Regioselective Catalyzed Modification of Poly(methylhydro)siloxane Using RuRh and RuPt Bimetallic Dendrimer-Encapsulated Nanoparticles

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ABSTRACT: RuRh and RuPt bimetallic dendrimer-encapsulated nanoparticles (DENs) were successfully prepared by a two-step process involving co-complexation, using ruthenium and rhodium or ruthenium and platinum complex ions with partially quaternized fifth-generation poly(amidoamine) (G5-Q), and then coreduction with $NaBH_4$. UV–vis, transmission electron microscope, and laser scattering analyses were used to characterize the bimetallic alloy DENs. The regioselective synthesis of multifunctional hybrid poly(methylhydro)siloxane was achieved by the RuRh and RuPt alloy nanoparticle catalysts. The experimental results showed that the RuRh and RuPt bimetallic DENs presented higher catalytic activity than physical mixtures of their monometallic DENs, respectively. This should be due to synergistic electronic effect of RuRh and RuPt alloy catalysts. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 334–341, 2011

Key words: dendrimer; encapsulation; bimetallic nanoparticles; poly(methylhydro)siloxane; hydrosilylation; catalyst selectivity

INTRODUCTION

Over the past years, great attention has been paid to dendrimer-encapsulated nanoparticles (DENs). This is because they can be used as model systems to study structure-function relationships. The dendrimers as a template of preparing metal nanoparticles have provided new opportunities for catalysis.[1,2] The DENs not only retain the benefits of homogeneous catalysts, such as high catalytic activity and high selectivity, but may also have good reproducibility and accessibility of the metal site.[3,4]

In line with the prospect of the dendrimer-dispersed metal nanoparticles, bimetallic DENs have drawn a greater interest than monometallic and traditionally prepared catalytic particles, because the bimetallic DENs have demonstrated to be specific superior to those of monometallic and traditional ones in many systems when they are used as catalysts.[5–7] RuPt bimetallic DENs have been prepared via the template of fourth-generation hydroxyl-terminated poly(amidoamine) (PAMAM) dendrimers (G4-OH).[8,9] Preliminary results show that the nano-electrocatalyst of the RuPt alloy DENs immobilized on the oxidized surface of a glassy carbon electrode exhibits good electrocatalytic activity for the oxygen reduction reaction in the presence of methanol.[8] The methanol oxidation activity of 20 wt % G4-OH-RuPt/C (utilizing G4-OH dendrimers as a protective ligand in solution to produce carbon-supported RuPt bimetallic nanoparticles) catalyst is about 60% greater than that of E-Tek's commercially available 20 wt % RuPt catalyst.[10] Furthermore, the silica-supported bimetallic RuPt nanoparticle catalysts were prepared using G4-OH dendrimers and then separated from the dendrimer by deposition/thermal treatment steps. The kinetic evaluation was investigated for the selective hydrogenation of 3,4-epoxy-1-butene, which demonstrated that the bimetallic RuPt catalyst prepared by the co-complexation method exhibits a superior catalytic activity compared to the sequential one and is much more active than a conventional catalyst prepared by incipient wetness method.[9] In this regard, quaternized PAMAM dendrimer was chosen as a template, due to the advantage of preparing nearly monodispersed metallic DENs.[11,12] Scott et al.[13] reported the synthesis, characterization, and catalytic properties of PdAu bimetallic DENs by partially quaternized sixth-generation PAMAM dendrimers. The catalytic hydrogenation of allyl alcohol was significantly enhanced in the presence of the alloy and core/shell PdAu nanoparticles compared to the mixtures of their monometallic nanoparticles. In general, bimetallic

DENs can be made via three methods:[4] co-complexation, sequential loading, and partial displacement. The co-complexation method has been used to synthesize bimetallic alloy DENs, the bimetallic core/shell DENs could be devised by both sequential loading and partial displacement methods. However, although a few bimetallic DENs had been synthesized and demonstrated higher catalytic activity and/or better catalytic selectivity in homogeneous or heterogeneous catalytic reactions, more types of metallic DENs are yet to be studied and more applications of DENs, especially in macromolecular reactions are yet to be explored.

The purpose of this article is to investigate the syntheses and catalytic activities of RuRh and RuPt bimetallic DENs. Specially designed addition reaction of poly(methylhydro)siloxane (PMHS) and 1-hexene has been carried out to determine the regioselective catalyzed modification of multifunctional hybrid PMHS, which is important for three reasons.[14] First, PMHS is an excellent inorganic template because of its availability in various molecular weight ranges and well-defined microstructures. Second, evenly distributed Si—H bonds in PMHS can be viewed as chemical handles on which organic groups can be catalytically attached to generate hybrid polymers not achievable by physical mixing of individual phases. Finally, although the regioselective modification of monomeric species are well documented,[15–18] selective hydrosilylation of polyhydrosiloxanes is still a challenging task due to side reaction, such as redistribution of functional groups, self-dehydrocoupling, and crosslinking reactions, etc.

EXPERIMENTAL

Materials

Fifth-generation amine-terminated PAMAM dendrimer (G5-NH_2, with 128 primary amine groups on the terminal) having an ethylenediamine core was purchased in a methanol solution, which contained 10–25 wt % of G5-NH_2 from Dendritech (Midland, MI). Before use, the methanol was removed under vacuum at room temperature. $RuCl_3$ (98 wt %), $RhCl_3$ (98 wt %), K_2PtCl_4 (98 wt %), $NaBH_4$ (99 wt %), 1-hexene (99 wt %), and tetrahydrofuran (THF, 99 wt %) (The Aldrich Chemical, Milwaukee, WI) were used as received. PMHS (98 wt %, $M_w \approx 2000$, 33–35 Si—H units) obtained from Gelest (Morrisville, PA).

Synthesis of quaternized fifth-generation PAMAM dendrimers (G5-Q)

G5-NH_2 [2.5 g (0.087 mmol)] was reacted with 0.036 g (0.174 mmol), that is, twofold molar excess of 2-methylacryloyloxyethyl trimethylammonium chloride in methanol for 4 days at 50°C in a water bath. Then the methanol was removed by a rotary evaporator under a pressure of 8–12 mmHg, the residue was precipitated in 30 mL ether, and then the precipitate was redissolved in 10 times its weight of deionized water and dialyzed against water for 4 days. Amine colorimetry measurements[19] indicated that average 96 of the terminal primary groups were quaternized. Details of the synthetic technique to prepare partially quaternized dendrimers are outlined elsewhere.[20,21]

Preparations of RuRh and RuPt bimetallic DENs

The bimetallic RuRh and RuPt alloy DENs [G5-Q(RuxRhy) and G5-Q(RuxPty), where x/y = molar ratio for Ru/Rh or Ru/Pt] were synthesized by simultaneous co-complexation of two different metal ions, followed by a co-reduction step.[13] 16.2 mL of a 0.10 mM aqueous solution of G5-Q were added to 63.0 mL of deionized water in a 100-mL shake-flask, followed by adding a total volume of 0.60 mL of both 0.10M $RuCl_3$ and 0.10M $RhCl_3$ or 0.10M $RuCl_3$ and 0.10M K_2PtCl_4 solutions. After the system was continually stirred at 200 RPM for 24 h, 1.2 mL of a 0.5M $NaBH_4$ solution were slowly added into it with vigorous stirring and then stirred at 200 RPM for another hour.

Regioselective modification of PMHS

Regioselective catalytic modifications of PMHS were carried out in THF/water (v/v = 6/1) at the atmospheric pressure and room temperature (22°C). 10.0 mL (0.0074 mmol RuRh or RuPt) of the bimetallic DEN solution were placed into a 150-mL RB Schlenk flask fitted with a magnetic stirring bar and an adapter that was connected to the valve of a N_2 system, and then were added with 60 mL of THF, and 1.1 mL (18.3 mmol) of PMHS, respectively. After the system was purged with N_2 for 15 min, 2.4 mL (18.5 mmol) of 1-hexene were added by a 5-mL syringe under vigorous stirring to initiate the reaction, followed by slowly bubbling N_2 and stirring at room temperature. Samples were taken out via a 10-mL syringe matched needle-tubing connector at designated reaction times (RT), and then the product was separated from reaction mixture by high-speed centrifugation for 20 min, by which the bimetallic DENs precipitated. After the separation, the solvent was evaporated via a vacuum system at room temperature. The product was a white powder.

Characterization

UV–vis absorption spectra can be used for characterizing the course of the co-complexation of the two metals with the dendrimer and the subsequent reduction. The absorption spectra of the RuRh and RuPt bimetallic DENs during the forming course were determined with a Shimadzu UVmini-1240
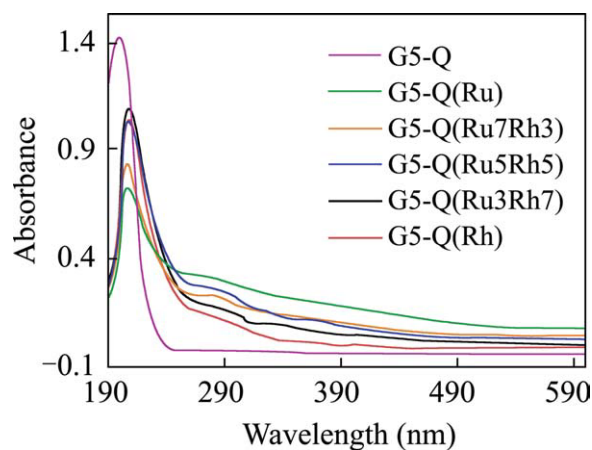
Figure 1 UV–vis spectra of RuRh bimetallic DENs with various Ru/Rh ratios. The total metal concentration in all cases was 0.1 mM, and the G5-Q concentration was 1.35 μM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

UV–vis spectrophotometer. The optical path length was 1.0 cm, and deionized water or aqueous dendrimer solution was used as the references. The measured concentrations of total metal and G5-Q were 0.1 mM and 1.35 μM (twofold dilution concentration of G5-Q template), respectively. The average particle diameter and the distribution of the DENs were measured by laser scattering analysis with a Microtrac Nanotrac^{TM} 150. Transmission electron micrographs were obtained using a LEO 912AB Transmission electron microscope (TEM). For TEM characterization, a water solution of the bimetallic DENs was dropped on a carbon-coated Cu grid and natural air drying. The composition and structure of modified polymer can be analyzed by FTIR and NMR spectra. FTIR measurements were carried out by a Bio-Rad Merlin FTS-3000 spectrophotometer via the KBr pellet method.^{1}H-NMR,^{13}C-NMR, and ^{29}Si-NMR spectra were recorded in CDCl$_3$ solvent on a Bruker-300 MHz NMR spectrometer at room temperature. Proton and carbon spectra were referenced internally to protonated and carbonated solvent shifts, respectively. For the convenience of analysis and characterization, the relevant spectra of FTIR, ^{1}H-NMR, ^{13}C-NMR, and ^{29}Si-NMR are listed as follows:

PMHS: FTIR v (cm^{-1}): 2970 (sp^{3}CH), 2170 (sp^3 SiH, m), 1260 (SiCH$_3$), 1099–1059 (SiO, s), <1000 (SiCH$_3$); ^{1}H-NMR δ (ppm): –0.001, 4.52; ^{13}C-NMRδ (ppm): 0.001; ^{29}Si-NMRδ (ppm): 8.41, –36.49.

Poly(methylhexyl)siloxane obtained by the RuRh catalyst system: FTIR v (cm^{-1}): 2970 (sp^{3}CH), 1260 (SiCH$_3$), 1099–1059 (SiO, s), <1000 (SiCH$_3$);^{1}H-NMRδ (ppm): 0.13, 1.23, 1.41, 1.58, 1.83; ^{13}C-NMRδ (ppm): –4.14, 1.46, 14.03, 22.63, 25.53, 29.63, 30.24, 31.86, 34.16, 67.9;^{29}Si-NMRδ (ppm): –22.15, 7.45.

Poly(methylhexyl)siloxane obtained by the RuPt catalyst system: FTIR v (cm^{-1}): 2970 (sp^{3}CH), 1260 (SiCH$_3$), 1099–1059 (SiO, s), <1000 (SiCH$_3$);^{1}H-NMRδ (ppm): 0.13, 1.23, 1.41, 1.58, 1.83; ^{13}C-NMRδ (ppm): –4.13, 1.46, 13.98, 22.61, 25.51, 29.56, 30.21, 31.80, 34.10, 67.8;^{29}Si-NMRδ (ppm): –22.14, 7.43.

RESULTS AND DISCUSSION

RuRh and RuPt bimetallic DENs prepared by co-complexation

The preparations of the RuRh and RuPt bimetallic DENs were carried out by simultaneously using two metal precursors, both RuCl$_3$ and RhCl$_3$ with G5-Q dendrimers, or both RuCl$_3$ and K$_2$PtCl$_4$ with G5-Q dendrimers, followed by NaBH$_4$ reduction. Partially quaternized PAMAM dendrimers as the template are due to some relationship problems associated with amine-terminated PAMAM dendrimers, metal ions selectively coordinate to the exterior amines, could be avoided.[13] The comparisons shown in both Figures 1 and 2 clearly demonstrate the evolution of the absorption peak along with the co-complexation of metal composition. In Figures 1 and 2, the characteristic absorption peak of G5-Q was at ∼ 197 nm; after the addition of a series of the bimetallic RuRh and RuPt nanoparticles, the peaks were shifted to 208 and 209 nm, respectively. The absorption peak intensities of G5-Q(RuxRhy) increased with decrease in the Ru/Rh ratios (Fig. 1); however, the ones of G5-Q(RuxPty) decreased with decrease in the Ru/Pt ratios (Fig. 2). Regardless of the Ru/Rh or Ru/Pt ratios, the absorption bands are of nearly exponential shape and this indicates the complete reduction of metal ions.[22] Moreover, it should be noted that the spectra of the resulting nanoparticles are
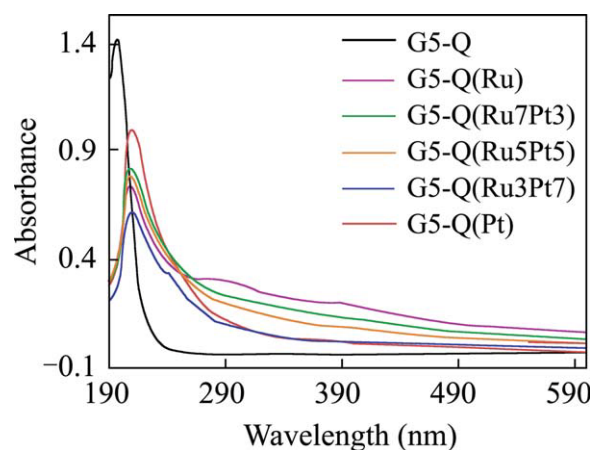

Figure 2 UV–vis spectra of RuPt bimetallic DENs with various Ru/Pt ratios. In all cases, the final concentrations of total metal and G5-Q were 0.1 mM and 1.35 μM, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

G5-Q (RuxRhy)	D (nm)	S (nm)
Ru	1.94	0.56
Ru7Rh3	4.02	1.16
Ru5Rh5	0.92	0.06
Ru3Rh7	4.68	1.27
Rh	1.59	0.86

different from those of the monometallic Ru or Rh or Pt nanoparticles. The change can be primarily attributed to the change in dielectric function caused by mixing the two different metal atoms. Therefore, the characteristic monotonic absorption spectra suggest that bimetallic nanoparticles are formed in the cavities of the dendrimers.[23]

The mean particle diameter (D) and the standard deviation (S) of the RuRh and RuPt bimetallic DENs prepared by the co-complexation route are shown in both Tables I and II, respectively. In Table I, the D is within 5 nm, and the S is less than 1.3 nm, which implies that the G5-Q can be used to the nearly monodispersed RuRh bimetallic DENs. In Table II, the particles have the D of smaller than 5 nm, and the S also of smaller than 2 nm, which shows that the G5-Q as a template was effective in assisting the synthesis of the RuPt bimetallic nanoparticles.

TEM study of the RuRh bimetallic DENs further confirms the above results. Figures 3 and 4 are TEM micrographs of the G5-Q(Ru5Rh5) and G5-Q(Ru7Pt3) DENs, respectively. In Figure 3, the microscopy demonstrates that the particle size is uniform. The formation of nearly monodispersed nanoparticles suggests the effectiveness of dendrimers acting as both nanoreactors for the preparation of nanoparticles and as nanoporous stabilizers for the prevention of aggregation. Specifically, in Figure 3, standardless quantitative analysis of three particles using the parallel lines resulted in an average particle size of around 1 nm. Similar to the RuRh case, bimetallic RuPt nanoparticles are well dispersed, and the particle shape is nearly spherical in Figure 4(a). Figure 4(b) further shows the corresponding size distribution histogram of the RuPt bimetallic nanoparticles, which demonstrates that

G5-Q (RuxPty)	D (nm)	S (nm)
Ru	1.94	0.56
Ru7Pt3	2.20	0.73
Ru5Pt5	3.93	1.50
Ru3Pt7	4.29	1.92
Pt	3.81	1.17

the nanoparticles display a Gaussian-like size distribution. The D and S of RuPt bimetallic DENs are 2.20 and 0.73 nm, respectively.

Regioselective modification

The regioselective modification of PMHS with 1-hexene was examined using bimetallic nanoparticles synthesized in the current work (Scheme 1). With the reaction proceeding, the colorless mixture solution gradually turned to be a homogeneous brownish yellow, and then became a milky latex, indicating the generation of poly(methylhexyl)siloxane.

The progress of the reaction was monitored with FTIR spectroscopy by following the disappearance of the Si—H absorption band at 2170 cm^{-1}, associated with starting materials, could be used to infer the catalytic activity of bimetallic DENs in the hydrosilylation reaction of PMHS with 1-hexene.[16]

Table III shows the reaction parameters for the hydrosilylation reaction of PMHS with 1-hexene using different bimetallic DENs as catalysts. For the RuRh bimetallic DENs, the effect of [substrate]/[catalyst] ratio on the conversion at 2 h can be seen in Table III (Ru5Rh5-1, Ru5Rh5, and Ru5Rh5-6). The conversion at 2 h decreased with increasing the ratio of the [substrate]/[catalyst]. This was due to increasing the substrate concentration when the ratio of the [substrate]/[catalyst] increased. Contrarily, the conversion shown in Table III increased with increasing the catalyst concentration (Ru5Rh5-2, Ru5Rh5, and Ru5Rh5-3). The effect of the temperature on the
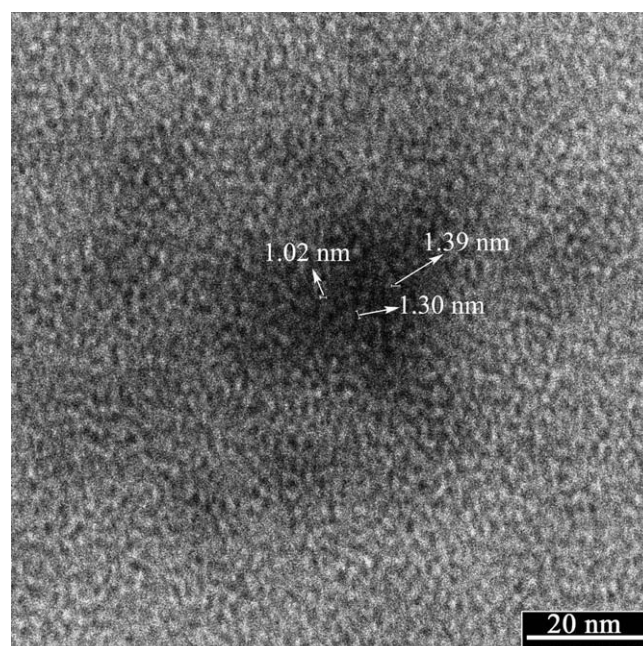

Figure 3 TEM micrograph of bimetallic G5-Q(Ru5Rh5) obtained by reduction of 50/50 ratio of Rh^{3+} and Rh^{3+} ions in the presence of G5-Q.
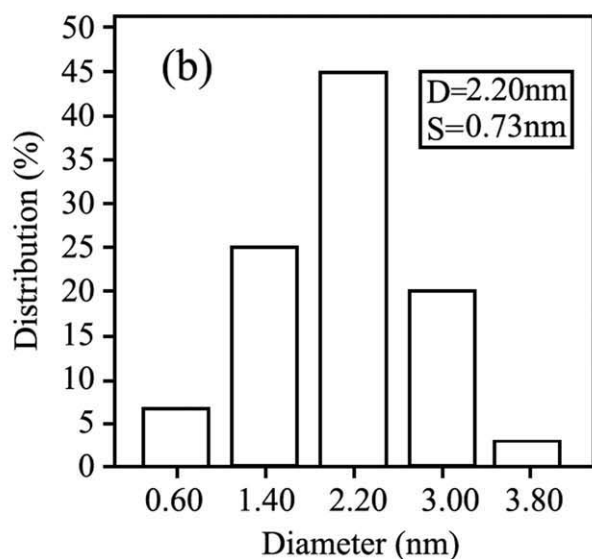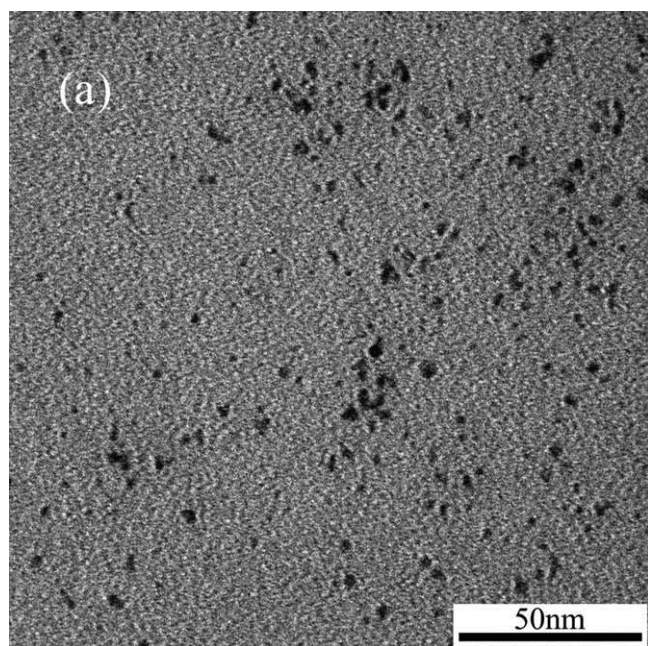
Figure 4 TEM micrograph of G5-Q(Ru7Pt3) (a) and the corresponding size distribution histogram (b).

conversion at 2 h is also shown in Table III (Ru5Rh5, Ru5Rh5-4, Ru5Rh5-5). The conversion apparently increased with the increase in the reaction temperature, because it enhanced the mass transfer between catalysts and substrates with increasing temperature.[24] Keeping the reaction parameters constant ([substrate]/[catalyst] ratio = 2500 : 1, [catalyst] = 100 μM, T = 22°C, and RT = 2 h), Table III shows that DENs containing Rh-rich DENs (Ru/Rh ratio of 7/3, 5/5, and 3/7) yielded in a higher conversion than those obtained from monometallic nanoparticles (the conversion from the Ru-only DENs is 44% and from the Rh-only DENs is 52%). The higher conversion from the RuRh DENs is the enhanced catalytic activity in the bimetallic catalysts, a synergistic electronic effect between metals.[25] Such synergistic electronic effect has also been observed in the RuPt system (Table III). The RuPt system presented a similar catalytic activity with above the RuRh DENs catalysts in the hydrosilylation reaction of PMHS with 1-hexene. However, the RuRh bimetallic DENs were found to be more effective catalysts than the RuPt DENs, which could be partially due to the smaller and narrower size distribution of the RuRh bimetallic nanoparticles. Furthermore, the highest conversion at 2 h in the RuRh system was achieved with a RuRh ratio of 5/5, whereas the RuPt system was a Ru/Pt ratio of 7/3. Those results suggest that the catalytic activities of bimetallic DENs were dependent on the metal composition of bimetallic nanoparticles and their activities were higher than those of the monometallic ones prepared by the same method.

Catalytic selectivity

NMR analyses can explain the regiospecificity of the above addition reaction. In general, the addition of Si—H bonds to alkene can take place either in an anti-Markovnikov (β-addition) fashion resulting in the silicon being attached at the terminal position or in a Markovnikov (α-addition) fashion resulting in
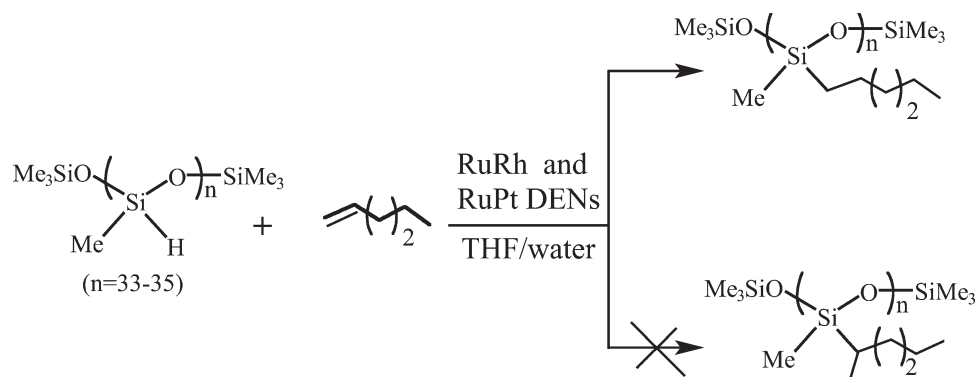
Scheme 1 RuRh and RuPt bimetallic DENs-catalyzed regioselective modifications of PMHS.

TABLE III
Reaction Parameters for the Hydrosilylation Reaction of PMHS with 1-Hexene using Different Bimetallic DENs as Catalysts

DENs	[Substrate]/ [catalyst] molar ratio	[Catalyst] (μM)	Reaction temperature (°C)	Conversion (%)[a] (reaction time, h)
Ru	2500 : 1	100	22	44 (2)
Ru7Rh3	2500 : 1	100	22	71 (2)
Ru5Rh5	2500 : 1	100	22	79 (2)
Ru5Rh5-1	1500 : 1	100	22	90 (2)
Ru5Rh5-2	2500 : 1	50	22	47 (2)
Ru5Rh5-3	2500 : 1	200	22	88 (2)
Ru5Rh5-4	2500 : 1	100	30	85 (2)
Ru5Rh5-5	2500 : 1	100	40	89 (2)
Ru5Rh5-6	5000 : 1	100	22	53 (2)
Ru3Rh7	2500 : 1	100	22	72 (2)
Rh	2500 : 1	100	22	52 (2)
Ru7Pt3	2500 : 1	100	22	69 (2)
Ru5Pt5	2500 : 1	100	22	63 (2)
Ru3Pt7	2500 : 1	100	22	57 (2)
Pt	2500 : 1	100	22	35 (2)

[a] Conversion was measured via quantitative FTIR method based on peak height ratio of v (sp3SiH, 2170 cm^{-1}) with v (sp3CH, 2970 cm^{-1}).

the silicon being attached at the iso-position of 1,2-alkene.

Figures 5 and 6 present the ^{1}H-NMR spectra of PMHS modified with 1-hexene when the reactions were carried out for 26 and 24 h, respectively.

The regioselective modification of PMHS was proceeded almost exclusively by β-addition of the Si—H group with the vinyl double bond. The virtual absence of the α-addition products may be seen in the ^{1}H-NMR spectra by the absence of the peak at 0.5 ppm,[16] which may be assigned to aliphatic methyl groups. In addition, ^{13}C-NMR spectra of PMHS revealed two new peaks at δ 25.5 (—CH$_2$CH$_2$Si) and
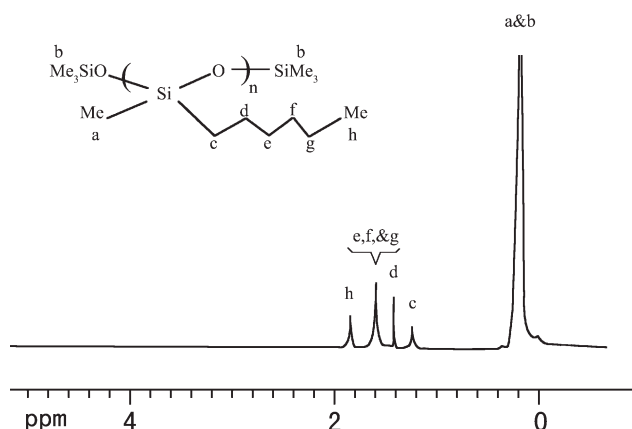

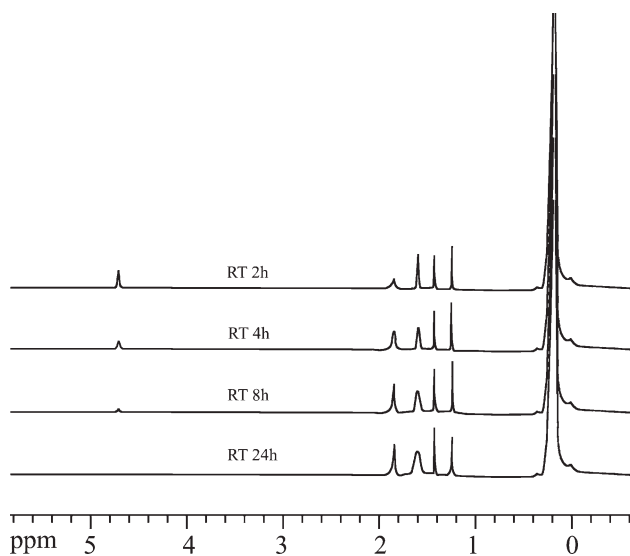**Figure 6** ^{1}H-NMR spectra of PMHS modified with 1-hexene using G5-Q(Ru7Pt3) catalyst with reaction times of 2, 4, 8, and 24 h.

δ 14.0 (—CH$_2$CH$_2$Si), which indicated exclusive β-silylation of 1-hexene at terminal carbons.

Figure 7 shows ^{29}Si-NMR spectrum of G5-Q(Ru5Rh5) catalyzed regioselective modification of PMHS in CDCl$_3$. The ^{29}Si-NMR analysis of the reaction mixture showed only a single peak at δ −22.15 (—CH$_2$$Si$Me) corresponding to hexyl-substituted silicon centers beside the peak at δ 7.45 originating from the terminal —OSiMe$_3$ group. The result was also found to be similar to ^{29}Si-NMR spectrum of G5-Q(Ru7Pt3) catalyzed regioselective modification of PMHS in CDCl$_3$.

Reaction kinetics

The reaction kinetics of the hydrosilylation reaction of PMHS with 1-hexene was studied using the quantitative FTIR method[16] based on the absorption measurements at the Si—H absorption band at 2170 cm^{-1}, with reference to the standard curve.
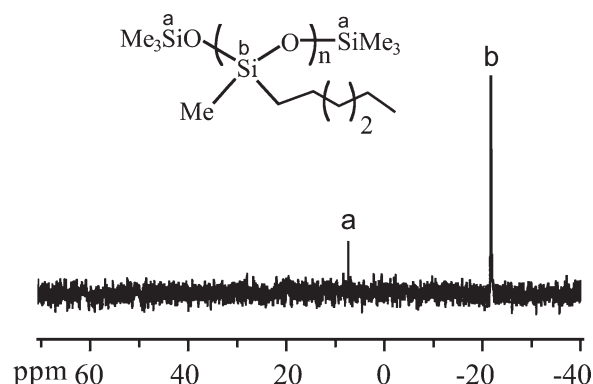

Figure 5 ^{1}H-NMR spectrum of G5-Q(Ru5Rh5) catalyzed regioselective modification of PMHS in CDCl$_3$.

Figure 7 ^{29}Si-NMR spectrum of G5-Q(Ru5Rh5) catalyzed regioselective modification of PMHS in CDCl$_3$.
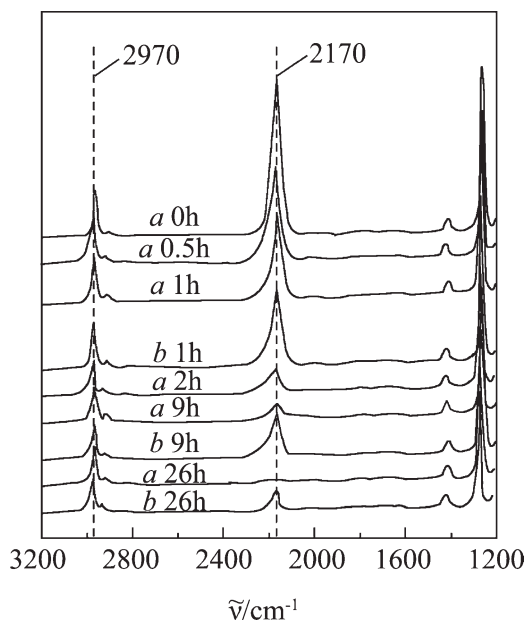
Figure 8 FTIR spectra of PMHS modified with 1-hexene using G5-Q(Ru5Rh5) (a) and physical mixture of G5-Q(Ru) + G5-Q(Rh) (b) catalysts after different reaction time.

Figures 8 and 9 are FTIR spectra of PMHS modified with 1-hexene using both G5-Q(Ru5Rh5) and G5-Q(Ru7Pt3) catalysts after different reaction time, respectively. Shown in Figures 10 and 11 are the corresponding plots of the conversion of the Si—H group with the reaction time for G5-Q(Ru5Rh5) and G5-Q(Ru7Pt3) catalyzed regioselective modifications of PMHS, respectively. It is seen that the rate of hydrosilylation reaction was all very large within 2
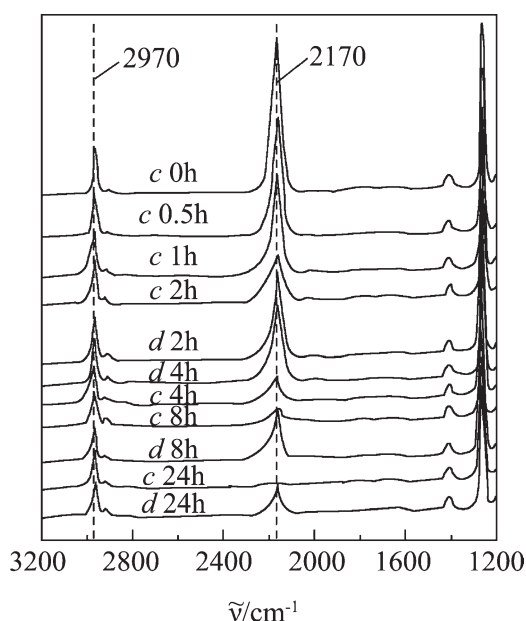

Figure 9 FTIR spectra of PMHS modified with 1-hexene using G5-Q(Ru7Pt3) (c) and physical mixture of G5-Q(Ru) + G5-Q(Pt) (d) catalysts after different reaction time.
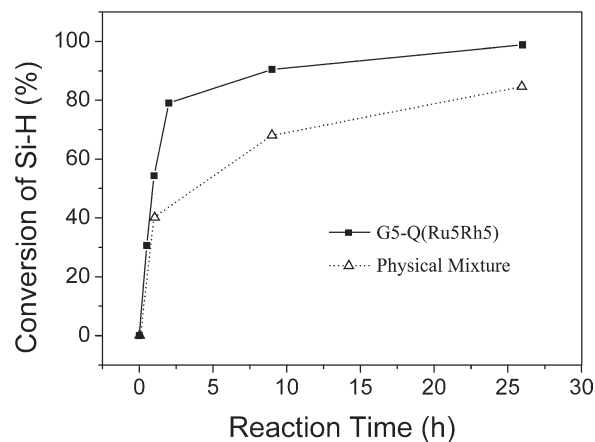
Figure 10 Conversion versus reaction time for G5-Q(Ru5Rh5) (■) and physical mixture of G5-Q(Ru) + G5-Q(Rh) (△) catalyzed regioselective modifications of PMHS. Conditions: substrate : metal ratio = 2500 : 1, [catalyst] = 100 μM, T = 22°C.

h and then slowed down. The Si—H conversion of PMHS catalyzed by the RuRh and RuPt systems can reach to 98.8% (26 h) and 99.3% (24 h), respectively. In addition, in Figures 10 and 11, we also note that the RuRh and RuPt alloy nanoparticles showed that their ability to hydrosilylate reaction of PMHS with 1-hexene was at higher rate than physical mixtures of their monometallic DENs with equal composition. Such an enhancement was believed to be due to synergistic electronic effect.[4]

Similar results may also be drawn from an examination of the ^{1}H-NMR spectroscopy variation with RT of 2, 4, 8, and 24 h (Fig. 6). It also showed the gradual disappearance of the peaks associated with Si—H (δ 4.68), and the appearance of the new peaks
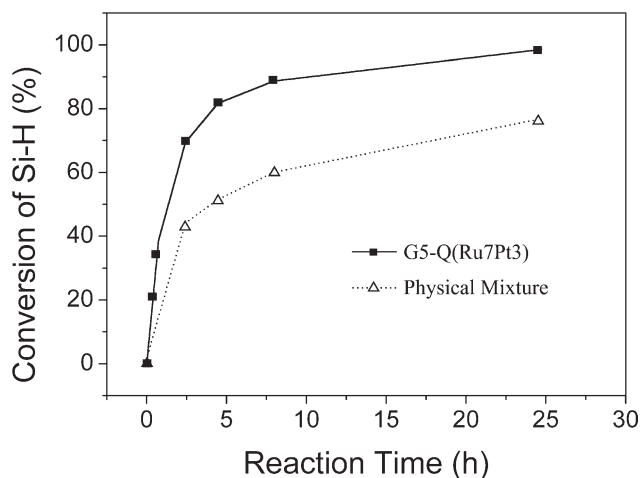

Figure 11 Conversion versus reaction time for G5-Q(Ru7Pt3) (■) and physical mixture of G5-Q(Ru) + G5-Q(Pt) (△) catalyzed regioselective modifications of PMHS. Conditions: substrate : metal ratio = 2500 : 1, [catalyst] = 100μM, T = 22°C.

in the methylene region (δ 1.2–1.6).[14] These measurements provide a direct evidence of the consumption of the Si—H functional groups during the modification of PMHS.

CONCLUSIONS

We have shown that bimetallic RuRh and RuPt alloy DENs can be synthesized by the co-complexation method, that is, Ru^{3+} and Rh^{3+} or Ru^{3+} and Pt^{2+} ions, were simultaneously complexed within the G5-Q, and then the resulting composites are reduced via $NaBH_4$. UV–vis spectroscopy suggests that the bimetallic RuRh and RuPt nanoparticles were formed in the template of G5-Q. Laser scattering analysis and TEM results show that the co-complexation method provides useful means for preparing well-dispersed bimetallic RuRh and RuPt alloy nanoparticles. The G5-Q(Ru5Rh5)- and G5-Q(Ru7Pt3)-catalyzed regioselective modifications of PMHS with 1-hexene, all displayed a high efficiency of hydrosilylation, confirmed by a quantitative FTIR method, and NMR analyses also identified the results.

References

1. Astruc, D.; Boisselier, E.; Ornelas, C. Chem Rev 2010, 110, 1857.
2. Ravoo, B. J. Dalton Trans 2008, 1533.
3. Pachón, L. D.; Rothenberg, G. Appl Organomet Chem 2008, 22, 288.
4. Peng, X.-H.; Pan, Q.-M.; Rempel, G. L. Chem Soc Rev 2008, 37, 1619.
5. Liu, D.; Monnier, J.; Williams, C. T. AIChE Annual Meeting, Conference Proceedings, 05AIChE: 2005 AIChE Annual Meeting and Fall Showcase, Conference Proceedings 2005; American Institute of Chemical Engineers, New York; p 11602.
6. Peng, X.-H.; Pan, Q.-M.; Rempel, G. L.; Wu, S. Catal Commun 2009, 11, 62.
7. Weir, M. G.; Knecht, M. R.; Frenkel, A. I.; Crooks, R. M. Langmuir 2010, 26, 1137.
8. García, I. L. E.; García, J. L.; Rodriguez, F. J.; Chapman, T. W.; Godinez, L. A. ECS Trans 2007, 3, 1.
9. Liu, D.; Jesús, Y. M. L.-D.; Monnier, J. R.; Williams, C. T. J Catal 2010, 269, 376.
10. Gu, Y.; Wu, G.; Hu, X.-F.; Chen, D. A.; Hansen, T.; zur Loye, H.-C.; Ploehn, H. J. J Power Sources 2010, 195, 425.
11. Oh, S.-K.; Kim, Y.-G.; Ye, H.; Crooks, R. M. Langmuir 2003, 19, 10420.
12. Kim, Y.-G.; Oh, S.-K.; Crooks, R. M. Chem Mater 2004, 16, 167.
13. Scott, R. W. J.; Wilson, O. M.; Oh, S.-K.; Kenik, E. A.; Crooks, R. M. J Am Chem Soc 2004, 126, 15583.
14. Chauhan, B. P. S.; Rathore, J. S. J Am Chem Soc 2005, 127, 5790.
15. Lewis, L. N.; Lewis, N. J Am Chem Soc 1986, 108, 7228.
16. Crivello, J. V.; Bi, D. J Polym Soc Part A: Polym Chem 1993, 31, 3121.
17. Marciniec, B.; Guliński, J.; Kopylova, L.; Maciejewski, H.; Grundwald-Wyspiańska, M.; Lewandowski, M. Appl Organomet Chem 1997, 11, 843.
18. Stein, J.; Lewis, L. N.; Gao, Y.; Scott, R. A. J Am Chem Soc 1999, 121, 3693.
19. Milun, A. J. Anal Chem 1957, 29, 1502.
20. Peng, X.-C.; Peng, X.-H.; Zhao, J.-Q.; Lin, Y.-W. Petrochem Technol 2005, 34, 986.
21. Peng, X.-C. PhD Dissertation: Synthesis and Application of Modified Poly(amidoamine) Dendrimer, South China University of Technology, Guangzhou, 2007; Chapter 3.
22. Chung, Y.-M.; Rhee, H.-K. J Mol Catal A: Chem 2003, 206, 291.
23. Chung, Y.-M.; Rhee, H.-K. Catal Lett 2003, 85, 159.
24. Lu, F.; Liu, J.; Xu, J. J Mol Catal A: Chem 2007, 271, 6.
25. Scott, R. W. J.; Datye, A. K.; Crooks, R. M. J Am Chem Soc 2003, 125, 3708.