using K_2CO_3 (0.33 g) as an acid-trap in CH_3CN (30 ml) at 82 °C for 24 h under N_2. The crude product was obtained by filtration and rotary evaporation. Finally, the product was washed with ethyl acetate-pentane (1:6) twice to remove the unreacted MAC and dried to obtain pure G2-M as light yellow powdery solid. The preparation route of G2-M is shown in Scheme 2.
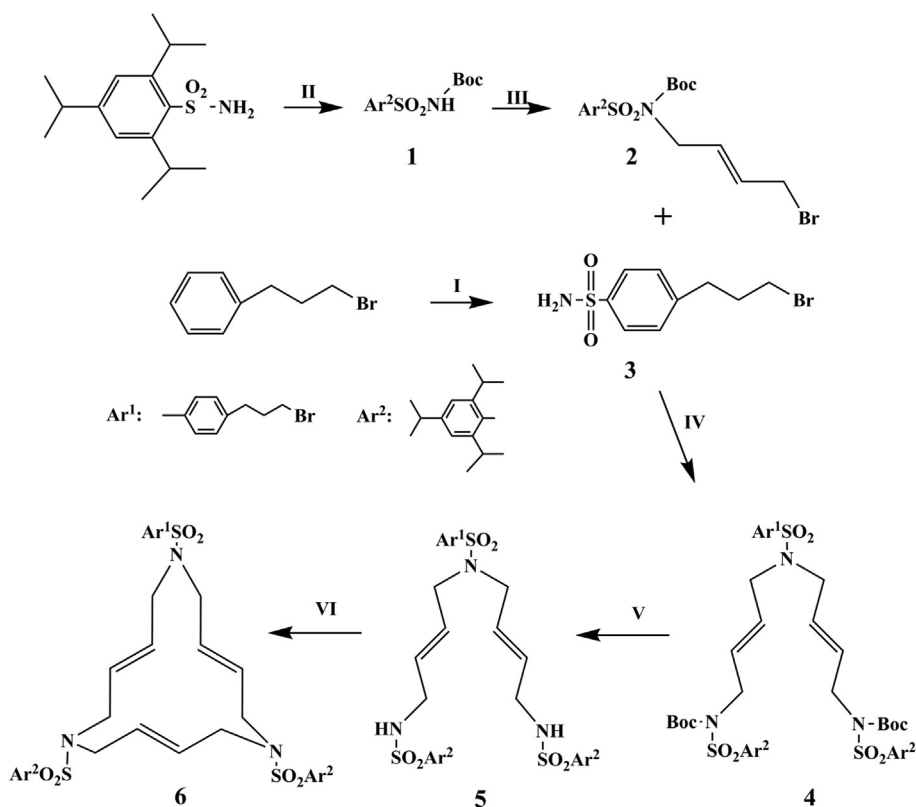
Scheme 1. The synthetic route of MAC.