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ARTICLE TYPE

A Ternary Rh Complex Catalyst Highly Active and Stable in Hydrogenation of Acrylonitrile-Butadiene Rubber

Peng Cao[a], Meng Wu[a], Rui Zou[a], Liqun Zhang[a,b], Dongmei Yue[a,b]*

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An Rh-based complex, T-Rh-PPh$_3$, was developed through a facile one-step process. The T-Rh-PPh$_3$ exhibited high activity and air stability in hydrogenation of acrylonitrile-butadiene rubber. The enhanced air stability can be ascribed to the phenolic hydroxyl structures in tannin.

The hydrogenation of acrylonitrile-butadiene rubber (NBR) is a significant process to improve and optimize the physical and chemical properties of the parent polymer[1]. The hydrogenated acrylonitrile-butadiene rubber (HNBR) not only retains the original excellent chemical, physical, and mechanical properties, but also has outstanding resistance to ozonolytic aging and oxidation, even at high temperatures[2, 3]. The homogeneous rhodium catalyst RhCl (PPh$_3$)$_3$, developed by Lanxess GmbH, Germany, exhibits remarkable activity and selectivity in NBR hydrogenation[4, 5]. However, the drawback of RhCl (PPh$_3$)$_3$ is that it is quite expensive and unstable owing to oxidation[6]. The as-prepared RhCl (PPh$_3$)$_3$ should be stored in inert-gas atmosphere, which is not convenient to its use and transportation. Therefore, in addition to the studies focusing on the recovery of Rh catalyst or preparation of novel homogeneous catalysts based on the less expensive metals[7, 8], significant efforts have been encouraged to design and develop a catalyst system that is inexpensive and has high activity and stability to reduce the cost and facilitate the process of HNBR preparation.

Tannin, one of the most abundant biomass resources, can be easily obtained from the extraction of plants[9, 10]. According to the chemical structures, tannin can chelate with many kinds of metal ions through its dense ortho-phenolic hydroxyls and scavenge free radicals so as to prevent metal species from oxidation. These properties imply that tannin could be used as an ideal stabilizer for metal species. Meanwhile, two adjacent phenol hydroxyls can be used as a bidentate ligand to bond with metal ions, obtaining a stable five-membered ring chelate and the third phenol hydroxyl of pyrogallol can promote this chelation process, so as to enhance the formation and stability of the complex[11-13]. Bi Shi group synthesized a serious of AuNP, Pt-based, and Pd-based catalysts using tannin as reductant, stabilizer or ligand[14-16]. Beside, seldom efforts have been made to improve the stability of catalysts, such as RhCl (PPh$_3$)$_3$, for the hydrogenation of NBR. Thus, to expand the applications of the tannin for stabilization of catalysts, a new stable Rh-based complex, T-Rh-PPh$_3$, is designed for the hydrogenation of NBR in this paper.

In the study, we first synthesized a novel Rh-based complex (T-Rh-PPh$_3$) by a facile and efficient one-step process. In this method, tannin acts as a stabilizer and ligand, and RhCl$_3$· 3H$_2$O is used as a precursor. The structure of the as-prepared catalyst was fully characterized by FTIR and ^{1}HNMR. The catalytic activity and stability of the obtained catalyst toward NBR hydrogenation were investigated.

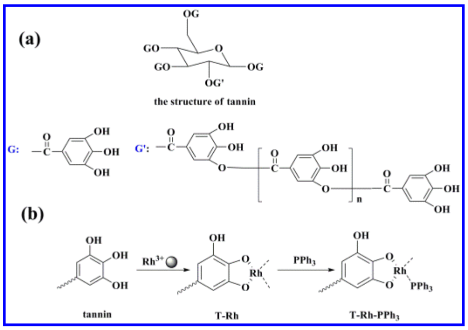


Fig. 1. (a) Molecular structure of tannin and (b) proposed route for preparation of T-Rh-PPh$_3$.

There are a large number of adjacent phenol hydroxyls at the B-rings of tannin (Fig. 1(a)) and the phenol hydroxyls can form chelate rings with many kinds of metal ions. The partly attached galloyl groups at the A-rings of tannin can enhance this chelating ability. Bi Shi demonstrated that tannin has high affinity towards many transition-metal ions including Pd (II), Pt (IV) and Au (III)[13, 17, 18]. A schematic flow diagram for the preparation of T-Rh-PPh$_3$ is shown in Fig. 1(b)[10].

Fig. 2(a) shows the FTIR spectra of T-Rh-PPh$_3$ and RhCl (PPh$_3$)$_3$. The peak at 3400 cm^{-1} can be attributed to the stretching vibration of the O–H bond from phenol hydroxyls (C–OH) or the vibration of the C–H bond in the benzene ring[10]. As shown in Fig. 2(a1), the peak for the stretching vibration of O–H is broader in the spectrum for T-Rh-PPh$_3$ than in the spectrum for RhCl (PPh$_3$)$_3$, an indication of the successfully chelating with Rh ion. The peaks in the wave number range of 1627-1454 cm^{-1} suggest the presence of aromatic rings, and the peak at 1454 cm^{-1} belongs to the special skeletal stretching vibration of the aromatic ring of tannin. Particularly, the strong peak at 1020 cm^{-1} is attributed to the stretching vibration of C-O single bond from tannin[19]. All these results demonstrate that tannin and Rh ion form a new complex through covalent bond.

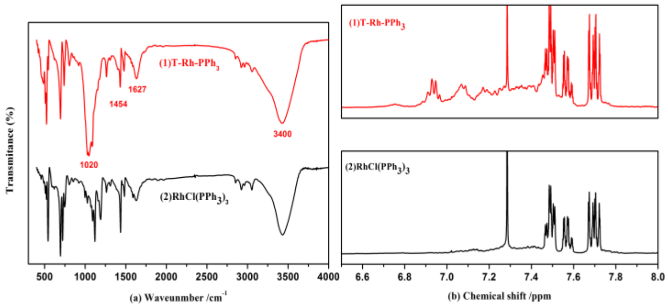


Fig. 2. (a) FTIR spectra of T-Rh-PPh$_3$ and RhCl (PPh$_3$)$_3$ and (b) ^{1}HNMR spectra of T-Rh-PPh$_3$ and RhCl (PPh$_3$)$_3$.

^{1}HNMR was used to further confirm the chemical chelation between Rh^{3+} and tannin, and the spectra are shown in Figure 2(b). The three peaks between 6.8 and 7.25 ppm are the characteristic peaks of the phenol hydroxyl group on the benzene ring, indicating that tannin is connected to the Rh ion by a chemical bond. The three peaks in the range 7.5 to 7.75 ppm are the PPh$_3$ proton characteristic peaks on the benzene ring.

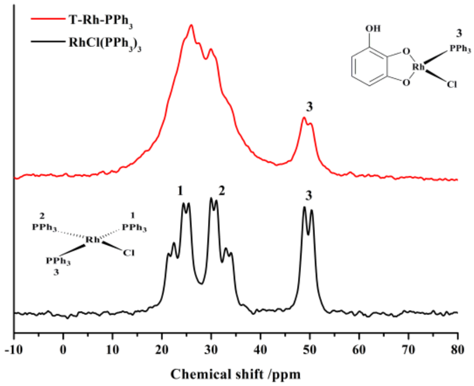


Fig. 3. Solid-state ^{31}P-NMR spectra of T-Rh-PPh$_3$ and RhCl(PPh$_3$)$_3$ catalysts (1D, pulse interval 5 s, spinning rate 11 kHz).

The solid-state ^{31}P-NMR spectrum of RhCl(PPh$_3$)$_3$ (Fig. 3) shows the center bands and can be divided into three parts, with chemical shifts of 49.7, 32.3, and 23.1 ppm. These peaks are attributed to three nonequivalent phosphorus atoms in the catalyst molecule (P1, P2, and P3)[20, 21]. However, the ^{31}P-NMR spectrum of T-Rh-PPh$_3$ differs significantly from that of RhCl(PPh$_3$)$_3$. In addition there is a signal at 49.7 ppm, which corresponds to the signal of the phosphorus atom P3. The main intensity is concentrated in a single broad peak at 26.0 ppm, which in comparison with the spectrum of the RhCl(PPh$_3$)$_3$ can be related to the phosphorus atom labeled as P1 and P2. Therefore, the results of ^{31}P-NMR suggest that two phosphine ligands P1 and P2 are substituted by ortho-phenolic hydroxyls of tannin and form the ternary catalyst of T-Rh-PPh$_3$ (see Fig. 3). Further, X-ray photoelectron spectra of Rh 3d peak were employed to analyze the change of Rh element for the both catalyst (Fig. S1)

T-Rh-PPh$_3$ was also tested by the FeCl$_3$ solution method to determine if there was any free tannin in the complex[22]. Low levels of tannin can react with FeCl$_3$ solution to form a black precipitate. First, the T-Rh-PPh$_3$ complex was dissolved in acetone, and then freshly prepared FeCl$_3$ reagent was added dropwise to the acetone solution. No black precipitate was observed; indicating that there was no free tannin in the T-Rh-PPh$_3$ complex. The results showed that tannin, PPh$_3$, and Rh ion form a ternary complex rather than a simple physical mixture.

It is well known that RhCl (PPh$_3$)$_3$ is unstable when it exposes to air environment for a long time. The catalytic activity of RhCl (PPh$_3$)$_3$ is gradually reduced by oxidative deterioration. In our experiments, both T-Rh-PPh$_3$ and RhCl (PPh$_3$)$_3$ were exposed to air for 2, 4, 8, and 20 days. Then they were used as catalysts for the hydrogenation of NBR under similar condition. The degree of hydrogenation results are shown in Fig. 3.

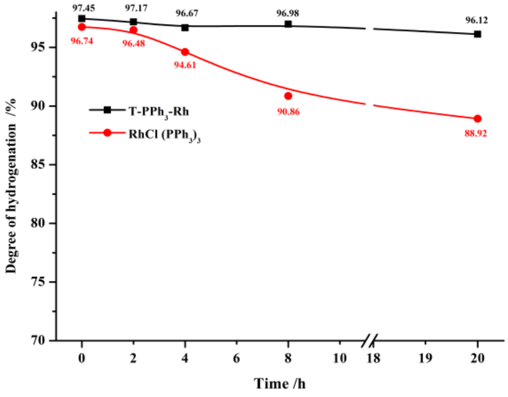
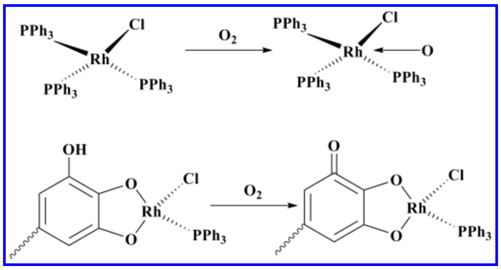


Fig. 4. Effect of time of exposure to air on degree of hydrogenation for T-Rh-PPh$_3$ and RhCl (PPh$_3$)$_3$. Reaction conditions: 120 mL of NBR glue solution (6 wt%), content of catalyst (0.2 wt%), H$_2$ pressure of 2.5 MPa, temperature of 120 ℃, and reaction time of 6.0 h.

Fig. 4 shows that the catalytic activity of T-Rh-PPh$_3$ remains at above 96% after laying aside for 20 days in air. However, the catalytic activity of RhCl (PPh$_3$)$_3$ drops to 88% after laying aside for 20 days. These results show that as-prepared T-Rh-PPh$_3$ is more stable in air than RhCl (PPh$_3$)$_3$, which is greatly convenient to its store and application.

The difference in resistance to oxidation between the two catalysts is attributed to their different chemical structures. The active state of RhCl (PPh$_3$)$_3$ is Rh$^+$, which can react with oxygen molecules to become the inactive species Rh^{3+}, with lower catalytic activity. However, the rhodium in T-Rh-PPh$_3$ combines with ortho phenolic hydroxyl and triphenylphosphine, and the partly uncoordinated phenolic hydroxyls can be oxidized into a quinone by oxygen molecules. Phenolic hydroxyl is a hydrogen donor and can inhibit the production of oxygen anions or hydroxyl radicals. It plays a significant role in protecting the active center Rh$^+$ from oxidation or delaying the oxidation by oxygen anions. Therefore, T-Rh-PPh$_3$ shows better resistance to oxidation than RhCl (PPh$_3$)$_3$ under the same conditions. We suppose the possible mechanism of the two catalysts oxidation in the air atmosphere is shown in Scheme 1.



Scheme 1. Supposed mechamism of the catalysts of RhCl $(PPh_3)_3$ and T-Rh-PPh_3 oxidation by O_2.

To evaluate the catalytic activity of as-prepared T-Rh-PPh_3 catalyst, the hydrogenation of NBR to produce HNBR was carried out. Fig. 5 illustrates the degree of hydrogenation for different loadings of the T-Rh-PPh_3 catalyst.

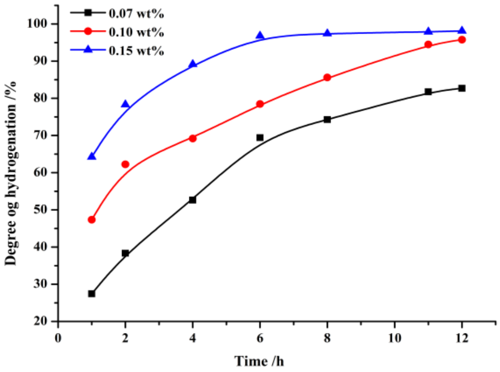


Fig. 5. Effect of catalyst concentrations for the T-Rh-PPh_3 on the degree of hydrogenation of NBR hydrogenation reaction. Reaction conditions: 120 mL of NBR glue solution (6 wt%), H_2 pressure of 2.5 MPa and temperature of 120 ℃.

It can be seen that the catalyst T-Rh-PPh_3 demonstrates high activity toward hydrogenation of NBR. With 0.15 wt% loading, T-Rh-PPh_3 shows a high degree of hydrogenation of 96.78% with 6 h, at temperature of 120 ℃. With the lowest loading of 0.07 wt%, a hydrogenation of 82.68% is obtained after 11 h at 120 ℃. These results show the T-Rh-PPh_3 has remarkable catalytic activity for the NBR hydrogenation.

For analyze the structure of hydrogenated NBR, FTIR and ^{1}HNMR spectra of HNBR and NBR were employed (Fig. S2). From the spectra, it can be seen that an enhanced intensity of the aliphatic protons is observed and the characteristic peaks (-CH-CN, acrylonitrile structural unit) remains unchanged. These results indicate that only the C=C takes place without reduction of the -CN by using the new catalyst T-Rh-PPh_3, a selective hydrogenation of NBR.

The effects of different reaction conditions on the degree of hydrogenation are summarized in Fig. S3. The results show that under the optimized conditions, the degree of hydrogenation can reach 97%.

In conclusion, the preparation and characterization of T-Rh-PPh_3 were studied. FTIR, ^{1}HNMR and ^{31}P-NMR showed that the tannin and triphenylphosphine were successfully incorporated into the framework of the T-Rh-PPh_3.The T-Rh-PPh_3 was used for the hydrogenation of NBR, exhibiting satisfactory catalytic activity, excellent selectivity, and good air stability. The hydrogenation results showed that under optimum conditions, a degree of hydrogenation of 97% was achieved. The enhanced air stability is the phenolic hydroxyls in tannin protect the active species Rh^+ from oxidation. This method can be expected to apply to other catalytic systems to improve their stability.

Experimental section

Synthesis of T-Rh-PPh_3

The used tannin is bayberry tannin, a kind of typical condensed tannin. The bayberry tannin was obtained from the barks of myrica by extraction with an acetone-water solution (1:1, v/v) and then spray dried[10].

First, 1 g of $RhCl_3{\cdot}3H_2O$, 3 g of tannin, and 200 mL of deionized water were added to a flask under vigorous stirring for 20 min to obtain a homogenous solution. Then, the pH value of the solution was adjusted by 2 mol/L HCl solution to 2-3 and the solution was stirred vigorously at 313 K for 6-10 h. Afterwards, 50 mL of triphenylphosphine ethanol solution was added, and the mixture was followed by stirring at 373 K for another 2-3 h. The product, T-Rh-PPh_3, was collected by filtration, washed, and dried in a vacuum oven.

For the purpose of comparison, the RhCl $(PPh_3)_3$ catalyst was prepared without the addition of tannin according to the procedure mentioned above. The Rh content in catalysts of $RhCl(PPh_3)_3$ and T-Rh-PPh_3 was determined by ICP-MS and amounted to be 10.49 wt % and 6.27 wt%, respectively.

Evaluation of activity of catalyst on NBR hydrogenation

A certain amount of NBR was dissolved in chlorobenzene to obtain an NBR solution. The NBR solution and catalyst were added to a 100-mL high-pressure stainless steel autoclave. Then the system was sealed and degassed with N_2 and H_2. Afterwards, the system was charged with H_2 to the desired pressure and then gradually heated to the desired reaction temperature. After the reaction, the autoclave was cooled down to room temperature. The product was precipitated with alcohol, washed with alcohol, and dried in a vacuum oven. The conversion of the double bonds, also called the degree of hydrogenation (HD), was calculated as

$$HD = (1 - [C{=}C]_t / [C{=}C]_0) \times 100\% \qquad (1)$$

where $[C{=}C]_t$ is the concentration of C=C bonds at reaction time t and $[C{=}C]_0$ is the initial double bond concentration. The hydrogenated NBR sample was analyzed by ^{1}HNMR[23].

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Notes and references

[a]*State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China. Fax: +86-010-64436201; Tel: +86-010-64436201; E-mail: caopbuct2010@.163.com*

[b]Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing 100029, China. *Fax: +86-010-64436201; Tel: +86-010-64436201; E-mail: yuedm@nail.buct.edu.cn.*

† Electronic Supplementary Information (ESI) available: X-ray photoelectron spectra of the Rh 3d region for various Rh catalysts. Effect of different control reation condition on degree of hydrogenation and FTIR and ^{1}HNMR spectra of NBR and HNBR. See DOI: 10.1039/b000000x/

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