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Reversible hydrogen-bond-selective phase transfer directed towards noble metal nanoparticles and its catalytic application

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Reversible phase transfer of noble metal nanoparticles (NMNPs) without the presence of phase transfer agents or supplementary reagents is a big challenge. Through a simple protocol, we demonstrated and expanded an easy, highly efficient, and continuously reversible hydrogen-bond-selective phase transfer directed towards thermoregulated ligand Ph₂P(CH₂CH₂O)₂₂CH₃-stabilized noble metal (Pt, Ru, Ir, Pd, and Au) nanoparticles in the aqueous/alcohols biphasic system. When thermoregulated ligand was integrated onto NMNP surface, it provided a better switchable surface hydrophobicity/hydrophilicity for the NMNPs. So the critical parameters controlling the phase transfer of NMNPs, such as temperature, gas atmosphere and organic solvent, were studied. With the help of TEM, UV-vis, and ICP-AES, the asprepared NMNPs (Pt, Ru, Ir, Pd, and Au) not only exhibited a high level of dispersion stability, but also had an almost constant size distribution (excluding Au-NPs) and very high phase transfer efficiency during the multiple reversible phase transfer processes. In addition, a simple mechanism with respect to the reason for the increase of Au nanoparticle size was discussed. Subsequently, the as-prepared Pt-NPs were used as the catalyst for the hydrogenation of diphenylacetylene (DPA). A complete semihydrogenation to stilbene and a better stereoselectivity to *cis*-stilbene were achieved. Additionally, the as-prepared Pt-NPs can be recycled for 13 times without evident loss in activity and selectivity. Therefore, our investigations supply a fundamental and systematic study of the reversibe phase transfer of NMNPs (Pt, Ru, Ir, Pd, and Au), and then also afford an attractive solution to the problem of separating and recycling the NMNPs catalysts.

1. Introduction

The strategy to reversibly transfer substances including amphiphilic molecules, polymers, and colloidal particles across the aqueous/oil interfaces is not only fascinating for the physically and chemically relevant process but also highly necessary for many innovative applications such as biological sensing,^{1,2} drug delivery,^{3,4} separation/purification of noble metal nanoparticles (NMNPs),^{5,6} and catalyst recycling.⁷ It is a thermodynamically practicable fact that colloidal particles prefer to attach to an aqueous/oil interface rather than readily cross it.^{8,9} since their surface wettability is not easy to change and their solvation energies are much higher than small molecules. Therefore, there are large numbers of methods proposed on the phase transfer of colloidal particles from aqueous to oil phase or vice versa, such as two-phase Brust-Schiffrin method,¹⁰ ligand exchange strategy,^{11,12} and amphiphilic polymer coating method.13 Although these methods have their own unique advantages, most of them, in terms of the effect of phase transfer, could neither obtain a wider application to different noble metal nanoparticles, nor

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possess a continuously reversible phase transfer process; additionally, the procedure of phase transfer needs two or more steps associated with the use of supplementary phase transfer agents, ligands, or reagents.

It is an inspired ingenious design to develop a simple and feasible work involving the intermolecular H-bonds. For example, Mao et al. directed hydrophobic colloidal particles coated with polylactide (PLA) and polyethylene glycol (PEG) to transfer from organic phase to aqueous via the intermolecular H-bonds.¹⁴ However, their design was not capable of reversibly transferring colloidal particles. In this case, the protocol, which could reversibly transfer colloidal particles and make *in situ* separation and/or recycling of colloidal particles possible, is crucial to nanoscience and nanotechnology.

It is of very high practical value to find or synthesize some special types of amphiphilic molecules such as thermoregulated ligands, which could drive the colloidal particles reversibly transfer between water and oil with the change of environment, such as temperature, $^{\rm 15,16}$ light, $^{\rm 17,18}$ or acidity.¹⁹ In our preliminary study,^{20,21} we depicted the phenomenon of Rh nanoparticle phase transfer as the change of temperature in the aqueous/1-butanol (or 1-pentanol) biphasic system. As for the mechanism of phase transfer and more in-depth, systematic work, we have not carried out. It is a very necessary and meaningful work, which is also challenging, to examine whether a phase transfer protocol is versatile for various metal nanoparticles. In this article, we aim

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at revealing and proving the essence of thermoregulated phase transfer, namely a reversible hydrogen-bond-selective phase transfer, and then expand phase transfer to different NMNPs (Pt, Ru, Ir, Pd and Au), thus further provide a systematic study of the easy, highly efficient and continuously reversible phase transfer in aqueous/alcohols biphasic system. Significantly, the evaluation of stereoselective hydrogenation of diphenylacetylene (DPA) makes our work more instructive in the liquid/liquid biphasic catalysis, especially the separation and recycling of nanostructured materials and catalysts.

2. Experimental

2.1 Materials.

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Dihydrogen hexachloroplatinate(IV) hexahydrate (H₂PtCl₆.6H₂O, 99.9%, metals basis), ruthenium(III) chloride hydrate (RuCl₃.xH₂O, 99.9%, PGM basis, Ru 38%), iridium(III) chloride hydrate (IrCl₃.xH₂O, 99.9%, metals basis), sodium tetrachloropalladate(II) hydrate(PdNa₂Cl₄.xH₂O, 99.95%, metals basis, Pd 30%), hydrogen tetrachloroaurate(III) trihydrate(HAuCl₄.3H₂O, ACS, 99.99%, metals basis, 49.5%) were purchased from Alfa Aesar, and then adding distilled water to dissolve each kinds of noble metal salts, completely, with a final concentration as 1 mg/mL. 1-Butanol was supplied from Fluka. 1-Pentanol, toluene and n-heptane were purchased from Kermel. 1-Hexanol and cyclohexanol were purchased from Tianjin Guangfu Fine Chemical Research Institute. 1-Heptanol was obtained from Energy Chemical. All these chemical agents were analytical reagent and purified by distillation from an appropriate drying agent under inert atmosphere for all synthetic process as well as the phase transfer process. Diphenylacetylene (DPA) was purchased from Alfa Aesar. Thermoregulated ligand Ph₂P(CH₂CH₂O)_nCH₃ (n=22) was prepared according to the method reported in the literature.²²

2.2 Synthesis of noble metal nanoparticles.

In a typical experiment, 1 mL of aqueous solution of $H_2PtCI_6.6H_2O$ (1.931 \times 10⁻⁶ mol), 4.52 mg of thermoregulated ligand $Ph_2P(CH_2CH_2O)_{22}CH_3$ (3.862 \times 10⁻⁶ mol), 3 mL of deionized water, 4 mL of 1-pentanol were added in a 75 mL teflon-lined standard stainless-steel autoclave and stirred under hydrogen (4 MPa) at 70 °C for 2 h. Then the reactor was cooled to room temperature and depressurized. The color of the aqueous phase changed from nearly colorless to brown, indicating the formation of Pt nanoparticles (Pt-NPs). The synthesis of Ru, Ir, Pd, Au nanoparticles (Ru-NPs, Ir-NPs, Pd-NPs, Au-NPs) followed the above protocol (see ESI⁺ for full experimental details).

2.3 Continuously reversible phase transfer.

All manipulations about the continuously reversible phase transfer of NMNPs were same, thus we would take Pt-NPs for instance. The fresh Pt-NPs solution (4 mL) and 1-pentanol (4 mL) were added into a 20 mL Schlenk tube, and then stirred and heated in a 70 $^{\circ}$ C thermostatic oil bath for several minutes under a nitrogen atmosphere. Soon we would observe the Pt-NPs transfer from aqueous to 1-pentanol. After that, the Schlenk tube was cooled to room temperature for enough

time, and the Pt-NPs could transfer from 1-pentanol phase to aqueous phase. Next, when further continued to heat up and cool down, the same phenomenon could be observed, repeatedly.

2.4 Measurement of phase transfer temperature

The as-prepared Pt-NPs solution (4 mL) and 1-pentanol (4 mL) were added into a 20 mL Schlenk tube under a nitrogen atmosphere. Then, the Schlenk tube was stirred and heated in a thermostatic oil bath. Raising temperature of the oil bath slowly, we can observe the phase transfer of Pt-NPs. When the aqueous phase was completely colorless and transparent, and then recorded the temperature. Repeated the procedure three times and averaged. Next, other organic solvents including 1-butanol, 1-hexanol, cyclohexanol, 1-heptanol, toluene, and *n*-heptane were used instead of 1-pentanol, respectively. The measurement of phase transfer temperature of other metal nanoparticles in different organic solvents was the same as Pt-NPs.

2.5 Phase transfer under different gas atmospheres.

Similarly, we used the Pt-NPs as an example. The fresh Pt-NPs solution (4 mL) and 1-pentanol (4 mL) were added into a 20 mL Schlenk tube, and then stirred and heated in a 70 $^\circ C$ thermostatic oil bath for half an hour under a nitrogen atmosphere. Afterward, the system was cooled to room temperature for several hours. The entire procedure should be kept attention. Next, we would respectively duplicate this operation under hydrogen, carbon monoxide, and air atmosphere.

2.6 Evaluation of phase transfer efficiency.

In brief, a series of experiments about the phase transfer efficiency after cooling for different time were performed. The freshly prepared NMNPs phase transfer between aqueous (4 mL) and 1-pentanol (4 mL) were carried out in a 75 mL teflon-lined standard stain-steel autoclave pressurized with a 2 MPa N₂, stirred and heated in a 70°C thermostatic oil bath for half an hour. Subsequently, the autoclave was placed in an icewater bath to cool for 0.5 h, 1 h, 2 h, 3 h, 4 h, 5 h, and 10 h, respectively, and then depressurized and obtained the 1-pentanol phase by simple phase separation. After microwave-assisted sample digestion of the obtained organic phase, we could calculate the metal content by ICP-AES analysis.

2.7 Catalytic application.

The hydrogenation reactions were carried out in a 75 mL teflon-lined standard stain-steel autoclave immersed in a thermostatic oil bath. The autoclave was charged with the asprepared Pt-NPs, water, 1-pentanol, DPA and *n*-decane (as internal standard) and flushed 5-6 times with 1 MPa H₂. The reactor was pressurized with H₂ up to the required pressure and held at the scheduled temperature for a fixed length of time. Then, the reactor was cooled to room temperature and depressurized. The upper 1-pentanol phase was separated by simple phase separation and immediately analyzed by GC and GC-MS.

2.8 Material characterization.

The size of NMNPs (Pt, Ru, Ir, Pd, and Au) was characterized by transmission electron microscopy (TEM). The solution containing the NMNPs (Pt, Ru, Ir, Pd, and Au) was diluted with

ethanol. Then, several drops of the solution were placed onto a carbon-coated copper grid, which was dried at ambient temperature. The TEM images were taken with a Philips Tecnai G^2 20 TEM at an accelerating voltage of 200 kV. All reported data were presented as mean values \pm standard deviation obtained from three replicates. The samples for the ultraviolet-visible (UV-vis) measurement were prepared via diluting the NMNPs solution by the addition of ethanol, with the resulting solutions analyzed in quartz cuvettes. The UV-vis instrument was a Ruili double beam UV-vis spectrophotometer with a spectral window range of 190 nm to 800 nm. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses of all metal elements were carried out on Optima 2000DV (Perkin Elmer, USA).

3. Results and discussion

3.1 Characterization.

Although we synthesized Rh nanoparticles using hydrogen as a reducer in a previous literature,²⁰ there were few reports, in the field of phase transfer, on the preparation of other metal nanoparticles using hydrogen reduction because it was not easy to achieve a sufficient dispersion stability and a narrow size distribution in the aqueous/organic biphasic system. For the study reported here, thermoregulated ligand



Fig 1. TEM micrographs and particle size histograms of different NMNPs: (A1-2) Pt-NPs, (B1-2) Ru-NPs, (C1-2) Ir-NPs, (D1-2) Pd-NPs, (E1-2) Au-NPs.

Ph₂P(CH₂CH₂O)₂₂CH₃ was extensively explored to synthesize NMNPs (Pt, Ru, Ir, Pd and Au) via hydrogen reduction method in an aqueous/1-pentanol biphasic system. Compared with other reduction methods such as using sodium borohydride, lithium aluminum hydride or lithium triethylborohydride as reducing agent, hydrogen reduction method for preparing NMNPs was very clean, nonpolluting and available to avoid the reduction of many chemical functional groups. Furthermore, 1-pentanol being the organic phase was not only an expedient solvent as it was polar enough to dissolve various inexpensive metal precursors, but also can effectively facilitate the formation of NMNPs.

It was very interesting that the as-prepared NMNPs displayed various colors (Fig S1, ESI⁺). Compared with the brown Pt-NPs, Pd-NPs had a nigger-brown color; Ir-NPs and Ru-NPs displayed a brownish black color; while Au-NPs had a pleasurable red color. The mixed solutions of thermoregulated ligand/metal precursors $(H_2 PtCl_6.6H_2O)$ RuCl₃.xH₂O, IrCl₃.xH₂O, PdNa₂Cl₄.xH₂O, HAuCl₄.3H₂O) in water-ethanol before reduction exhibited different UV-vis characteristic absorption peaks at 259 nm, 246 nm, 325 and 384 nm, 346 nm, and 304 nm, respectively, due to the charge-transfer transition between metal ions and thermoregulated ligand (Fig S2, ESI⁺). And then after reduction, the disappearances of their characteristic absorption peaks showed the formation of nanoparticles. As for Au-NPs solution, however, a new broad absorption peak emerged at 524 nm, which was similar to previous literature report.²³

TEM micrographs and particle size histograms of different NMNPs (Pt, Ru, Ir, Pd, and Au) (see Fig 1) showed that the asprepared NMNPs (Pt, Ru, Ir, Pd, and Au) had a mean diameter of 1.9 ± 0.4 nm, 1.7 ± 0.4 nm, 2.0 ± 0.3 nm, 3.4 ± 0.6 nm, and 4.8 ± 1.5 nm, respectively, and displayed a good particle dispersibility. Such results sufficiently confirmed that our synthesized protocol could provide a facile and versatile strategy to prepare NMNPs (Pt, Ru, Ir, Pd, and Au) with a comparatively narrow size distribution and good dispersion stability in the aqueous/1-pentanol biphasic system.

3.2 Effect of phase transfer parameters: organic solvents, temperature, and gas atmospheres.

Seven different solvents, namely 1-butanol, 1-pentanol, 1hexanol, cyclohexanol, 1-heptanol, toluene, and n-heptane, were employed as the organic phase in this study. Owing to a suitable hydrophile-lipophile balance in the amphiphilic ligand Ph₂P(CH₂CH₂O)₂₂CH₃ and based on the cloud point of this amphiphilic molecule in water, the as-prepared NMNPs (Pt, Ru, Ir, Pd, and Au) successfully performed the transfer from aqueous to alcohols, however, gave rise to a partial transfer in toluene and had a failure transfer in *n*-heptane (e.g., Ir-NPs for different organic solvents, Fig S3, ESI⁺). Furthermore, we also measured the as-prepared NMNPs phase transfer temperature in different organic solvents (Table 1). It was very clear that different NMNPs had an identical or a slight difference in terms of transfer temperature in the same organic solvent, while the same metal nanoparticles produced a distinct transfer temperature in various organic solvents.

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Table	1.	The	phase	transfer	temperature	of	NMNPs	in
aqueo	us/	orga	nic solv	ents. [ª]				

Organic solvents	Phase transfer temperature of different NMNPs				different
	Pt	Ir	Ru	Pd	Au
1-butanol	46 ℃	46° ℃	47 ℃	46 ℃	45 ℃
1-pentanol	49 ℃	51° C	52° C	52 ℃	51° C
1-hexanol	51° C	54° C	62 °C	54 °C	55° ℃
cyclohexanol	57 ℃	59° C	65 ℃	60 °C	60 ℃
1-heptanol	61° C	62° C	69° C	62 °C	63 ℃
toluene	partial	partial	partial	partial	partial
<i>n</i> -heptane	no	no	no	no	no

[a] For each organic solvent, "partial" indicates a partially phase transfer, and "no" indicates that no phase transfer occurred.

already realized thermoregulated ligand We had $Ph_2P(CH_2CH_2O)_nCH_3$ -stabilized (n = 16 and 22) Rh nanoparticle phase transfer in the aqueous/1-butanol (or 1-pentanol) biphasic system, but the mechanism of phase transfer was not clear. As we know, polyethylene glycol (PEG) has a good solubility in water and alcohols due to the formation of intermolecular H-bonds. Moreover, the transfer of PEG molecules from water to organic solvents is an endothermic process. This phenomenon had been reported.²⁴ Analogous to this transfer mechanism, the general principle of such behavior of the as-prepared NMNPs can be schematically depicted as follows (Fig 2). The system consists of aqueous and organic phases, namely the upper 1-pentanol phase and the lower water phase. They are immiscible with each other and separated into two layers with a clear interface. The asprepared NMNP is in the water phase at room temperature. Afterward, the water/1-pentanol mixture is heated gradually to a higher temperature under stirring. Then we can observe that the as-prepared NMNP is transferred into the upper 1pentanol phase due to the cleavage of H-bonds in water phase and the regeneration of H-bonds in 1-pentanol phase. As soon as the system is cooled to room temperature, the as-prepared NMNP could return to the aqueous phase. What's more, this process is continuously reversible. Mao et al. demonstrated the hydrogen-bond-selective method for directing hydrophobic NPs to transfer from organic to aqueous phase via ligand exchange strategy.¹⁴ More recently, a work about the transfer of large gold nanoparticles from water to organic solvents using thiolated polyethylene glycol (PEG-SH) as a phase transfer agent was also reported.²⁵ However, their design did not reversibly transfer colloidal particles. By contrast with previous aimlessly choosing organic media, the above explanation and proven provided a theoretically and experimentally significant predication for our further work.

In order to systematically study the thermoregulated phase



Fig 2. General principle of thermoregulated ligand $Ph_2P(CH_2CH_2O)_{22}CH_3$ -stabilized NMNPs phase transfer

transfer system, several experiments about the NMNPs stability in different gas atmospheres, such as carbon monoxide, hydrogen, nitrogen and air, during the phase transfer process, were performed. Obviously, the NMNPs preserved phase transfer property without any visible aggregation under the atmosphere of carbon monoxide, hydrogen, and nitrogen (Fig S4-6, ESI⁺). However, all NMNPs lost the ability to transfer from aqueous to organic solvent due to amounts of agglomeration in air (Fig S7, ESI⁺). The liable oxidizability of thermoregulated phosphine ligand at high temperature in air resulted in its failure to stabilize NMNPs.

3.3 Continuously reversible phase transfer and phase transfer efficiency evaluation.

In our work, thermoregulated ligand could not only stabilize NMNPs very well through a strong ligand-nanoparticle interaction, but also play a role of phase transfer agent by means of changing temperature. With these thoughts in mind, we did a series of experiments to verify the continuously reversible phase transfer ability in aqueous/1-pentanol biphasic system.

Fig 3 showed that the reversible phase transfer of the asprepared NMNPs, after one cycle of heating and cooling, could be easily observed between aqueous and 1-pentanol without any sign of aggregation, visually. Moreover, we could know that (Fig S8-12, ESI⁺) the as-prepared NMNPs had a narrow size distribution during the phase transfer process. Careful analysis of the diameter of the NMNPs revealed that Pt-NPs, Ru-NPs, Ir-NPs, and Pd-NPs had a slight decrease (1.8 ± 0.4 nm, 1.6 ± 0.3 nm, 1.9 ± 0.4 nm, and 3.1 ± 0.5 nm, respectively), while Au-NPs had an evident increase (a mean diameter of 8.7 \pm 2.2 nm). In addition, the test of ICP-AES in the lower aqueous phase had been performed when metal nanoparticles transferred into the upper 1-pentanol phase; the result indicated that most of thermoregulated ligand Ph₂P(CH₂CH₂O)₂₂CH₃ (up to 92%) moved into the upper 1pentanol phase with nanoparticles during the phase transfer step. Subsequently, six consecutive cycles of heating and



Fig 3. Continuously reversible phase transfer photographs for the as-prepared NMNPs: (A) Pt-NPs; (B) Ru-NPs; (C) Ir-NPs; (D) Pd-NPs; (E) Au-NPs, in the aqueous (the lower)/1-pentanol (the upper) biphasic system.

cooling were carried out. To our surprise, the as-prepared NMNPs successfully achieved the goal. It was noteworthy that the lower aqueous phase displayed completely clear and transparent without any color after each heating (Fig 3). The test of ICP-AES showed that there were no metallic residues for Ru, Ir, Pd, and Au, and the Pt content in the aqueous phase was no more than 0.1 %. According to the TEM image information (Fig S8-12, ESI⁺), their mean diameters (Pt, Ru, Ir and Pd) had a further slight decrease (a diameter of 1.7 ± 0.3 nm, 1.5 ± 0.3 nm, 1.8 ± 0.4 nm, and 3.1 ± 0.5 nm, respectively), but Au-NPs had a relatively larger mean diameter of 10.3 ± 2.4 nm. Similar results have been reported in the literature.²⁶ The available experimental data showed that our protocol was also effective when metal nanoparticles were about 10 nm.

More explanations for this behavior of Au-NPs could be found from a few literature reports.^{27,28} Two possible pathways can be considered. The first involved stepwise aggregation in which smaller nanoparticles became "activated", and then these "activated" particles were slowly subjected to those large particles leading to larger particles creation until the supply of smaller nanoparticles was exhausted. The second implied that these particles underwent decomposition in dilute solution and at elevated temperatures to produce larger nanoparticles due to the inherent instability of these phosphine ligand stabilized Au-NPs. Given the two possible pathways, we respectively added doubling and tripling amount of thermoregulated ligand to the as-prepared Au-NPs aqueous solution for obtaining better stabilizing effect, and then performed a six consecutive reversible phase transfer experiment. In that case, the TEM measurements (Fig S13, ESI⁺) indicated a similar size distribution of the resulting Au-NPs. Such results, to some extent, provided a contrary evidence for the second possible pathway.

We performed a test of ICP-AES, which had a detectable limitation of 5 $\mu g/L$ to accurately ascertain metallic residues



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Fig 4. The NMNPs transfer efficiency from 1-pentanol to aqueous after a reversible phase transfer.

in the upper organic phase after a reversible phase transfer process. To our surprise, all NMNPs phase transfer efficiencies were more than 99.9% (Fig 4). It was important to note that the larger the metal nanoparticles, the faster the phase transfer rate. As we know, one of the main disadvantages of soluble NMNPs catalysts in liquid/liquid biphasic system is the problem of separating the catalyst from the products. our protocol, in which the NMNPs catalysts transfer into organic phase to catalyze the reaction at higher temperature and return to aqueous to be separated from the products at lower temperature, affords an attractive solution to this problem.

3.4 The catalytic hydrogenation of DPA.

Semihydrogenation of alkynes is a key reaction in organic chemistry, which has been widely used in the synthesis of bioactive molecules, flavors, and natural products.^{29,30} Seeing that our protocol provided an easy, highly efficient, and continuously reversible phase transfer ability for NMNPs, we firstly employed the as-prepared Pt-NPs as catalysts for the hydrogenation of DPA to evaluate the catalytic activity, selectivity, and reusability.

Various reaction conditions for the hydrogenation of DPA were studied and the results were summarized in Table 2. The effect of reaction temperature was investigated in the range of 40-80 °C at 1 MPa H₂ for 20 min (Table 2, Entry 1-5). With the increasing of reaction temperature, the conversion of DPA increased from 19% to approximately 100%, and the stereoselectivity to cis-stilbene (Cis-ST) had a slight decrease. In the range from 0.5 to 3 MPa (Table 2, Entry 4, 7, 8, 9), we can know that the stereoselectivity to cis-stilbene also had a slight decrease. To our surprise, the product of complete hydrogenation to diphenylethane (DPE) had not been detected during the process of changing reaction conditions. Therefore, the as-prepared Pt-NPs exhibited a very high catalytic activity the semihydrogenation of DPA and a better to stereoselectivity to cis-stilbene.

Once the optimal reaction condition was selected, it was employed for other metal nanoparticles in the hydrogenation

Table 2. Semihydrogenation of	DPA using the a	s-prepared Pt-
NPs. ^a		

DP	DPA			ans-ST cis-ST		
	Temp		DPA	Selectivity	/ (%) ^[c]	
Entry	(°C)	(MPa)	conv. (%) ^[b]	Trans-ST	Cis-ST	
1	40	1	19	11	89	
2	50	1	34	12	88	
3	60	1	67	12	88	
4	70	1	> 99	14	86	
5	80	1	> 99	19	81	
6 ^[d]	70	1	59	14	86	
7	70	0.5	66	13	87	
8	70	2	> 99	17	83	
9	70	3	> 99	17	83	

^a Reaction conditions: 1-pentanol 4 mL, water 4 mL containing 1.931×10^{-3} mmol Pt-NPs, DPA/Pt = 500 (molar ratio), 100 mg of *n*-decane as internal standard, 20 min. ^b Determined by GC ^cDiphenylethane (DPE) was not found. ^d Reaction time, 10 min.

of DPA. The results (Table S1, ESI⁺) indicated that Au-NPs didn't show any catalytic activity, while Ru-NPs and Ir-NPs exhibited a very low catalytic activity. As for Pd-NPs, however, it produced a very high stereoselectivity to *cis*-stilbene up to 99%, though there was a relatively low catalytic activity compared with Pt-NPs. To our satisfaction, all the catalysts were able to achieve the separation from products, and successfully recycled.

Next, the reusability of the as-prepared Pt-NPs was examined. After reaction, the upper 1-pentanol phase was separated from the lower catalyst-containing phase by simple phase separation. And the lower catalyst-containing phase was directly reused in the next reaction run. Under the identical reaction conditions to entry 4 in Table 2, the recovered Pt-NPs were reused for 13 times without evident decrease in



Fig 5. Recycling efficiency of the as-prepared Pt-NPs for the stereoselective semihydrogenation of DPA

conversion and stereoselectivity (Fig 5). In general, the as-
prepared Pt-NPs catalyst exhibited a very high turnover
number (TON) of 7400 for the semihydrogenation of DPA,
which was far superior to most of the hitherto known catalysts,
such as Pd, ^{31,32} Pt, ³³ Ru, ³⁴ and Rh. ³⁵

4. Conclusions

In summary, we report on an easy, highly efficient, and continuously reversible phase transfer process directed towards NMNPs (Pt, Ru, Ir, Pd, and Au) in an aqueous/1pentanol biphasic system. By comparing a series of organic solvents (alcohols, toluene, and *n*-heptane), we reveal the essence of thermoregulated phase transfer, namely a reversible hydrogen-bond-selective process. Due to the special structure of thermoregulated ligand Ph₂P(CH₂CH₂O)₂₂CH₃, suitable gas atmospheres (carbon monoxide, hydrogen, nitrogen) are found decisive for the successful phase transfer of NMNPs. After six cycles of reversible phase transfer, the NMNPs (Pt, Ru, Ir, and Pd) size and distribution almost remain constant, while the size of Au-NPs has an obvious increase. With the aid of ICP-AES, we can know that the phase transfer efficiency of NMNPs from 1-pentanol to aqueous or vice versa isn't less than 99.9%. In contrast with other reversible phase transfer protocols,^{36,37} which needed supplementary phase transfer agents, ligands, or reagents, our protocol has almost the best reversible phase transfer ability. Moreover, we successfully demonstrate the feasibility of separation and recycling of the as-prepared Pt-NPs catalyst, which exhibits exceptionally high catalytic activity, better stereoselectivity, and excellent reusability in the semihydrogenation of DPA. Herein, we anticipate that our protocol not only provides an innovative avenue for the development of the NMNPs phasetransfer technology but also is found to be very effective for the in situ separation and recycling of NMNPs catalysts.

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Insert Table of Contents Graphic and Synopsis Here

We mainly expanded an easy, highly efficient, and continuously reversible hydrogen-bond-selective phase transfer directed towards noble metal (Pt, Ru, Ir, Pd, and Au) nanoparticles.

