

Supported Pd Nanocatalysts onto Ionic Silica-Coated Magnetic Particles for Catalysis in Ionic Liquids[†]

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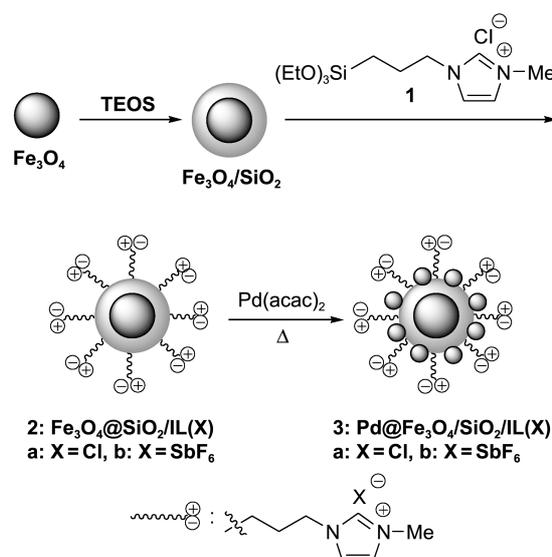
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Due to size effects as well as structure/function relationships, metal nanoparticles (NPs) account for such excellent catalytic activity in so many reactions that the nanoparticle catalysts are attracting tremendous interest.¹ However, such NPs having very active surface atoms, can often lead to kinetic liability with respect to inter-particle aggregating to their bulk forms, which undoubtedly are apt to decrease catalytic activity. This problem has been approached by a variety of methods, e.g., the addition of additive stabilizers or supporting the NP catalysts on solid materials.^{1d-1f} As quasi-homogeneous catalysts, additive-stabilized NP catalysts show high catalytic activity, but difficulty separating them for reuse limits their practical applications. In contrast, solid-supported NP catalysts allow easy recycling as they work heterogeneously, but they often display significant loss of catalytic activity.

Ionic liquids (ILs) are attracting considerable attention as an alternative medium for catalysis as well as for the formation of nanomaterials.² Since the first report by Dupont *et al.* on the formation of NP catalysts in ILs,³ many studies have suggested that imidazolium-based ILs stabilize NP catalysts electrostatically and/or by coordination involving the imidazolium cations.⁴ Indeed such imidazolium-based ILs are believed to be effective stabilizers for NP catalysts, but the inevitable self-aggregation has been determined in some cases to result in loss of catalytic activity. One promising solution is immobilization of NP catalysts on high-surface-area nanosupports, which not only stabilize the NP catalysts, but also make easy the recovery and reuse of the NP catalysts. Recently, Kou *et al.* have reported that NP catalysts supported on vinyl-imidazolium salt/styrene copolymers show increased stability in ILs.⁵ Quite recently, we also found that palladium NP catalysts supported on imidazolium-functionalized ionic carbon nanotubes show an extraordinary stability with high catalytic activity for hydrogenations of olefins in an isopropanol (IPA)/IL biphasic solvent system.⁶ Since it has been known that imidazolium-based ionic liquids have head-to-tail arrangements,⁷ it would be reasonable to assume that the high stability of these supported NP catalysts in ionic liquid may largely be related with the discriminative formation of micelle-like frameworks *via* an alternative head-to-tail ar-

rangement of ionic liquid over the imidazolium-functionalized nanosupport materials, which could prevent self-aggregation of NP catalysts. Based on these considerations, we reasoned that the palladium NPs supported on the ionophilic spherical magnetite coated with imidazolium-functionalized silica (hereafter denoted as Pd@Fe₃O₄/SiO₂/IL) would invoke secondary interactions with ILs to form micelle-like spherical ionic multilayers. This approach allowed stable catalyst dispersion without aggregation of the supported palladium NP catalysts in a medium of IL. Moreover, we also hypothesized that the micelle-like spherical ionic multilayer would form molecular gates for the substrate's diffusion, making the reaction rate largely dependent on the effective size of the applied substrates.⁸ Utilizing a magnetite core in the supported catalysts achieves the additional advantages of highly efficient recovery and reuse. In the present paper, we report the synthesis of the recoverable ionophilic Pd@Fe₃O₄/SiO₂/ILs, showing substrate-size-dependant kinetics for the hydrogenations of *trans*-stilbene and styrene in ILs. Scheme 1 and Figure 1 show preparation and characterization data of palladium nanocatalysts supported on magnetite coated with imidazolium-functionalized silica



Scheme 1. Preparation of palladium nanocatalysts supported on magnetic nanoparticles coated with imidazolium salt-functionalized silica.

[†]This paper is dedicated to Professor Eun Lee on the occasion of his honourable retirement.

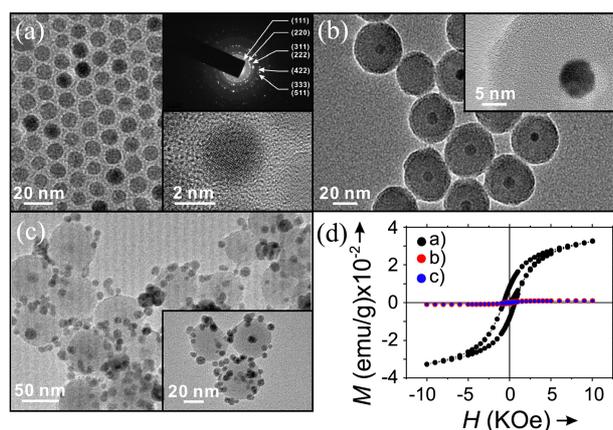


Figure 1. (a) HRTEM image for monodisperse Fe₃O₄ nanocrystals, their SAED pattern, and the lattice fringe of single nanocrystal (inset). (b) HRTEM image for IL-functionalized Fe₃O₄@SiO₂/IL(Cl) **2a**. No phase change over the mother particles was observed after silica coating and IL functionalization (inset). (c) HRTEM image for Pd@Fe₃O₄/SiO₂/IL(SbF₆) **3b**. (d) Field-dependant magnetization data at 300 K for each composites (●: Fe₃O₄, ●: Fe₃O₄@SiO₂/IL(Cl) **2a**, ●: Pd@Fe₃O₄/SiO₂/IL(SbF₆) **3b**).

(For details, see supporting information).

The monodisperse spherical magnetic nanocrystals, Fe₃O₄, having an average diameter of 6 nm, were first prepared from iron(III) chloride hexahydrate, according to the reported procedure.⁹ Figure 1(a) shows the typical HRTEM, high resolution trans-electron spectroscopy, image of monodisperse Fe₃O₄ nanocrystals exhibiting peaks in the corresponding selected area electron diffraction (SAED) (Figure S1) and powder X-ray diffraction (PXRD) patterns that well match the reflections of the spinel magnetite Fe(II)Fe(III)₂O₄, including the minor body-centered cubic (bcc) phase of Fe(0) (2θ = 43.16°) (Figure S5). The silica-coated magnetite NPs (Fe₃O₄@SiO₂) were prepared through the water-in-oil microemulsion technique using tetraethyl orthosilicate (TEOS).¹⁰ Grafting of the pre-synthesized triethoxysilane-functionalized imidazolium chloride **1** on the Fe₃O₄/SiO₂ surface afforded the ionic Fe₃O₄@SiO₂/ILs **2** having chloride anion. HRTEM images in Figure 1(b) confirm the core/shell structure of the Fe₃O₄@SiO₂/ILs **2** with the diameter ratio of 1:5. Most of the NPs are spherical with average diameter distribution around 30 nm. The mother core appears darker than the shell due to the difference in Debye-Waller factors arising from the distinct metal oxide types.¹¹ Finally, palladium NPs were deposited onto the ionic Fe₃O₄@SiO₂/ILs **2** to afford the supported palladium nanoparticle catalysts **3a**. Anion exchange with NaSbF₆ afforded the hydrophobic Pd@Fe₃O₄/SiO₂/ILs **3b** having SbF₆ anion. As shown in Figure 1(c), the palladium NPs with an average size of 7 nm were well deposited on the ionic supports. In data obtained by X-ray photoelectron spectroscopy, XPS, (Figure S3), both **3a** and **3b** show the characteristic Pd(0) peaks with Pd 3d_{3/2} and Pd 3d_{5/2} binding energies at 341 and 335 eV. Moreover, the best Rietveld result from the PXRD pattern of Pd@Fe₃O₄/SiO₂/ILs **3b** shows that no phase was observed except a face-centered cubic (fcc)

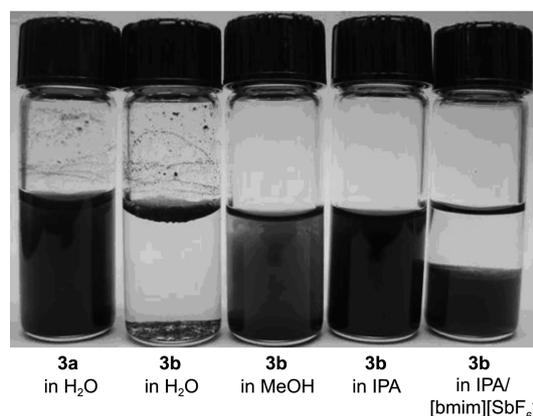


Figure 2. Photograph of the Pd@Fe₃O₄/SiO₂/ILs **3a** and **3b** in various solvent systems. The catalyst, Pd@Fe₃O₄/SiO₂/IL **3b**, are dissolved in the bottom layer of [bmim][SbF₆] ionic liquids.

phase of 7 nm-Pd(0) NPs (Figure S5). The elemental compositions of Pd@Fe₃O₄/SiO₂/ILs **3a** and **3b** were cross-confirmed by energy dispersive spectroscopy (EDS) and inductively coupled plasma-mass spectroscopy (ICP-MS) (Table S1), indicating palladium content of 3.04 mmol g⁻¹ for **3a** and 2.61 mmol g⁻¹ for **3b**. Furthermore, the magnetic properties of the Pd@Fe₃O₄/SiO₂/ILs **3a** and **3b** were confirmed by measuring the magnetization as a function of field (Figure 1(d)) allowing magnetic-assisted separation.

We first investigated the dispersion of Pd@Fe₃O₄/SiO₂/ILs **3a** and **3b**, into various solvents, for instance, water, methyl alcohol, IPA and IPA/[bmim][SbF₆] (where bmim = 1-butyl-3-methylimidazolium). As shown in Figure 2, the stable dispersions of Pd@Fe₃O₄/SiO₂/ILs **3b** with SbF₆ anion are observed in various solvents having a relatively low dielectric constant (ϵ): an IL medium of [bmim][SbF₆] ($\epsilon < 10$, RT),¹² IPA ($\epsilon = 18$, RT), MeOH ($\epsilon = 30$, RT) and water ($\epsilon = 80$, RT),¹³ in order of apparent solubility. Pd@Fe₃O₄/SiO₂/ILs **3a** possessing quite hydrophilic surfaces are well dispersed in water.¹⁴ As we observed in IL-functionalized CNTs,⁶ the hydrophobic Pd@Fe₃O₄/SiO₂/ILs **3b** were preferentially dispersed in a [bmim][SbF₆] layer of IPA/[bmim][SbF₆], which allowed catalysis in IPA/[bmim][SbF₆] biphasic solvent system.

We next investigated the catalytic activity of the Pd@Fe₃O₄/SiO₂/IL **3b** in monophasic IPA and biphasic IPA/[bmim][SbF₆] solvent systems for the hydrogenation of *trans*-stilbene and styrene, which were chosen as model compounds to examine the effects of substrate size on reaction rate. Although, there might be intrinsic reactivity discrepancy between these substrates, we assumed that compared with styrene, the *trans*-stilbene with pedal-like motion might have a two-fold effective size or even more (Figure S8), which might restrict the continuous diffusion through the micelle-like molecular gates formed *via* secondary interactions between ionophilic Pd@Fe₃O₄/SiO₂/ILs **3b** with [bmim][SbF₆]. Styrene could relatively be positive, overcoming such a short-range coulombic barrier of ordered zwitterions, as shown in Figure 3(a). Thus, the substrate selectivity on reaction rate, which is partly a result of steric conditions, should be noted in reaction

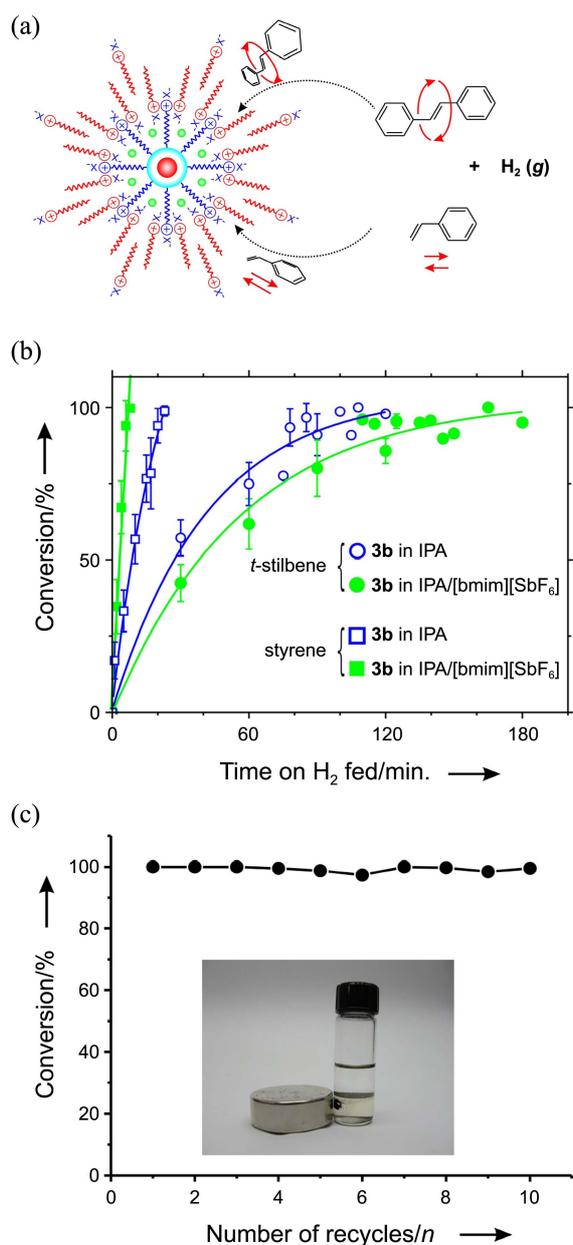


Figure 3. (a) Schematic presentation for formation of the substrate selective micellar molecular-gates over ionophilic Pd@Fe₃O₄/SiO₂/IL **3b** through shared π - π stacks of the ionic liquids. (b) The conversions (%) of substrates, *trans*-stilbene and styrene, vs time (minute) on hydrogen fed (1 atm) over the different catalyst systems. Reaction conditions: olefin/Pd molar ratio (100), P_{H_2} = 1 atm, and T = 25 °C. (c) Demonstration of magnetic separation of Pd@Fe₃O₄/SiO₂/IL **3b** in biphasic IPA/[bmim][SbF₆].

monitoring.

The hydrogenations were carried out in the presence of 1 mol % of catalyst (based on Pd content) under 1 atm H₂ pressure. The typical conversion-time profiles are presented in Figure 3(b) showing the experimental and fitted curves (also see Table S2). A negative apparent order toward both substrates could be rationalized from the regime of Langmuir-Hinshelwood kinetics, assuming a competitive adsorption of the reactants with weak non-dissociative adsorption of H₂.¹⁵

For the hydrogenation of *trans*-stilbene, it has been found that the catalytic activity (TOF: mol_{substrate}/mol_{Pd} per hour) of Pd@Fe₃O₄/SiO₂/ILs **3b** in monophasic IPA (TOF = 46 hr⁻¹) is slightly higher than that in biphasic IPA/[bmim][SbF₆] (TOF = 30 hr⁻¹). In contrast, styrene proceeded almost 3 times faster in biphasic IPA/[bmim][SbF₆], with a TOF of 833 hr⁻¹, than in monophasic IPA, where TOF was 275 hr⁻¹. Comparison of the catalyst activities from the same solvent system indicated that hydrogenation rates of *trans*-stilbene are slower than those of styrene, *i.e.*, TOF_{styrene}/TOF_{stilbene} ratios are 6 in IPA and 28 in IPA/[bmim][SbF₆]. If we assume that the TOF_{styrene}/TOF_{stilbene} ratio in IPA comes from the intrinsic reactivity differences of those substrates, a simple numerical calculation (833/30 × 6) indicates the TOF_{styrene} would be 4.6 times faster than the TOF_{stilbene} in IPA/[bmim][SbF₆]. These results suggest, as we hypothesized, that the supported ionophilic catalyst Pd@Fe₃O₄/SiO₂/ILs **3b** form micelle-like molecular channels with an ionic liquid, and the diffusion process of substrate into the active sites of palladium catalysts play a crucial role in the rate-determining step, which might be affected by the effective size of travelling substrates. Finally, we investigated the recyclability of the Pd@Fe₃O₄/SiO₂/ILs **3b**. It has been frequently observed that because of the mutual solubility between IL and the applied organic solvent used for product extraction, the catalysts immobilized in an ionic liquid often leached into the organic solvent. Moreover, separation of nanoparticulate materials generally requires special cautions because of their quasi-homogeneity in IL-medium. Fortunately, the supported Pd@Fe₃O₄/SiO₂/ILs **3b** on magnetite core was effectively separated magnetically (Figure 3(c)), and recycled 10 times in the hydrogenation of styrene without any significant loss of catalytic activity.

In conclusion, we have synthesized recyclable palladium nanocatalysts supported on ionophilic magnetite coated with imidazolium salt-functionalized silica. The catalytic activity of the supported palladium nanocatalysts is highly dependent on the effective size of the substrates. This suggests the formation of a micelle-like secondary structure, which acts as fences for nanoparticle aggregation as well as size-selective micellar gates. The supported palladium nanoparticle catalysts can be recovered magnetically, and reused 10 times without any loss of catalytic activity.

Experimental Section

Preparation of Pd@Fe₃O₄/SiO₂/ILs **3a and **3b**.** A solution of Pd(acac)₂ (0.2 g) and IL-functionalized silica/magnetic NPs (0.5 g) in dioctylether (20 mL) was heated to 250 °C and maintained for 1 hr. After cooling to RT, the resulting nanoparticles were collected magnetically and washed with excess chloroform. This washing procedure was repeated three times. The final nanoparticles were dried *in vacuo* to give Pd@Fe₃O₄/SiO₂/ILs **3a**. Anion exchange of **3a** with SbF₆⁻ provided Pd@Fe₃O₄/SiO₂/ILs **3b**. To a suspension solution of Pd@Fe₃O₄/SiO₂/ILs **3a** (90 mg, Cl moiety 0.58 mmol/g) in acetone 50 mL, NaSbF₆ 90 mg (6 eq.) was added and the reaction mixture was stirred vigorously for 24 hours

at room temperature. After then, the anion exchanged Pd@Fe₃O₄/SiO₂/ILs **3b** (solid content: 1.2 g) was collected using magnet and washed with acetone repeatedly (5 times), dried *in vacuo*.

A Typical Procedure for Catalytic Hydrogenation. To suspension of catalyst, Pd@Fe₃O₄/SiO₂/IL **3b** (1.0 mol % based on Pd contents) in IPA/[bmim][SbF₆] (8 mL/2 mL) was added *trans*-stilbene (1.0 mmol). The resulting mixture was stirred vigorously under 1 atm of H₂ (balloon) at room temperature. After completion the reaction by GC analysis, the upper IPA layer was separated, and ionic liquid layer was extracted with IPA (5 mL × 3). During this step, the catalyst was holded by magnet to prevent catalyst loss. The recovered Pd@Fe₃O₄/SiO₂/IL **3b** in [bmim][SbF₆] was reused for the next run by addition of fresh IPA and substrate.

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