NANO-MICRO LETTERS ARTICLE
www.nmletters.org

RuRh Bimetallic Nanoparticles Stabilized by 15-membered Macrocycles-terminated Poly(propylene imine) Dendrimer: Preparation and Catalytic Hydrogenation of Nitrile–Butadiene Rubber

Yang Wang, Xiaohong Peng*

(Received 16 October 2013; accepted 16 December 2013; published online 06 January 2014)

Abstract: A new fourth-generation poly(propylene imine) dendrimer (G4-M) containing 32 triolefinic 15-membered macrocycles on the surfaces has been synthesized. The bimetallic RuRh dendrimer-stabilized nanoparticles (DSNs) were first prepared within G4-M by a co-complexation route. The new G4-M dendrimer has been characterized by 1H nuclear magnetic resonance, infrared radiation, and elemental analysis. The dendrimer-stabilized bimetallic ions and reduction courses were analyzed by UV-vis spectroscopy. High-resolution transmission electron microscopy and energy dispersive spectrometer were used to characterize the bimetallic nanoparticle size, size distribution, and particle morphology. The RuRh bimetallic DSNs showed high catalytic activity for the hydrogenation of nitrile-butadiene rubber.

Keywords: G4-M dendrimer; RuRh bimetallic nanoparticles; Catalytic hydrogenation; Nitrile-butadiene rubber

Citation: Yang Wang and Xiaohong Peng, “RuRh Bimetallic Nanoparticles Stabilized by 15-membered Macrocycles-terminated Poly(propylene imine) Dendrimer: Preparation and Catalytic Hydrogenation of Nitrile–Butadiene Rubber”, Nano-Micro Lett. 6(1), 55-62 (2014). http://dx.doi.org/10.5101/nml.v6i1.p55-62

Introduction

In recent years, bimetallic nanoparticles has attracted a great deal of attention among scientists due to their applications in numerous catalytic reactions, including catalytic reforming reactions, hydrogenation, pollution control, and alcohol oxidation [1-2]. This is because the addition of a second metal is an important approach for tailoring the electronic and geometric structures of nanoparticles that would make it possible not only to obtain catalysts with improved catalytic activity owing to a synergistic effect but also to create new types of catalysts, which may not be achieved by monometallic catalysts [3-5].

Dendrimer has a stereoregular, highly branched and well-defined structure. Therefore, it can act as nanoparticle template to form encapsulated metal nanoparticle catalyst [6]. Moreover, the dendrimer surface stabilized metal nanoparticle catalyst (DSNs) can be obtained when connecting the catalytic active centers to the surface of the end-functional dendrimer [7]. Normally the preparation of nanoparticles within the dendrimers involves two processes. Firstly, the metal ions coordinated with the dendrimer template, and then the metal nanoparticles were synthesized by the reduction of metal ions into the neutral atoms [8]. The 6-nm Au/Pt bimetallic nanoparticles, which were stabilized by polyaryl ether trisacetic acid ammonium chloride dendrimer (G3NACl) and used as catalysts for the hydrogenation of 3-phenoxybenzaldehyde and nitrobenzenes, were synthesized by Yang *et al.* [9]. The catalytic capability of bimetallic nanoparticles is higher

---

Department of Polymer Science and Engineering, South China University of Technology, Guangzhou 510640, P.R. China
*Corresponding author. E-mail: pxhpf@scut.edu.cn

than that of physical mixtures of monometallic Pt and Au nanoparticles. The double bonds in the nitrogen containing triolefinic 15-membered macrocyclic ligand are excellent ligands for transition metal atoms. In addition, the macrocyclic ligands possess excellent anti-oxide property and tend to coordinate with metal atoms to form complexes, which is beneficial to stabilize and recover the metal nanoparticles [10]. Using new dendrimers with triolefinic 15-membered macrocycles at the end of the dendron as stabilizers for preparing metallic nanoparticles provides the advantage of minimal surface deactivation for catalytic applications. The phosphorus dendrimers containing 15-membered azamacrocycles on the surfaces were utilized as stabilizers to prepare 2.5-7.9 nm Pd catalysts by Sebastian *et al.* [11]. The Pd catalysts were efficient, could be recovered and reused in Mizoroki-Heck reaction in homogeneous and heterogeneous manner.

In this paper, RuRh bimetallic DSNs were first prepared by a co-complexation route with fourth-generation 15-membered azamacrocycles-terminated poly(propylene imine) (PPI) dendrimer as stabilizer. The end-functional dendrimer was used to control the particles size, to enhance dispersity and to prevent agglomeration. The hydrogenation of nitrile-butadiene rubber (NBR) was carried out to investigate the catalytic activity of bimetallic DSNs catalysts. The results showed that the RuRh bimetallic DSNs exhibited enhanced catalytic activities compared with the physical mixtures of corresponding monometallic DSNs.

Experimental sections

Materials

$RuCl_3$(99 wt%),$RhCl_3$(99 wt%), $NaBH_4$(99 wt%), $RhCl(PPh_3)_3$(99 wt%), TPP(99 wt%)were obtained from the Shanghai Chemical Reagents Company. The NBR(N31, ACN: 33.5 wt%) was obtained from the Shanghai Nessen international Trading Co., Ltd. The G4 poly(propylene imine) dendrimers with a diaminobutane core were purchased from SyMO-Chem B.V in the Netherlands. The nitrogen-containing triolefinic 15-membered macrocycles was synthesized as described in reference with some changes [12].

Instruments

High-resolution transmission electron microscopy (HRTEM) micrographs having a point-to-point resolution of 0.23 nm were obtained using JEOL JEM-2100UHR transmission electron microscope equipped with an ISIS-300 X-ray energy dispersive spectrometer (EDS). UV-vis was analysed using Beckman UNICAM UV-500 UV–vis spectrophotometer. A Bio-Rad FTS3000 FTIR spectrometer was used to carry out FTIR analysis.

Synthesis of 15-membered azamacrocycles-terminated fourth-generation PPI dendrimers (G4-M)

The 15-membered azamacrocycles (0.84 g, 8.4×10^{-1} mmol) and the fourth-generation PPI (G4-NH_2)(46 mg, 1.31×10^{-2} mmol) were added to K_2CO_3 (0.58 g, 4.2 mmol) in CH_3CN (35 mL). The mixture was stirred for 24 h at 90℃ under argon. The solvent was evaporated, and the residue was digested with dichloromethane. Salts were eliminated by passing through Celite, and the filtered solution was evaporated. The residue was washed with ethyl acetate-pentane (1:6) for three times and dried to afford G4-M as a white solid.

Preparations of RuRh bimetallic DSNs

G4-M(RuRh) DSNs were synthesized by simultaneous co-complexation of two different metal ions, followed by a single reduction step. Firstly, G4-M(0.12 g, 3.65×10^{-3} mmol) was dissolved in 50 mL THF to yield a dendrimeric solution. Secondly, co-complexation of metal ions with dendrimers was carried out by adding a total volume of 1.0 mL of both 0.10 M $RuCl_3$ and 0.10 M $RhCl_3$ solutions to the THF solution of G4-M in a 100 mL shake-flask. After stirring at 200 rpm for 24 h, 5.0 mL of 0.5 M $NaBH_4$ solution was added dropwise under vigorous stirring, and then the mixture was stirred at 200 rpm for 1 h. Finally, the pH value of the solution was adjusted to 7∼8 with 0.1 M HCl aqueous solution.

Hydrogenation reactions

As described in Ref. [13], the hydrogenation of NBR was carried out in a 0.3 L autoclave reactor. A certain amount of NBR (3.6 g) dissolved in the chlorobenzene (150 mL) was first added to the reactor, and the mixture was degassed with N_2 (2.4 L/min) for three times at room temperature with the agitating speed of 400 rpm. A measured volume of bimetallic DSNs solution (DSNs/NBR = 0.35 wt%) was added to the NBR mixture when the temperature was 100℃. The hydrogen gas was introduced to the reactor by a hydrogen adapter and maintained at 5.5 MPa. The hydrogenation temperature (100℃) and the agitating speed (800 rpm) were maintained constant for 9 h. The system was cooled down after a given reaction time. The methanol was added to the system to flocculate the rubber, and the final product was obtained after drying the rubber in vacuum. The organic solutions were evaporated, and the bimetallic DSNs catalysts were recovered and reused in the next run under the same condition. There was no evidence for DSNs aggregation after the hydrogenation reaction, indicating that the catalysts were stable within the reaction periods. The degree of hydrogenation (HD) was calculated by the absorption constant (k) based on the strength of the characteristic peaks from the IR spectrum [14]. (Fig. S1 in supporting information)

Gel fraction measurements

The gel fraction measurements were carried out by use of a solvent extraction technique, the details of which have been described [15]. Briefly, 0.2 g of dried film of hydrogenated NBR was first cast and then mixed with 25 ml chlorobenzene for 24 h. The dissolved portion is determined gravimetrically from the amount of solids remaining in the supernatant after the centrifugation of the mixture system at 10000 rpm for 30 min. The gel fraction is the percentage of the insoluble polymer in the total film sample.

Results and discussion

Figure 1 shows the UV-vis absorption spectra of Ru and Rh metals during the process of co-complexation and the subsequent reduction. The characteristic absorption peak of G4-M was at 293 nm, after the addition of Ru^{3+} and Rh^{3+}, the peak was shifted to 297 and 298 nm, respectively (Fig. 1(a)). The UV-vis data indicated the interaction between the metallic ions (Ru^{3+}, Rh^{3+}) and the tertiary amine groups of G4-M dendrimer [16]. The presence of metallic ions (Ru^{3+}, Rh^{3+}) coordinated to the endocyclic olefins of macrocycle can be deduced from the 1H nuclear magnetic resonance (1HNMR) spectra [17]. The free G4-M presented signals for the endocyclic olefinic protons at δ ~5.70-5.80 (Fig. S2(a)), whereas some strong upfield shifts were observed up to δ ~2.50-3.40 (depending on the proton considered) (Fig. S2(b)) for metallic ions complexes. After reduction of the composite of Ru^{3+} and Rh^{3+}, the absorption peak at 297 nm turned weaker. Figure 1(b) presents a series of UV-vis spectra of the RuRh bimetallic nanoparticles with various Ru/Rh ratios (G4-M(RuxRhy), where x/y = Ru/Rh molar ratio). As the content of Rh in the bimetallic nanoparticles increased, the intensity of the absorption peak at 296 nm increased, but the peak at 362 nm gradually decreased. That the absorption bands are of nearly exponential shape indicates the complete reduction of metal ions [18]. Moreover, it should be noted that the spectra of the resulting nanoparticles are different from those of the monometallic nanoparticles that attributed to the change in dielectric function caused by mixing two different metal atoms [19]. Therefore, it can be suggest that bimetallic nanoparticles are formed with the G4-M dendrimers as stabilizer.

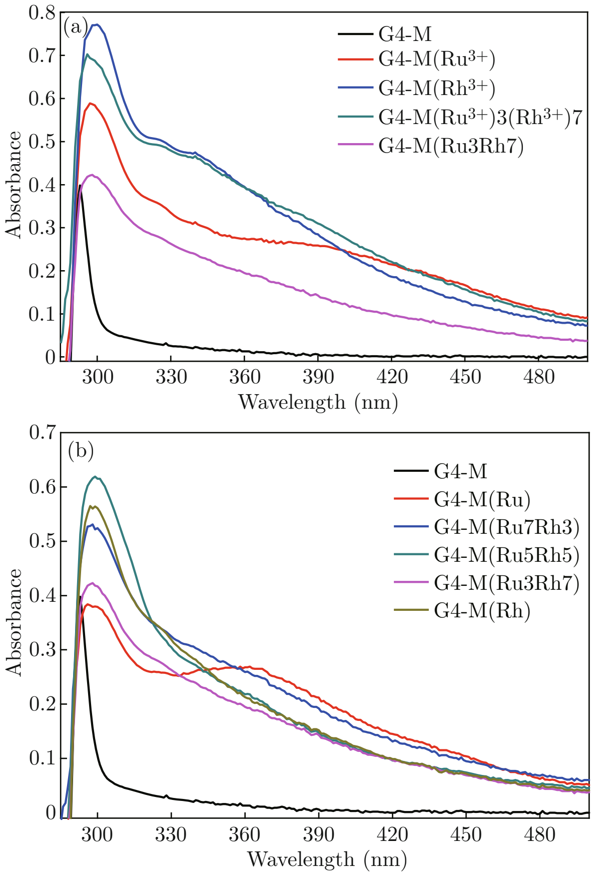

Fig. 1 (a) Variations in the UV–vis spectra of Ru and Rh metals during the course of co-complexation and the subsequent reduction; (b) UV-vis spectra of G4-M(RuxRhy) with various Ru/Rh ratios. In all cases, the final concentrations of total metal and G4-M were 0.07 mM and 1.97 × 10^{-5} M, respectively.

The HRTEM micrographs of G4-M(RuRh) are shown in Fig. 2. The monometallic (Ru, Rh) and RuRh bimetallic nanoparticles prepared by the reduction of co-complexation metal ions demonstrated a Gaussian-like size distribution, and the shape of nanoparticles is nearly uniform and almost spherical. The average diameter of the metallic nanoparticles was 3.3 ± 1.1 nm, 8.5 ± 2.6 nm, 6.1 ± 1.4 nm, 4.5 ± 1.5 nm and 7.7 ± 2.1 nm for G4-M(Rh) (Fig. 2(a)), G4-M(Ru) (Fig. 2(b)), G4-M(Ru7Rh3) (Fig. 2(c)), G4-M(Ru5Rh5) (Fig. 2(d)), and G4-M(Ru3Rh7) (Fig. 2(e)), respectively. The results demonstrated that the average size of metallic nanoparticles does not depend on the Ru/Rh ratio.

HRTEM results of G4-M(Ru5Rh5) further confirmed the bimetallic nature of the obtained RuRh nanoparticles. Due to rapid reduction of precursors, the nanoparticles were not well crystallized; however, some results could be obtained according to XRD (Fig. S3 in Supporting information). The lattice spaces of 0.223 nm and 0.272 nm which correspond to Rh (111) (Fig. 3(c)) and Ru (111) (Fig. 3(b)) respectively, were both found

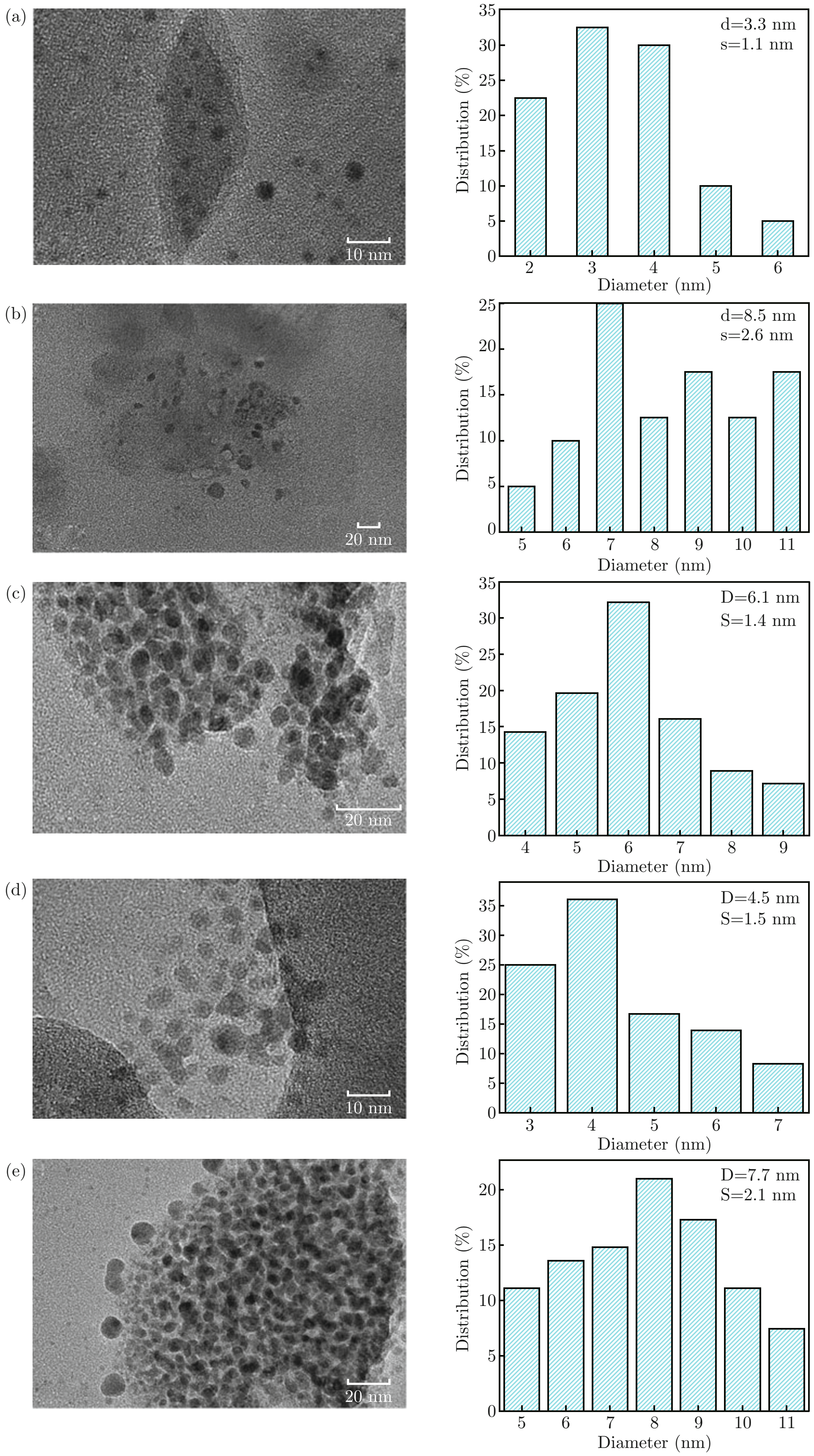

Fig. 2 HRTEM images and the corresponding size distribution histograms of G4-M(Rh) (a); G4-M(Ru) (b); G4-M(Ru7Rh3) (c); G4-M(Ru5Rh5) (d) and G4-M(Ru3Rh7) (e) nanoparticles.

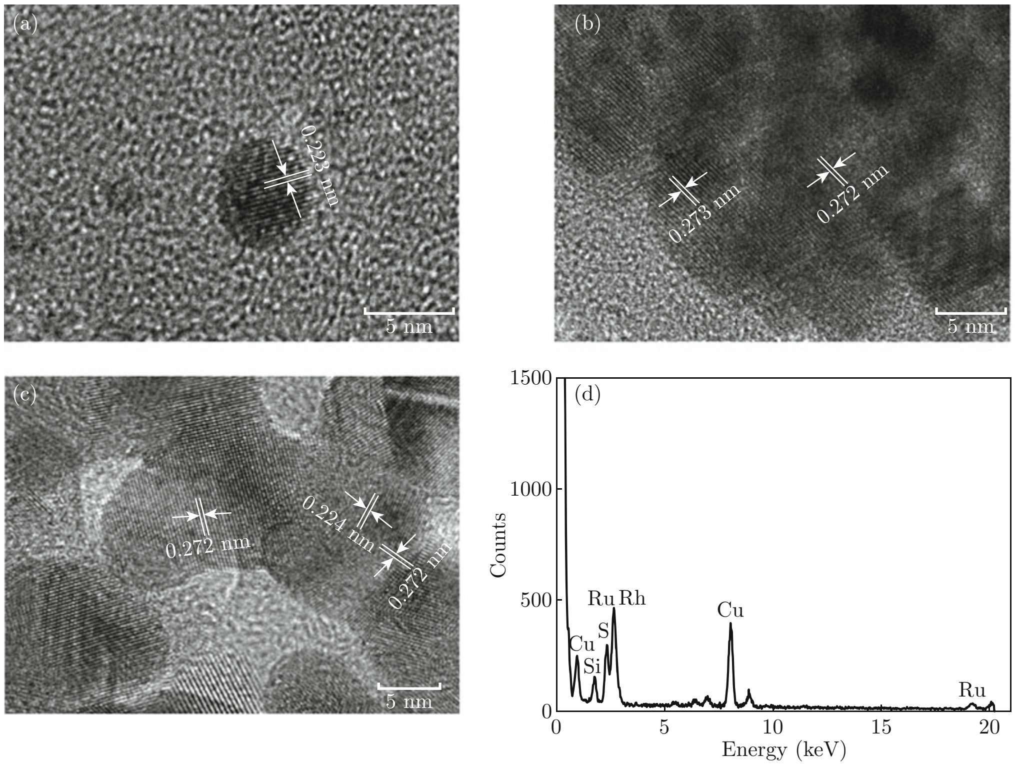

Fig. 3 HRTEM images of G4-M(Rh) (a); G4-M(Ru) (b); G4-M(Ru5Rh5) (c); EDS analysis for the G4-M(Ru5Rh5) bimetallic nanoparticles (d).

by HRTEM as shown in Fig. 3(c), indicating that Rh and Ru components co-exist in sole particle. The EDS was also used to confirm that the nanoparticles were indeed alloy of Ru and Rh in G4-M(Ru_5Rh_5) (Fig. 3(d)). Ru and Rh were detected at 2.56 keV and 2.70 keV respectively in similar studies [20].

The gel fraction measurement of hydrogenated NBR was determined through a solvent extraction technique. It was observed that HNBR sample was completely dissolved into chlorobenzene and no precipitate was found after rigorous centrifugation. In addition, the deviation between the weight of HNBR sample (W_1) and the weight of HNBR in sample-chlorobenzene solution after centrifugation (W_2) did not exceed 1.5%. These results indicated that there was no gel formation in the resultant HNBR product and confirmed the advantage of Wilkinson's catalyst [13], that is, the RuRh bimetallic DSNs can effectively suppress the crosslinking of NBR during the hydrogenation reaction.

In this study, the catalytic capability of the catalyst was represented by HD which was determined via FT-IR spectra. Figure 4 shows a set of representative FT-IR spectra of NBR with different HD. The absorption peaks at 2236 cm^{-1}, 970 cm^{-1} and 917 cm^{-1} corresponds to the cyano group (C≡N), the 1, 4-trans double bond and the 1, 2-vinyl terminal bond. The intensity of the peak attributed to the olefinic double bond at both 970 cm^{-1} and 917 cm^{-1} decreased gradually with an increasing in the degree of hydrogenation. There is a new peak at 723 cm^{-1} assigned to the saturated (-CH2-)n, n>4, while the peak at 2236 cm^{-1} is unchanged [14]. This explains the RuRh bimetallic DSNs catalyst can achieve the target of hydrogenation NBR.

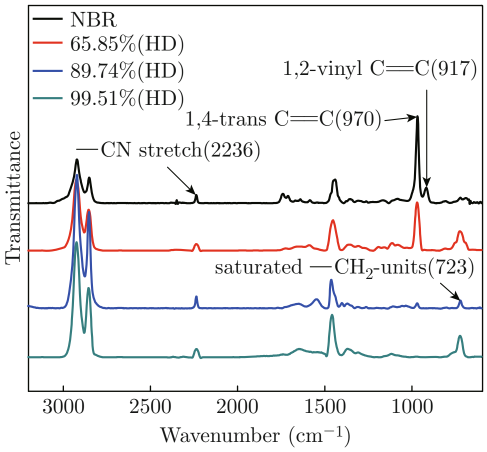

Fig. 4 A set of representative FT-IR spectra of NBR with different extent of hydrogenation. Conditions: NBR = 3.6 g, bimetallic DSNs/NBR = 0.35 wt%, 800 rpm of agitation, 100℃ 5.5 MPa of H_2 (Reaction time: 9 h).

Figure 5 shows the quantitative HD of NBR with the RuRh bimetallic DSNs and the physical mixtures of Ru and Rh monometallic ones as hydrogenation catalyst, respectively. Monometallic Ru DSNs yielded the lowest HD (65.85%). The HD of NBR which was catalytic hydrogenated by the physical mixtures of Ru and Rh monometallic nanoparticles basically linearly increased with the increase in Rh content. Although the diameter of Rh monometallic DSNs was smaller than that of the RuRh bimetallic DSNs (Fig. 2(a) and Fig. 3), the RuRh bimetallic DSNs (Ru/Rh ratios of 7/3, 5/5 and 3/7) gave larger HD than the relative physical mixtures of Ru and Rh monometallic DSNs. The maximum HD (99.51%) was obtained when the Ru/Rh ratio was 3/7. The higher catalytic activity of the bimetallic DSNs may be attributed to synergistic electronic effect [18]. According to Pauling [21], the electronegativity of rhodium (2.28) is larger than that of ruthenium (2.20). The electronic interaction between these two different metals would allow the Rh to attract electrons from Ru, which could make the electron density of Ru become lower. This effect could make the bimetallic cluster more active than monometallic ones because the NBR with double bond favors the electron-deficient surface. The dendrimer branches can be used as selective gates to control the access of small molecules (substrates) to the encapsulated (catalytic) nanoparticles [16]. The NBR could not contact the catalyst due to the high molecular weight, however, the catalytic capability of the bimetallic nanoparticles was very strong, and the maximum HD could be 99.51%. These results suggested that the bimetallic nanoparticles formed on the surface of the G4-M dendrimers.

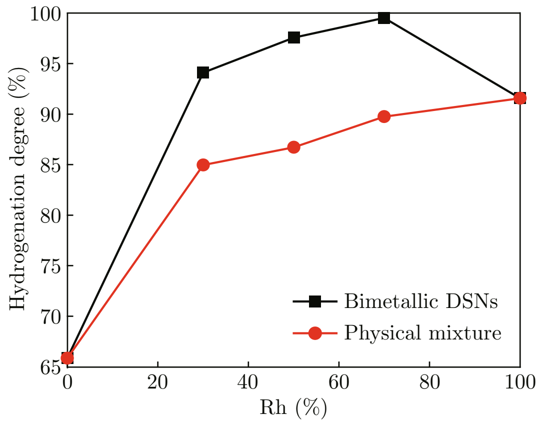

Fig. 5 Hydrogenation degree of NBR as a function of the molar ratio of rhodium in RuRh bimetallic DSNs and the physical mixtures of Ru and Rh monometallic ones. Conditions: NBR=3.6 g, bimetallic DSNs/NBR = 0.35 wt%, 800 rpm of agitation, 100°C, 5.5 MPa of H_2 (Reaction time: 9 h).

The HD of NBR catalyzed by G4-M(Ru3Rh7) bimetallic nanoparticles and Wilkinson's catalyst ($RhCl(PPh_3)_3$) versus reaction time was shown in Fig. 6(a). For each type of catalyst, there was an increase in the HD with the reaction time and the maximum HD (99.59%) can be reached, the rate of hydrogenation reaction was all very large within 2 h and then slowed down. The HD and hydrogenation reaction rate of G4-M(Ru3Rh7) nanoparticles are higher than those of Wilkinson's catalyst ($RhCl(PPh_3)_3$). These results may be due to the synergistic electronic effect [22] and the advantage of the minimal surface deactivation provided by the bimetallic DSN [11]. Figure 6(b) shows the HD of NBR catalyzed by G4-M(Ru3Rh7) bimetallic nanoparticles in the different cycles. Only slight loss of catalytic activity was observed within 3 cycle times. The HD reached the minimum of 49.35% after 5 cycle times, which could be attributed to the loss of the amount of the catalyst. The initial amount of catalyst was 12.6 mg, while 7.1 mg was recovered after the fifth cycle.

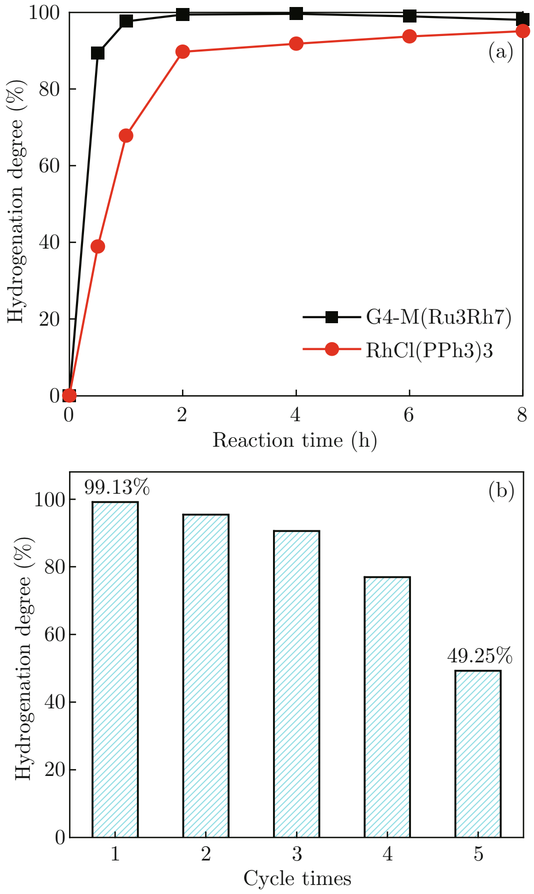

Fig. 6 (a) Hydrogenation degree versus reaction time for G4-M(Ru3Rh7) and $RhCl(PPh_3)_3$ catalyzed hydrogenation of NBR. Conditions: NBR = 3.6 g, catalysis/NBR=0.35 wt %, $RhCl(PPh_3)_3$/TPP is 10 wt%, 800 rpm of agitation, 100°C, 5.5 MPa of H_2; (b) Hydrogenation degree of NBR catalyzed by G4-M(Ru3Rh7) in different cycles.

Conclusions

A new fourth-generation PPI dendrimer containing 32 triolefinic 15-membered macrocycles on the surfaces has been prepared. The monodispersed RuRh bimetallic nanoparticles stabilized by G4-M dendrimer with the size of 4.5 ± 1.5 nm, 6.1 ± 1.4 nm, 7.7 ± 2.1 nm were successfully prepared and used as catalysts for the hydrogenation of NBR. No cross-linking is found in the final hydrogenated product. The UV–vis absorbance spectra and catalytic hydrogenation activities of the RuRh bimetallic nanoparticles are different not only from those of their monometallic nanoparticles but also from those of their physical mixtures. The G4-M(Ru3Rh7) bimetallic nanoparticles exhibited higher catalytic hydrogenation activity than the Wilkinson's catalyst, and can be recycled for three time with slight loss of activity. These results suggest that the end-functional dendrimer can be used as template for the preparation of metal nanoparticle catalysts.

Acknowledgements

This work was supported financially by the National Natural Science Foundation of China (Project No. 51273071).

References

[1] A. K. Singh and Q. Xu, "Synergistic catalysis over bimetallic alloy nanoparticles", Chem. Cat. Chem. 5(3), 652-676 (2013). http://dx.doi.org/10.1002/cctc.201200591

[2] D. F. Yancey, E. V. Carino and R. M. Crooks, "Electrochemical synthesis and electrocatalytic properties of Au@Pt dendrimer-encapsulated nanoparticles", J. Am. Chem. Soc. 132(32), 10988-10989 (2010). http://dx.doi.org/10.1021/ja104677z

[3] J. H. Sinfelt, "Structure of bimetallic clusters", Acc. Chem. Res. 20(4), 134-139 (1987). http://dx.doi.org/10.1021/ar00136a002

[4] D. Mott, J. Luo, P. N. Njoki, Y. Lin, L. Y. Wang and C. J. Zhong, "Synergistic activity of gold-platinum alloy nanoparticle catalysts", Catalysis Today. 122(3-4), 378-385 (2007). http://dx.doi.org/10.1016/j.cattod.2007.01.007

[5] H. L. Jiang and Q. Xu, "Recent progress in synergistic catalysis over heterometallic nanoparticles", J. Mater. Chem. 21, 13705-13725 (2011). http://dx.doi.org/10.1039/C1JM12020D

[6] R. W. J. Scott, O. M. Wilson, S. K. Oh, E. A. Kenik and R. M. Crooks, "Bimetallic palladium-gold dendrimer-encapsulated catalysts", J. Am. Chem. Soc. 126(47), 15583-15591 (2004). http://dx.doi.org/10.1021/ja0475860

[7] D. Astruc, E. Boisselier and C. Ornelas, "Dendrimers designed for functions: from physical, photophysical, and supramolecular properties to applications in sensing, catalysis, molecular electronics, photonics, and nanomedicine", Chem. Rev. 110 (4), 1857-1959 (2010). http://dx.doi.org/10.1021/cr900327d

[8] W. M. Knecht, M. A. Frenkel and R. M. Crooks, "Structural analysis of PdAu dendrimer-encapsulated bimetallic nanoparticles", Langmuir 26(2), 1137-1146 (2010). http://dx.doi.org/10.1021/la902233h

[9] W. Zhang, L. Li, Y. K. Du, X. M. Wang and P. Yang, "Gold/Platinum bimetallic core/shell nanoparticles stabilized by an frchet-type dendrimer: preparation and catalytic hydrogenations of phenylaldehydes and nitrobenzenes", Catal Lett. 127(3-4), 429-436 (2009). http://dx.doi.org/10.1007/s10562-008-9725-9

[10] A. Serra-Muns and R. Pleixats, "Tsuji-trost allylations with palladium recovery by Phosphines/Pd(0)-Triolefinic macrocyclic catalysts", J. Organomet. Chem. 695(8), 1231-1236 (2010). http://dx.doi.org/10.1016/j.jorganchem.2010.01.033

[11] E. Badetti, A. M. Caminade, J. P. Majoral, M. Moreno-Mañas and R. M. Sebastian, "Palladium(0) nanoparticles stabilized by phosphorus dendrimers containing coordinating 15-membered triolefinic macrocycles in periphery", Langmuir 24(5), 2090-2101 (2008). http://dx.doi.org/10.1021/la7013418

[12] S. Cerezo, J. Cortès, D.Galvan, E. Lago, C. Marchi, E. Molins, M. Moreno-Mañas, R. Pleixats, J. Torrejón and A. Vallribera, "Preparation of nitrogen-containing 15-membered triolefinic macrocycles: (E,E,E)-1,6,11-tris(arylsulfonyl)- 1,6,11-triazacyclopentadeca- 3, 8, 13 -Trienes ", Eur. J. Org. Chem. 2, 329-337 (2001). http://dx.doi.org/10.1002/1099-0690(200101)2001:2$<$329::AID-EJOC329$>$3.0.CO;2-N

[13] H. Wang, Q. M. Pan and G. L. Rempel, "Organic solvent-free catalytic hydrogenation of diene-based polymer nanoparticles in latex form: Part I. Preparation of nano-substrate ", J. Polym. Sci. Pol. Chem. 50(22), 4656-4665 (2012). http://dx.doi.org/10.1002/pola.26277

[14] P. Martin, N. T. McManus and G. L. Rempel, "A detailed study of the hydrogenation of nitrile-butadiene rubber and other substrates catalyzed by Ru(II) complexes", J. Mol. Catal. A: Chem. 126(2-3), 115-131 (1997). http://dx.doi.org/10.1016/S1381-1169(97)00102-7

[15] Y. He, E. S. Daniels, A. Klein and M. S. El-Aasser, "Grafting behavior of n-butyl acrylate onto poly (butadiene-co-styrene) latexes", J. Appl. Polym. Sci. 65(3), 511-523 (1997). http://dx.doi.org/10.1002/(SICI)1097-4628(19970718)65:3<511::AID-APP11>3.0.CO;2-#

[16] R. M. Crooks, M. Q. Zhao, L. Sun, V. Chechik and L. K. Yeung, "Dendrimer-encapsulated metal nanoparticles: Synthesis, characterization, and applications to catalysis", Acc. Chem. Res. 34(3), 181-190 (2001). http://dx.doi.org/10.1021/ar000110a

[17] S. Cerezo, J. Cortes, E. Lago, E. Molins, M. Moreno-Manas, T. Parella, R. Pleixats, J. Torrejon and A. Vallribera, "The first transition metal complexes of 15-membered triolefinic macrocycles: (E,E,E)-1,6,11-tris(arenesulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triene complexes of palladium(0), platinum(0), and silver(I)", Eur. J.

Inorg. Chem. 8, 1999-2006 (2001). http://dx.doi.org/10.1002/1099-0682(200108)2001:8$<$1999::AID-EJIC1999$>$3.0.CO;2-V

[18] Y. M. Chung and H. K. Rhee, "Partial hydrogenation of 1, 3-cyclooctadiene using dendrimer-encapsulated Pd-Rh bimetallic nanoparticles", J. Mol. Catal. A: Chem. 206(1-2), 291-298 (2003). http://dx.doi.org/10.1016/S1381-1169(03)00418-7

[19] Y. M. Chung and H. K. Rhee, "Pt-Pd bimetallic nanoparticles encapsulated in dendrimer nanoreactor", Catal Lett. 85(3-4), 159-164 (2003). http://dx.doi.org/10.1023/A:1022181327349

[20] X. H. Peng, Q. M. Pan and X. R. Lu, "Regioselective catalyzed modification of poly(methylhydro)siloxane using RuRh and RuPt bimetallic dendrimer-encapsulated nanoparticles", J. Appl. Polym. Sci. 122(1), 334-341 (2011). http://dx.doi.org/10.1002/app.34178

[21] N. Toshima and T. Yonezawa, "Bimetallic nanoparticles - novel materials for chemical and physical applications", N. J. Chem. 22(11), 1179-1201 (1998). http://dx.doi.org/10.1039/A805753B

[22] X. H. Peng, Q. M. Pan and G. L. Rempel, "Bimetallic dendrimer-encapsulated nanoparticles as catalysts: a review of the research advances", Chem. Soc. Rev. 37(8), 1619-1628 (2008). http://dx.doi.org/10.1039/b716441f