Pt-Ni alloy catalysts for highly selective anti-Markovnikov alkene hydrosilylation

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Alkene hydrosilylation with homogeneous catalysts is an industrially important reaction for the preparation of organosilicon compounds such as silicone-based release coatings, surfactants, adhesives and molding products [1,2]. Moreover, alkene hydrosilylation is used for cross-linking of silicone polymers, and for coupling of silanes and siloxanes to organic polymers. For decades, noble metal based catalysts (e.g., Pt [3–7], Pd [8], Rh [9], etc. [10]) have been widely used in this class of reactions. However, the use of precious metals catalysts with a relatively low turn-over number (TON) represents a critical barrier to industrial applications. Although examples of non-noble metals (e.g., Fe [11–21], Co [22], etc.) have been widely reported, the separation and recycling of catalysts still remains difficult. To improve the separation and recycle ability of catalysts, researchers have developed supported metal nanoparticles (NPs) (e.g., Pt [23–27], Au [28], etc. [29]) as heterogeneous catalysts for hydrosilylation with the potential for high activity, high selectivity, wide applicability and recycle ability. However, the studies have been largely limited to single metal nanostructures and bimetallic catalysts are rarely explored to date.

Bimetallic NPs with well-defined surface structure, sizes, compositions, and crystal facets have been widely applied to organic reactions [30], water splitting [31], fuel cells [32], and so on [33]. Importantly, bimetallic nanostructures could exhibit superior activity, selectivity and stability to those of a pure single metal for a practical reaction, possibly due to the synergistic effects between two constituent metals [34–42]. Moreover, partial replacement of noble metal with cheap transition metals could help lower cost and improve atomic efficiency.

Herein we synthesized a series of bimetallic Pt_{1-x}Ni_x

($x=0, 0.33, 0.5, 0.66, 0.83, 1$) NPs [35,41,43] with tunable compositions. We found the composition of these Pt_{1-x}Ni_x NPs played an important role in their catalytic performance in alkene hydrosilylation. We further demonstrated that there existed no obvious shape-activity relationship between PtNi NPs with different morphologies in the two model hydrosilylation reactions under the same reaction conditions. Compared with Pt catalyst, which is only used for hydrosilylation of alkenes with chlorine, ketone, hydroxyl, amide and so on, octahedral PtNi alloy not only has broader functional group compatibility, such as bromine, ether and epoxyp propane, but also allows green and facile coupling of silanes and siloxanes to yield new functionalized products.

Pt_{1-x}Ni_x octahedral NPs were synthesized by a modified synthetic literature procedure [35,41] (see details in the Supplementary information). Their representative transmission electron microscopy (TEM) images (Fig. 1a) displayed a narrow size distribution of the as-prepared PtNi NPs (Fig. S1b). The high resolution TEM (HRTEM) images and Fourier transform (FFT) images (Fig. 1b) showed that the as-prepared PtNi NPs were single-crystals. The high-resolution TEM images display clearly resolved lattice fringes with an interplanar spacing of 0.219 nm, corresponding to the {111} lattice spacing of Pt-Ni alloy. The corresponding element mapping images (Fig. 1c) and the compositional line scanning profiles (Fig. S2) show that Pt and Ni elements are distributed evenly throughout individual PtNi octahedral NPs. The energy dispersive X-ray (EDX) analysis shows the atomic percentage content of Pt is 52% (Fig. S3).

By varying the molar ratios of Pt(acac)₂/Ni(acac)₂, the compositions of Pt_{1-x}Ni_x NPs could be finely tuned (Fig. 1d–f) while their sizes remained in the range of 7–8 nm

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Figure 1 Characterization of $\text{Pt}_{1-x}\text{Ni}_x$ octahedral NPs. (a) TEM image, (b) HRTEM image and (c) HAADF-STEM image of PtNi NPs and corresponding element maps showing the distribution of Pt (red) and Ni (yellow). TEM images of as-prepared (d) Pt_2Ni , (e) PtNi_2 , (f) PtNi_5 .

(Fig. S1). When $\text{Pt}(\text{acac})_2$ and $\text{Ni}(\text{acac})_2$ were the only metal precursors, Pt NPs of 8.5 nm and Ni NPs of 9.1 nm were obtained, respectively (Fig. S4). The X-ray diffraction (XRD) patterns (Fig. S5) of the as-obtained $\text{Pt}_{1-x}\text{Ni}_x$ NPs show that typical peaks could be indexed to {111}, {200}, and {220} diffraction peaks, which locate between those of the standard Pt (JCPD-04-0802) and those of Ni (JCPD-04-0850) peak [35,41]. When the atomic percentage content of Ni increased, the peaks of $\text{Pt}_{1-x}\text{Ni}_x$ shifted continuously from the Pt standard peaks to the corresponding Ni standard ones. The composition of the as-obtained Pt/Ni NPs were further analyzed and confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Table S1). In addition, the different morphologies of the prepared PtNi alloy including truncated octahedral and cubic NPs were also prepared and confirmed by TEM according to the reference method [31,43]. The XRD peaks of the PtNi all lie between the peak positions of pure Pt and Ni NPs.

The as-prepared $\text{Pt}_{1-x}\text{Ni}_x$ NPs were then supported on carbon black and used to catalyze the alkene hydrosilylation reaction under optimal conditions to probe their structure-activity and structure-selectivity relationship. Initial hydrosilylation experiments were conducted with a mixture of 1-hexene (0.48 mol L^{-1}) and $(\text{EtO})_3\text{SiH}$

(0.4 mol L^{-1}) using $\text{Pt}_{1-x}\text{Ni}_x$ NP catalysts in toluene solution. All reactions were performed with 0.5 mol% mass loading containing Pt and Ni in total catalysts. The reaction conversion of $(\text{EtO})_3\text{SiH}$ and selectivity were evaluated by gas chromatograph-mass spectrometer analysis. Fig. 2a and b showed the conversions of $(\text{EtO})_3\text{SiH}$ versus time during the reaction catalyzed by different catalysts at 50°C . We found that the PtNi/C catalyst showed the highest catalytic activity among all $\text{Pt}_{1-x}\text{Ni}_x$ catalysts. Meanwhile, the Pt/C reference catalyst showed a lower activity than the Pt_2Ni and PtNi catalysts, implying the Ni could promote the catalytic activity of the NP catalysts for the alkene hydrosilylation reaction. However, when the content of Ni continues to increase, the conversions of $(\text{EtO})_3\text{SiH}$ decreased and the orders of activity for the as-prepared catalysts were $\text{PtNi} > \text{PtNi}_2 > \text{PtNi}_5 > \text{Ni}$. Not surprisingly, Ni NPs were inactive. All these findings demonstrate that Pt is the intrinsic active component for the reaction [25,26], and Ni plays a positive role in promoting activity. As shown in Fig. 2c, the conversion of $(\text{EtO})_3\text{SiH}$ versus time for the PtNi catalyst at 90°C is much higher than at 50 and 70°C . To understand the hydrosilylation of 1-hexene mediated by different shapes of PtNi NPs/C, we also prepared PtNi NPs/C with three different shapes, the octahedral, truncated

Figure 2 Hydrosilylation of 1-hexene with $(\text{EtO})_3\text{SiH}$. (a, b) Conversion of $(\text{EtO})_3\text{SiH}$ versus time using different PtNi_x . (c) Effect of different temperatures using PtNi NPs. (d) Conversion of $(\text{EtO})_3\text{SiH}$ versus time with PtNi octahedral, truncated octahedral and cubic NPs. All catalysts were with 0.5 mol% mass loading of total metal containing Pt and Ni in total catalysts and 0.5%, 0.33%, 0.25%, 0.17%, 0.08% and 0% mass loading of Pt of $\text{Pt}_{1-x}\text{Ni}_x$ ($x = 0, 0.33, 0.5, 0.66, 0.83, 1$), respectively.

octahedral and cubic (Fig. S6). As shown in Fig. 2d, the activity of the octahedral PtNi/C catalyst is comparable to that of the cubic PtNi and higher than that of truncated octahedral PtNi . The activities of PtNi NPs with different morphologies for hydrosilylation reaction show no obviously periodic trends in the shape-activity relationship, which might arise from mutual influence on morphologies of nanoparticle and size of substrate molecule for the reaction.

We have further explored $\text{Pt}_{1-x}\text{Ni}_x$ NPs for hydrosilylation of styrene to produce triethoxy(phenethyl)silane. The reactions carried out with $\text{Pt}_{1-x}\text{Ni}_x$ catalysts show that PtNi/C catalyst exhibits the highest activity, with yield of 96% and correspondingly ~88% selectivity of

anti-Markovnikov product at 32 h (Table 1). At the same time, we examined the influence of reaction temperature on the hydrosilylation of styrene (Fig. S7). We found that the reaction at 90°C was fully completed in the shortest time than at 70 and 50°C (Table 1), but the by-product, which is detrimental to selectivity, was significantly increased, indicating the selectivity of the reaction decreased. We also studied the influence of shapes including the octahedral, truncated octahedral and cubic PtNi NPs for the hydrosilylation of styrene (Table 2), but did not see an apparent dependence of activity and selectivity of the hydrosilylation on the shapes.

We further evaluated the stability of the PtNi/C NPs. When the reaction was finished, the used PtNi/C catalyst

Table 1 Hydrosilylation of styrene with $(\text{EtO})_3\text{SiH}$

Catalyst	Reaction conditions	Yield (selectivity) ^a of 2b
Pt	0.4 mol L ⁻¹ , 50°C, 50 h	91% (86%)
Pt ₂ Ni	0.4 mol L ⁻¹ , 50°C, 32 h	95% (89%)
PtNi	0.4 mol L ⁻¹ , 50°C, 32 h	96% (88%)
PtNi ₂	0.4 mol L ⁻¹ , 50°C, 42 h	83% (87%)
PtNi ₅	0.4 mol L ⁻¹ , 50°C, 32 h	56% (62%)
Ni	0.4 mol L ⁻¹ , 50°C, 32 h	8% (ND)
PtNi	0.4 mol L ⁻¹ , 70°C, 28 h	96% (85%)
PtNi	0.4 mol L ⁻¹ , 90°C, 15 h	99% (82%)

a) Yields and selectivities are determined by GC-MS analysis.

Table 2 Hydrosilylation of styrene with $(\text{EtO})_3\text{SiH}$ catalyzed by various morphology catalysts

Entry	Catalyst of PtNi	Reaction conditions	Yield (selectivity) ^a
1	Octahedral	0.4 mol L ⁻¹ , 50°C, 35 h	98% (83%)
2	Truncated octahedral	0.4 mol L ⁻¹ , 50°C, 35 h	98% (81%)
3	Cubic	0.4 mol L ⁻¹ , 50°C, 35 h	98% (78%)

a) Yields and selectivities are determined by GC-MS.

could be easily separated by centrifugation from the reaction mixture for the next cycle use. The PtNi/C NPs exhibits excellent reusability for at least five times without apparent decay of activity (Table S2). TEM image of the used PtNi NPs/C catalyst displayed that the size, morphology and dispersity of the PtNi catalyst were largely preserved (Fig. S8), suggesting excellent stabilities of the NPs under the reaction condition.

To investigate the limitations of PtNi NPs, selected terminal alkenes bearing functional groups were chosen to examine the catalytic hydrosilylation (Scheme 1). Functionalized alkene with bromine (**1**) was converted to the corresponding anti-Markovnikov products in good yield (85%) and high selectivity (98%). Alkene with ether and epoxypropane (**2**) was fully converted into the corresponding anti-Markovnikov product in 96% yield and 99% selectivity. Furthermore, reactions of allyl alcohol with unprotected OH group (**3**) and allylamine with unprotected NH₂ group (**4**) were tolerant to some extent. These results confirmed that the hydrosilylation of selected terminal alkenes with $(\text{EtO})_3\text{SiH}$ displayed a good yield and selectivity under the reaction conditions with

Scheme 1 Functionalized hydrosilylation products from $(\text{EtO})_3\text{SiH}$ using catalyst PtNi.

the green and facile one-pot method.

In summary, we have prepared a series of Pt_{1-x}Ni_x ($x = 0, 0.33, 0.5, 0.66, 0.83, 1$) NPs with tunable compositions, which were used to catalyze the alkene hydrosilylation. The bimetallic PtNi catalyst with the Pt to Ni molar ratio of 1:1 exhibited superior activity and selectivity for the hydrosilylation of 1-hexene and styrene with $(\text{EtO})_3\text{SiH}$. This octahedral PtNi/C catalyst displayed good reusability without observable decay of activity and selectivity *via* the recyclability test. Furthermore, we further investigated the substrate scope of the hydrosilylation reactions, indicating that the octahedral PtNi alloy exhibits broader functional group compatibility and allows green and facile coupling of silanes and siloxanes to produce new functionalized products.

Received 4 January 2018; accepted 19 April 2018;
published online 10 May 2018

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Acknowledgements We sincerely thank Professor Yadong Li and Dingsheng Wang for their fruitful discussions and helpful suggestions in conducting this work and writing this paper. Some Pt(acac)₂ and Ni(acac)₂ raw materials were also obtained freely from their laboratory.

This work was supported by the National Natural Science Foundation of China (21671021) and the Fundamental Research Funds for the Central Universities (2015ZCQ-LY-03).

Author contributions Li Q and Duan X designed and engineered the samples; Li Q, Ji S and Li M performed the experiments and the characterizations. Li Q and Ji S wrote the paper with support from Duan X.

All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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铂镍合金催化烯烃的高选择性氢硅反马氏加成反应

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摘要 铂基催化剂已广泛应用于烯烃的硅氢加成反应, 但贵金属铂因其稀有而价高, 成为其工业化应用的障碍. 为了降低成本和提高原子效率, 我们采用了廉价的镍金属来代替金属铂. 本文合成了一系列具有可调成分和形貌的双金属铂镍催化剂, 发现其在温和条件下对烯烃的硅氢加成反应表现出优越的活性和选择性. 此外, 还发现八面体的铂镍纳米合金不仅能应用于具有不同的官能团烯烃, 而且还有利于有机硅和硅烷偶联剂的绿色化学制备, 开发出更多的新产品.