Demonstration of a magnetic and catalytic Co@Pt nanoparticle as a dual-function nanoplatform†

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Co@Pt nanoparticles as a bifunctional nanoplatform system for the hydrogenation of various unsaturated organic molecules under mild conditions and also for magnetic separation and recycling are demonstrated.

Nanoparticles (NPs) with extremely large surface areas can possess various functions, such as catalytic, magnetic, electronic and optical properties. In particular, with the emerging interest in developing versatile NPs for nanoplatform technologies, NPs exhibiting more than two functions are highly desirable for simultaneous and efficient technological applications. NPs with a core–shell structure are one of the promising candidates for integrating multiple functionalities into a single NP system.[1] Such core–shell nanostructures have been shown to be very useful for enhancing or modifying the properties of NPs, such as the surface plasmonic effect observed in the SiO_2@Au nanoshell and bimetallic nanocatalysts, for example the Co–Rh system.[2] Although the large surface area of NP-based catalysts is the key component of their catalytic activity,[3–5] as the size of the particle decreases to a nanometer scale, its separation step becomes harder and particle agglomeration during the reaction or separation process becomes a troublesome issue.[5] To circumvent such problems in nanocatalyst synthesis, various possibilities have been examined. For example, catalytic Pt NPs can be stabilized by large organic polymers or encapsulated within porous materials such as zeolites.[6] Herein, we present the core–shell Co@Pt NP and demonstrate both the catalytic activity (hydrogenation) of its Pt shell and the superparamagnetism of its Co core, which allows for the convenient separation and recycling of the nanocatalyst (Fig. 1). To our knowledge, our study is one of the first demonstrations of magnetically recovering heterogeneous catalytic NPs,[7] although examples of homogenous organometallic catalysts ligated with magnetic NPs have been reported previously.[8]

Our core–shell-type platinum NP catalyst (**1**) can provide advantages over single Pt component-based systems: Firstly, it is "atomically economical" because precious Pt metal can be conserved by replacing the interior of the NPs with other, inexpensive core metals.[9] Secondly, the additional functionality of the magnetic cobalt core[10] plays a critical role in the separation and recycling of the catalyst.

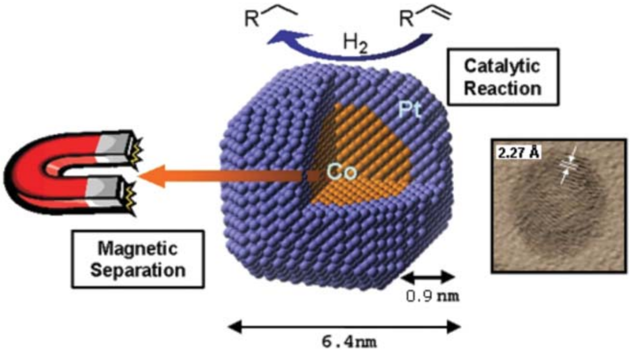

Fig. 1 The dual functionality of Co@Pt core–shell NPs. Insert: The HRTEM image of a single NP. 2.27 Å represents the lattice constant of the Pt shell.

The core–shell type-cobalt–platinum NPs were prepared by a redox transmetalation reaction between $Pt(hfac)_2$ and cobalt NPs.[11] The platinum forms a shell around the cobalt core and the shell surface is stabilized by dodecyl isocyanide capping molecules (Fig. 1). After the formation of the core–shell structure, the NP retains its magnetic properties, with a blocking temperature (T_B) of 15 K and a coercivity of 660 Oe at 5 K, indicating single domain superparamagnetism at room temperature. The particle size averages 6.4 nm with a cobalt core diameter of 4.6 nm; its overall stoichiometry being $Co_{0.45}Pt_{0.55}$. According to elemental analysis and high resolution transmission electron microscopy (HRTEM) data, the thickness of the Pt layer is about $\sim$0.9 nm, which corresponds to $\sim$4 layers of Pt.[11] A particle size of 6.4 nm was chosen because it gives a high colloidal stability while keeping a high surface area of Pt and strong magnetism. It is desirable to minimize the use of Pt as much as possible for economic reasons. In contrast, if the particle becomes too small (*e.g.* < 5 nm), the cobalt core also becomes smaller and does not have a strong enough magnetism for magnetic recycling processes. In short, our rationale for selecting the NP composition and size was to have 1: a high surface area for the Pt shell with minimum use of it, 2: retention of high magnetism for recycling purposes and 3: high colloidal stability for the dispersion of the nanocatalysts into the reaction solution. Since our core–shell cobalt–platinum NPs are well dispersed in a typical organic medium, we investigated the catalytic activity and recyclability of **1** towards hydrogenation, using 1-decene as a model substrate (Table 1).

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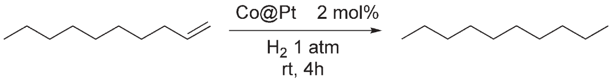
Table 1 Catalytic hydrogenation of 1-decene by **1** with catalyst recycling[a]



Run	1	2	3	4	5	6	7
Yields(%)[b]	100	100	100	100	100	100	100

[a] Reaction conditions: Substrate 0.25 mmol, 1-decene/Pt atom = 50 (2 mol%), toluene 0.1 mL, 1 atm H_2 (using toy balloon), room temperature. [b] Determined by GC and GC–MS.

When the hydrogenation of 1-decene in the presence of a catalytic amount of **1** under a H_2 atmosphere was carried out for 4 h at room temperature (see ESI† for details†), a complete conversion of 1-decene to *n*-decane was observed (Table 1, run 1).

Another functional feature of our core–shell NPs is the manner in which the catalyst recycles itself by magnetic auto-separation. Initially, all the black-colored Co@Pt nanocatalysts were collected on the central part of a stirring bar due to magnetic attraction (Fig. 2(a)1). However, when **1** was stirred in solution, it was fully dispersed by the centrifugal force (Fig. 2(a)2), giving rise to the desired nanocatalytic functions.

When stirring ceased, **1** spontaneously returned to the stirring bar through magnetic interaction (Fig. 2(a)3–5).[11] After the catalytic reaction and catalyst isolation process, the recovered **1** can be directly reused in subsequent hydrogenation reactions (Fig. 2(b)).

In fact, the reused NPs retained the same catalytic activity as that of freshly prepared NPs after up to seven cycles (Table 1, runs 2–7). For comparison, we performed the catalyst recycling experiments by using platinum on activated carbon (Pt/C) as the catalyst under the same hydrogenation conditions applied to **1**, except the reaction time (1 h per cycle). The catalytic activity of Pt/C started to diminish from 100 to 76% conversion after the second cycle, even though the total exposure period of Pt/C in the catalytic process was much shorter than that of **1** (3 h *vs.* 28 h).[12] TEM analysis clearly shows that the particle size and composition of **1** was unchanged, and that no aggregation occurred during or after the recycling procedure (Fig. 3 and ESI†).

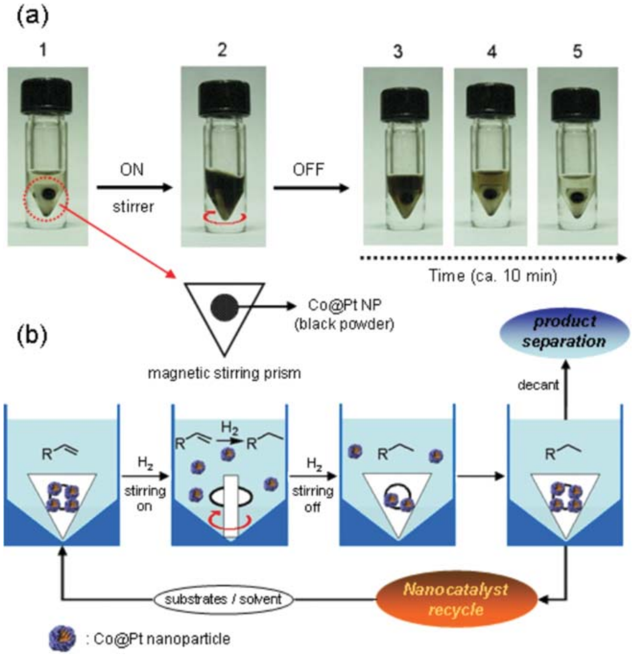


Fig. 2 (a) Visualization of the nanocatalyst collection process using a magnetic bar (details of the stirring bar are graphically presented): (1) Nanocatalyst on the magnetic bar. (2) During stirring. (3–5) Collection of NPs on the magnet after reaction. (b) Schemes for the procedures of catalyst reaction and the recycling.

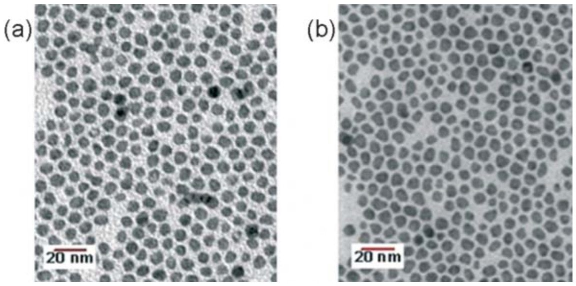


Fig. 3 TEM image of **1** showing the conservation of core–shell structure and monodispersity without deformation: (a) Before reaction. (b) After recycling.

We further investigated the scope of the substrates as well as the chemoselectivities of the Co@Pt NP catalytic hydrogenation system. The results are summarized in Table 2.‡

Catalyst **1** smoothly promotes the hydrogenation of various olefins and alkynes under very mild conditions. The position and structure of the olefins did not affect the reactivity of **1** towards them: terminal, internal, conjugated or isolated (Table 2, entries 1–4). The catalytic hydrogenation of alkynes into their corresponding saturated alkanes was facile, regardless of whether internal or terminal alkynes were used (Table 2, entries 5–8). However, the reaction of diphenylacetylene did not proceed as rapidly as expected, probably due to the unfavorable steric interaction between the two phenyl groups of the diphenylacetylene and the capping molecules on the surface of the NPs (Table 2, entry 9). One interesting thing to note is that this catalytic system exhibited near perfect selectivity when reducing the carbonyl group of aldehydes to the corresponding alcohol upon hydrogenation in the presence of ketone. For example, when benzaldehyde and cyclohexanone were applied to this hydrogenation, only benzaldehyde was converted to benzyl alcohol (Table 2, entries 10 and 11). Hydrogenation of 2-cyclohexenone and cinnamaldehyde was carried out using this catalytic system, and cyclohexanone and hydrocinnamalcohol were obtained, respectively, which also confirms the selectivity of the process (Table 2, entries 12 and 13).[5b] This type of dramatic selectivity can be explained as follows: The sterically less-hindered carbonyl group of aldehydes, compared to ketones, might more readily approach to the catalytic surface of **1** by minimizing its possible unfavorable steric interaction with the capping molecules. Interestingly, the nitro group could also be reduced to an amine group without any noticeable catalytic deactivation (Table 2, entries 14 and 15).[13]

In summary, we have demonstrated the efficacy of Co@Pt NPs as a bifunctional nanoplatform system for the hydrogenation of various unsaturated organic molecules under mild conditions, and also demonstrated their magnetic separation and recycling

Table 2 Hydrogenation of various substrates[a]

Entry	Substrate	Product	Time/h	Conversion (%)[b]
1	1-Decene	*n*-Decane	4	100
2	1,5,9-Decatriene	*n*-Decane	4	100
3	Cyclododecene	Cyclododecane	4	100
4	Styrene	Ethylbenzene	6	100
5	1-Octyne	*n*-Octane	8	100
6	4-Octyne	*n*-Octane	10	100
7	3-Phenylpropyne	Propylbenzene	4	100
8	1-Phenylpropyne	Propylbenzene	4	100
9	Diphenylacetylene	1,2-Diphenylethane	14	17
10	Benzaldehyde	Benzylalcohol	16	100
11	Cyclohexanone	—	12	0
12	Cinnamaldehyde[c]	Hydrocinnamylalcohol	10	100[c]
13	2-Cyclohexenone	Cyclohexanone	7	100
14	Nitrobenzene	Aniline	4	100
15	2-Bromonitrobenzene	2-Bromoaniline	16	100[d]

[a] Reaction conditions: Substrate 0.25 mmol, substrate/Pt atom = 50 (2 mol%), toluene 0.1 mL, 1 atm H_2 (using toy balloon), room temperature. [b] Determined by GC and GC–MS. [c] Mixture of partially and fully hydrogenated products. [d] Containing less than 1% of debrominated product.

capabilities. This kind of bifunctional core–shell NP may provide useful applications in various types of transition metal-based catalytic reaction.

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‡ It is noteworthy that we have not observed any hydrogenation product from the capping molecule in any of these catalytic reactions.

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