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Heterogeneous Catalysis

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Metal–Ligand Core–Shell Nanocomposite Catalysts for the Selective Semihydrogenation of Alkynes**

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In recent years, hybrid nanocomposites with core–shell structures have increasingly attracted enormous attention in many important research areas such as quantum dots,[1] optical,[2] magnetic,[3] and electronic[4] devices, and catalysts.[5–9] In the catalytic applications of core–shell materials, core-metals having magnetic properties enable easy separation of the catalysts from the reaction mixtures by a magnet.[5] The core-metals can also affect the active shell-metals, delivering significant improvements in their activities and selectivities. However, it is difficult for core-metals to act directly as the catalytic active species because they are entirely covered by the shell. Thus, few successful designs of core–shell nanocomposite catalysts having active metal species in the core have appeared to date.[10] Recently, we have demonstrated the design of a core–shell catalyst consisting of active metal nanoparticles (NPs) in the core and closely assembled oxides with nano-gaps in the shell, allowing the access of substrates to the core-metal. The shell acted as a macro ligand (shell ligand) for the core-metal and the core–shell structure maximized the metal–ligand interaction (ligand effect), promoting highly selective reactions.[11] The design concept of core–shell catalysts having core-metal NPs with a shell ligand is highly useful for selective organic transformations owing to the ideal structure of these catalysts for maximizing the ligand effect, leading to superior catalytic performances compared to those of conventional supported metal NPs.

Semihydrogenation of alkynes is a powerful tool to synthesize (Z)-alkenes which are important building blocks for fine chemicals, such as bioactive molecules, flavors, and natural products.[12] In this context, the Lindlar catalyst (Pd/$CaCO_3$ treated with $Pb(OAc)_2$) has been widely used.[13] Unfortunately, the Lindlar catalyst has serious drawbacks including the requirement of a toxic lead salt and the addition of large amounts of quinoline to suppress the over-hydrogenation of the product alkenes. Furthermore, the Lindlar catalyst has a limited substrate scope; terminal alkynes cannot be converted selectively into terminal alkenes because of the rapid over-hydrogenation of the resulting alkenes to alkanes.[13c] Aiming at the development of environmentally benign catalyst systems, a number of alternative lead-free catalysts have been reported.[14,15] Recently, we also developed a lead-free catalytic system for the selective semihydrogenation consisting of SiO_2-supported Pd nanoparticles (PdNPs) and dimethylsulfoxide (DMSO), in which the addition of DMSO drastically suppressed the over-hydrogenation and isomerization of the alkene products even after complete consumption of the alkynes.[16] This effect is due to the coordination of DMSO to the PdNPs. DMSO adsorbed on the surface of PdNPs inhibits the coordination of alkenes to the PdNPs, while alkynes can adsorb onto the PdNPs surface because they have a higher coordination ability than DMSO. This phenomenon inspired us to design PdNPs coordinated with a DMSO-like species in a solid matrix. If a core–shell structured nanocomposite involving PdNPs encapsulated by a shell having a DMSO-like species could be constructed, it would act as an efficient and functional solid catalyst for the selective semihydrogenation of alkynes.

Herein, we successfully synthesized core–shell nanocomposites of PdNPs covered with a DMSO-like matrix on the surface of SiO_2 (Pd@MPSO/SiO_2). The shell, consisting of an alkyl sulfoxide network, acted as a macroligand and allowed the selective access of alkynes to the active center of the PdNPs, promoting the selective semihydrogenation of not only internal but also terminal alkynes without any additives. Moreover, these catalysts were reusable while maintaining high activity and selectivity.

Pd@MPSO/SiO_2 catalysts were synthesized as follows. Pd/SiO_2 prepared according to our procedure[16] was stirred in *n*-heptane with small amounts of 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) and water at room temperature. Next, methyl-3-trimethoxysilylpropylsulfoxide (MPSO) was added to the mixture and the mixture was heated. The slurry obtained was collected by filtration, washed, and dried in vacuo, affording Pd@MPSO/SiO_2 as a gray powder. Altering the molar ratios of MPSO to Pd gave two kinds of catalysts: Pd@MPSO/SiO_2-1 (MPSO:Pd = 7:1), and Pd@MPSO/SiO_2-2 (MPSO:Pd = 100:1).

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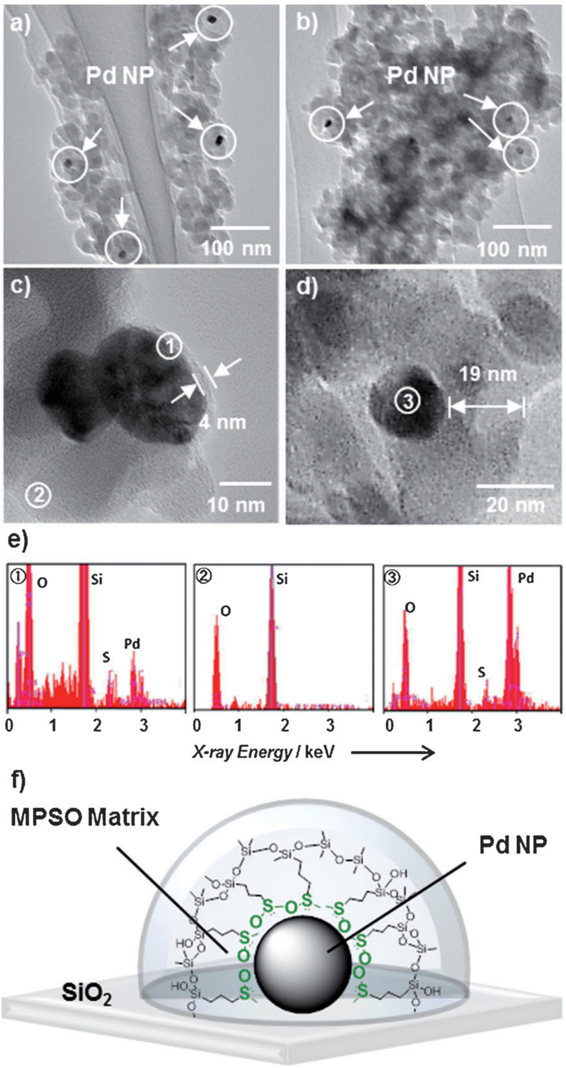


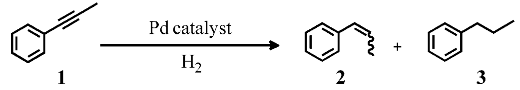
Figure 1. TEM images of a),c) Pd@MPSO/SiO_2-1 and b),d) Pd@MPSO/SiO_2-2. e) Representative EDS spectra at points indicated in (c) and (d). f) Illustration of the core–shell structured Pd@MPSO/SiO_2.

Transmission electron microscope (TEM) images of Pd@MPSO/SiO_2 showed that PdNPs having a mean diameter of 17 nm were covered by the shell structure (Figure 1 a and b). The average thicknesses of the shell area of Pd@MPSO/SiO_2-1 and Pd@MPSO/SiO_2-2 were 4 nm and 19 nm, respectively (Figure 1 c and d). Energy dispersive X-ray spectroscopy analysis (EDS) of Pd@MPSO/SiO_2 revealed that sulfur atoms could only be detected in the shell around the PdNPs (Figure 1 c–e). The molar ratios of sulfur to Pd in Pd@MPSO/SiO_2-1 and Pd@MPSO/SiO_2-2 were 5.6 and 23.8, respectively, from elemental analysis. ^{13}C CP/MAS NMR spectroscopy showed that the chemical shift of the carbon atoms proximal to the sulfoxide group of MPSO were downfield of those of free MPSO, suggesting the coordination of sulfoxide groups of MPSO to PdNPs.[17] The sulfoxide coordination was also confirmed by CO pulse adsorption measurements, which found that no CO was adsorbed on the PdNPs in Pd@MPSO/SiO_2, whereas the adsorption of CO occurred when using Pd/SiO_2 in place of Pd@MPSO/SiO_2.[18] From these combined results, it can be said that PdNPs were successfully covered with the MPSO matrix and formed core–shell structures on SiO_2 (Figure 1 f). In a control experiment, when MPSO was introduced to the SiO_2 surface before the loading of PdNPs onto the SiO_2 (Pd/MPSO-SiO_2), the core–shell structure was not formed.[17] This result supports that the building of the core–shell structure of Pd@MPSO/SiO_2 is triggered by the coordination of the sulfoxide group of MPSO to the PdNPs on the SiO_2, followed by the condensation of silyl ether groups of the MPSO. Furthermore, the thickness of the shell could be altered by changing the ratio of Pd to MPSO.

The catalytic activities of Pd@MPSO/SiO_2 were tested in the hydrogenation of 1-phenyl-1-propyne (**1**; Table 1). Pd@MPSO/SiO_2-1 showed high selectivity in the semihydrogenation of **1**, and 1-phenyl-1-propene (**2**) was obtained in an excellent yield (97 %) with high stereoselectivity (Z:E = 97:3, entry 1). Interestingly, when the reaction time was prolonged after complete consumption of **1**, the over-hydrogenation of **2** to *n*-propylbenzene (**3**) hardly occurred, while the high selectivity for **2** was maintained (entry 2). This result is quite different from other reported catalyst systems where the hydrogenation of alkene products occurred after full conversion of alkynes.[13,14] Pd@MPSO/SiO_2-2 also exhibited high selectivity for **2** although the catalytic activity was low (Table 1, entry 6). In contrast, the use of the catalyst precursor Pd/SiO_2 and Pd/MPSO-SiO_2 which do not have core–shell structures resulted in low selectivities for **2**, in which the undesired product **3** was easily (entries 7–10). In addition, commercially available Pd catalysts, such as Pd/C, Pd/Al_2O_3, and Pd/TiO_2 also gave low selectivities for **2** (entries 11–16). These phenomena clearly show that the coordination of the methyl sulfoxide moiety in the shell to the core PdNPs successfully allows the selective semihydrogenation while suppressing the over-hydrogenation of **2**. Furthermore, Pd@MPSO/SiO_2-1 was highly durable. After the reaction, the spent Pd@MPSO/SiO_2-1 was easily separable from the reaction mixture by filtration. Inductively coupled plasma (ICP) analysis revealed that no leaching of Pd species into the reaction mixture occurred (detection limit: 0.1 ppm). The Pd@MPSO/SiO_2-1 was reusable while maintaining its high catalytic activity and selectivity (Table 1, entries 3–5). TEM images and X-ray absorption fine structure (XAFS) analysis confirmed that the core–shell structure of the Pd@MPSO/SiO_2-1 used was similar to that of fresh catalyst and no aggregation of Pd nanoparticles was observed, supporting the excellent reusability of Pd@MPSO/SiO_2-1.[17]

Pd@MPSO/SiO_2-1 was also applicable to the semihydrogenation of a wide range of internal alkynes (Table 2). Various aromatic and aliphatic internal alkynes were converted into the corresponding alkenes in over 97 % yields. For example, (Z)-3-hexen-1-ol (leaf alcohol) and (Z)-methyl jasmonate, which are commercially important products for fragrances, were obtained in excellent yields (Table 2, entries 7 and 8). In all cases, the over-hydrogenation and isomerization of the products barely occurred and high selectivity for (Z)-alkenes was maintained even after complete consumption of the alkynes. Moreover, Pd@MPSO/

Table 1: Semihydrogenation of 1-phenyl-1-propyne using various Pd catalysts.[a]



Entry	Catalyst	*t* [min]	Conv. [%][b]	Yield of **2** [%][b]	*Z*:*E*[b]	Yield of **3** [%][b]
1	Pd@MPSO/SiO_2-1	120	>99	97	97:3	3
2	Pd@MPSO/SiO_2-1	180	>99	97	97:3	3
3[c]	Pd@MPSO/SiO_2-1	120	>99	97	97:3	3
4[d]	Pd@MPSO/SiO_2-1	120	>99	97	97:3	3
5[e]	Pd@MPSO/SiO_2-1	120	>99	97	97:3	3
6	Pd@MPSO/SiO_2-2	120	2	2	97:3	0
7	Pd/MPSO-SiO_2	15	>99	72	92:8	28
8	Pd/MPSO-SiO_2	25	>99	0	–	>99
9	Pd/SiO_2	7	>99	73	92:8	27
10	Pd/SiO_2	15	>99	0	–	>99
11[f]	Pd/C	10	>99	71	94:6	29
12[f]	Pd/C	20	>99	0	–	>99
13[f]	Pd/Al_2O_3	8	>99	75	96:4	25
14[f]	Pd/Al_2O_3	15	>99	0	–	>99
15[f]	Pd/TiO_2	7	>99	75	95:5	25
16[f]	Pd/TiO_2	15	>99	0	–	>99

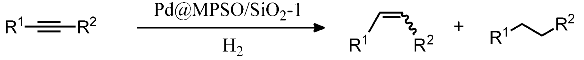
[a] Reaction conditions: **1** (0.5 mmol), Pd catalyst (Pd: 0.2 mol%), MeOH (5 mL), H_2 (1 atm), 30°C. [b] Determined by GC using an internal standard technique. [c] Reuse 1. [d] Reuse 2. [e] Reuse 3. [f] Purchased from WAKO pure chemicals (Pd: 5 wt%).

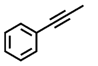
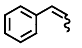
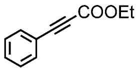
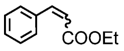
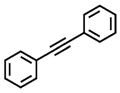
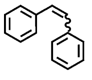
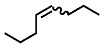
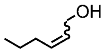
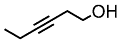
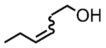
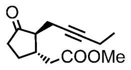
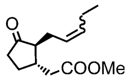
SiO_2-1 worked well under gram-scale reaction conditions: 10 mmol (1.16 g) of **1** was converted into **2** in 95% yield (isolated in 92% yield, $Z:E = 97:3$; entry 2).

The catalytic activity of Pd@MPSO/SiO_2 was investigated in the semihydrogenation of terminal alkynes, which has been challenging because terminal alkenes are more reactive than internal alkenes, easily resulting in the over-hydrogenation of alkene products even using the conventional Lindlar catalyst.[13c] When using ethynylbenzene as a model substrate, the use of Pd@MPSO/SiO_2-1 gave low selectivity for styrene (Table 3, entry 1). On the other hand, Pd@MPSO/SiO_2-2 showed excellent selectivity for the semihydrogenation of ethynylbenzene, affording styrene in 97% selectivity at full conversion (entry 2). This result can be explained by a thicker sulfoxide network around the PdNPs in Pd@MPSO/SiO_2-2 compared to Pd@MPSO/SiO_2-1, which sufficiently suppressed the coordination of the reactive terminal alkene to afford high selectivity for the terminal alkene.[19]

With Pd@MPSO/SiO_2-2 in hand, the semihydrogenation of a wide range of terminal alkynes was investigated. Ethynylbenzenes bearing electron-donating and electron-withdrawing groups were selectively hydrogenated to the corresponding terminal alkenes with excellent selectivities and reducible functional groups, such as halogen, aldehyde, and nitro moieties were compatible in the reaction (Table 3, entries 4–9). Various aliphatic terminal alkynes were also efficiently converted into the terminal alkenes without isomerization into internal alkenes (entries 10–16), confirming the wide applicability of Pd@MPSO/SiO_2-2.

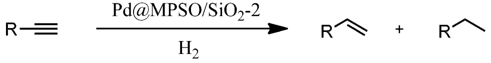
Table 2: Semihydrogenation of internal alkynes using Pd@MPSO/SiO_2-1.[a]

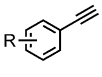
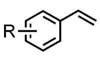
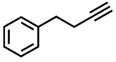
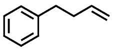
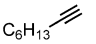
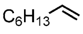
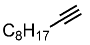
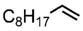
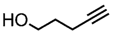
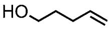
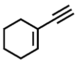
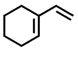
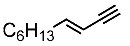
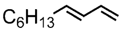
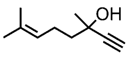
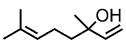


Entry	Substrate	Product	*t* [h]	Conv. [%][b]	Yield [%][b] Alkene	*Z*:*E*	Alkane
1			2	>99	97	97:3	3
2[c]			8	>99	95	97:3	5
3[d]			6	>99	98	97:3	2
4[d]			6	>99	99	98:2	1
5[d]			6	>99	98	98:2	2
6[e]			6	>99	98	95:5	2
7			3	>99	99	98:2	1
8[d]			8	>99	98	97:3	2

[a] Reaction conditions: alkyne (0.5 mmol), Pd@MPSO/SiO_2-1 (0.02 g, Pd: 0.2 mol%), MeOH (5 mL), H_2 (1 atm), 30°C. [b] Determined by GC using an internal standard technique. [c] Pd@MPSO/SiO_2-1 (0.1 g, Pd: 0.05 mol%), **1** (10 mmol), MeOH (40 mL), H_2 (1 atm), 30°C. [d] Reaction was conducted at 40°C. [e] THF was used as a solvent.

Table 3: Semihydrogenation of terminal alkynes using Pd@MPSO/SiO$_2$-2.[a]



Entry	Substrate	Product		T	t	Conv.	Yield [%][b]	
				[°C]	[h]	[%][b]	Alkene	Alkane
1[c]			R = H	30	1	> 99	82	18
2			R = H	30	6	> 99	97	3
3[d]			R = H	30	6	> 99	96	4
4			R = 4-CH$_3$	40	3	> 99	96	4
5			R = 4-OMe	50	10	> 99	96	4
6[e]			R = 4-NH$_2$	30	8	> 99	95	5
7			R = 4-Br	40	6	> 99	97	3
8[f]			R = 4-CHO	50	10	> 99	97	3
9[e]			R = 2-NO$_2$	30	6	> 99	95	5
10				40	3	> 99	97	3
11				40	6	> 99	97	3
12				40	5	> 99	97	3
13[f]				40	9	> 99	95	5
14				40	7	> 99	97	3
15[f]				50	12	> 99	95	5
16				50	10	> 99	99	1

[a] Reaction conditions: alkyne (0.5 mmol), Pd@MPSO/SiO$_2$-2 (0.02 g, Pd: 0.2 mol%), H$_2$ (1 atm), *n*-hexane (5 mL). [b] Determined by GC using an internal standard technique. [c] Pd@MPSO/SiO$_2$-1 was used as a catalyst. [d] Reuse. [e] A solvent mixture of *n*-hexane (3 mL) and toluene (2 mL) was used. [f] THF (5 mL) was used as a solvent.

In conclusion, we developed highly functionalized core–shell Pd@MPSO/SiO$_2$ catalysts consisting of PdNPs in the core and a DMSO-like matrix in the shell. The design of PdNPs encapsulated by a sulfoxide network as a shell ligand led to the selective coordination of alkynes to PdNPs, providing excellent activity and selectivity for the semihydrogenation of both internal and terminal alkynes. High selectivity of internal and terminal alkenes could be obtained by tuning the thickness of the shell ligand. Furthermore, the Pd@MPSO/SiO$_2$ catalyst was separable and reusable without any loss of its efficiency.

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