



Ordered Mesoporous Carbon Supported Colloidal Pd Nanoparticle Based Model Catalysts for Suzuki Coupling Reactions: Impact of Organic Capping Agents

Ha Rim Choi,^[a] Hyunje Woo,^[b] Seongwan Jang,^[b] Jae Young Cheon,^[a] Chungho Kim,^[c] Jongnam Park,^[c] Kang Hyun Park,^{*[b]} and Sang Hoon Joo^{*[a]}

Recent advances in the field of nanoscience have enabled the preparation of high-surface-area supported catalysts with precise control over the individual structural components. As such, a range of factors that affect the catalytic reactivity, such as the size, shape, and composition of the nanoparticles (NPs), have been identified. Herein, high-surface-area model catalysts that were based on colloidal Pd NPs and a hexagonally ordered mesoporous carbon support were prepared and the impact of various organic capping agents for the Pd NPs on their catalytic activity towards Suzuki coupling reactions was investigated. Colloidal Pd NPs (diameter: 3 nm) were synthesized with different organic capping agents, oleylamine (OA) and trioctylphosphine (TOP), and they were subsequently incorporated into the mesopores of CMK-3 mesoporous carbon to yield OA-Pd/CMK-3 and TOP-Pd/CMK-3 nanocatalysts, re-

spectively. The OA-Pd/CMK-3 catalyst was treated with acetic acid to generate a supported catalyst with surfactant-free Pd NPs (OA-Pd/CMK-3-A). Structural characterization revealed that the Pd NPs were uniformly dispersed throughout the mesopores of the CMK-3 support and the particle size and crystallinity of the Pd NPs were preserved following the incorporation. All of the Pd/CMK-3 nanocatalysts exhibited higher activity than commercial activated carbon supported Pd catalysts in Suzuki coupling reactions. The catalytic activities of the three Pd/CMK-3 nanocatalysts were in the following order: OA-Pd/CMK-3-A > OA-Pd/CMK-3 > TOP-Pd/CMK-3. This result suggested that the presence and type of surfactants had a significant effect on the catalytic activity. The OA-Pd/CMK-3-A catalyst also showed high activity for various substrates and good recycling ability in Suzuki coupling reactions.

Introduction

The recent drive towards sustainable chemistry and environmentally benign processes within the chemical industry has led to ever-increasing demands for catalyst systems that exhibit high activity and selectivity with long-term stability.^[1,2] To accomplish this goal, the identification of molecular factors that affect catalytic performance is of prime importance, thus highlighting the need for well-defined model catalysts.^[3] Recent advances in nanoscience have enabled the preparation of supported catalysts in a well-defined manner.^[4–7] Metallic nanoparticles (NPs) can be prepared by colloidal synthesis with controllable size, shape, and composition,^[8,9] whereas ordered mesoporous supports can be prepared with precisely tailored pore sizes and connectivity.^[10,11] The integration of these two catalytic entities has led to the preparation of 3D supported model catalysts.^[12–15] The individual properties of 3D nanocatalysts can be independently controlled on the molecular scale; thus, these 3D nanocatalysts have paved the way for the rational determination of a range of factors that affect catalytic reactivity, such as NP size, shape, and composition. Organic capping agents, which are used to prevent the aggregation of NPs and affect their size and shape, are important—yet rarely explored—variables in nanocatalysts.^[16–18] The functional groups on such organic capping agents can potentially dictate their interactions with metallic NP surfaces, which, in turn, alters the bonding modes of the adsorbents during the catalytic reactions, thereby affecting the catalytic consequences.

Suzuki coupling reactions are of paramount importance in the chemical and pharmaceutical industries because they can provide a one-step method for assembling complex molecular architectures.^[19–22] Homogeneous Pd complexes have been extensively studied as catalysts for Suzuki coupling reactions and

[a] H. R. Choi,* J. Y. Cheon, Prof. S. H. Joo
School of Nano-Bioscience and Chemical Engineering
KIER-UNIST Advanced Center for Energy and
Low-Dimensional Carbon Materials Center
Ulsan National Institute of Science and
Technology (UNIST)
UNIST-gil 50, Ulsan 689-798, Republic of Korea
Fax: (+82) 52-217-2509
E-mail: shjoo@unist.ac.kr

[b] H. Woo,* S. Jang, Prof. K. H. Park
Department of Chemistry and Chemistry Institute for
Functional Materials
Pusan National University
Busan 609-735 (Republic of Korea)
E-mail: chemistry@pusan.ac.kr

[c] C. Kim, Prof. J. Park
Interdisciplinary School of Green Energy and
KIER-UNIST Advanced Center for Energy
Ulsan National Institute of Science and
Technology (UNIST)
UNIST-gil 50, Ulsan 689-798 (Republic of Korea)

[*] These authors contributed equally to this work.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/cctc.201200220>.

the catalytic mechanisms under homogeneous reaction conditions are now well-established.^[19] However, homogeneous catalytic systems are prone to a range of problems, including the difficulties that are associated with the separation of the catalysts from the reaction mixture and catalyst recycling. Conversely, heterogeneous catalytic reactions allow for easy separation and recycling of the catalysts, thus enabling the sustained use of these catalysts. In this regard, the development of heterogeneous Pd catalysts for Suzuki coupling reactions has been actively pursued by using nanoporous supports, such as zeolites,^[23] mesoporous silicas,^[24–27] and layered double hydroxides.^[28] Carbon based supports have been particularly favored owing to their stability under basic reaction conditions; so far, activated carbons,^[29] graphene,^[30] and carbon nanotubes^[31] have been exploited for Suzuki coupling reactions, with activated carbon supports being the most prevalent choice. However, these activated carbons species are predominantly microporous in nature and their pore-size distribution is broad. Consequently, the active sites and sizes of the incorporated Pd catalysts are non-uniform, which hampers the systematic investigation of structure–property relationships by using these catalysts.

Ordered mesoporous carbon (OMC) materials, which are typically synthesized by using a nanocasting method with mesoporous silicas as hard templates, have emerged as a new class of porous carbon supports. These OMCs have uniform mesopores with sizes of 2–10 nm and exhibit high surface areas (up to 2000 m²g⁻¹) and pore volumes.^[32–35] Thus, OMCs are ideally suited as model carbon-based supports for catalytic applications. In particular, in the case of liquid-phase reactions that involve bulky substrates, the large, interconnected mesopores of OMCs may be advantageous over microporous supports. OMC-supported Pd NP catalysts that were prepared by an impregnation/reduction method have demonstrated promising activity for Heck and Ullmann coupling reactions,^[36,37] as well as for hydrogenation reactions.^[38]

Herein, we report the preparation of 3D high-surface-area Pd/CMK-3 model catalysts based on colloiddally synthesized, uniform Pd NPs and a hexagonally ordered CMK-3 mesoporous carbon support. This synthesis is the first example in which two well-defined catalytic building blocks are integrated to prepare carbon supported model catalysts. In addition, the impact of surface-capping agents for Pd NPs on Suzuki coupling reactions was also investigated. Two types of colloidal Pd NPs with similar particle sizes but different organic capping agents, that is, oleylamine (OA) and trioctylphosphine (TOP), were synthesized. These OA- and TOP-capped Pd NPs (OA-Pd NPs and TOP-Pd NPs, respectively) were incorporated into the mesopores of CMK-3 by using a sonication-induced capillary-inclusion method, thus affording OA-Pd/CMK-3 and TOP-Pd/CMK-3 nanocatalysts, respectively. The OA-Pd/CMK-3 catalyst was further treated with acetic acid (OA-Pd/CMK-3-A) to generate surfactant-free Pd NPs. Structural characterization revealed that the Pd NPs were uniformly dispersed throughout the mesopores of the CMK-3 supports and the particle size and crystallinity of the Pd NPs were preserved subsequent to this incorporation. All of the evaluated Pd/CMK-3 nanocatalysts exhibit-

ed higher activity than the commercially available activated carbon supported Pd catalysts in Suzuki coupling reactions. A comparison of three Pd/CMK-3 catalysts showed that the organic capping agents for the Pd NPs had a significant effect on their catalytic activity, in the order: OA-Pd/CMK-3-A > OA-Pd/CMK-3 > TOP-Pd/CMK-3. Furthermore, the OA-Pd/CMK-3-A catalyst showed high activity for various substrates and good recycling ability in Suzuki coupling reactions.

Results and Discussion

Synthesis of Pd NPs with various organic capping agents

Two types of Pd NPs were prepared by using either OA or TOP as organic capping agents. OA and TOP are surfactants that are widely used as capping agents and are versatile for the synthesis of highly monodisperse metals and metal–oxide NPs.^[39] The OA-Pd NPs were synthesized by using a mixture of OA and oleic acid (OAc) as a surface-capping agent and tetrabutylammonium borohydride (TBAB) as a reducing agent.^[40] Based on a previous report,^[40] only the OA surfactants were coordinated to the surfaces in the final Pd NPs when a surfactant mixture of OA and OAc was used for synthesizing the Pd NPs. In the case of TOP-Pd NPs, the TOP-Pd complexes thermally decomposed at high temperatures (300 °C) to generate TOP-Pd NPs.^[41]

Figure 1 shows TEM images of the two types of Pd NPs. The TEM image of the OA-Pd NPs (Figure 1a) shows that the OA-Pd NPs were highly monodisperse with an average particle size of 3.0(±0.3) nm (for the particle size distribution, see the Supporting Information, Figure S1a). A high-resolution TEM (HRTEM) image of the OA-Pd NPs (Figure 1b) revealed that they consisted of a mixture of single-crystalline and polycrys-

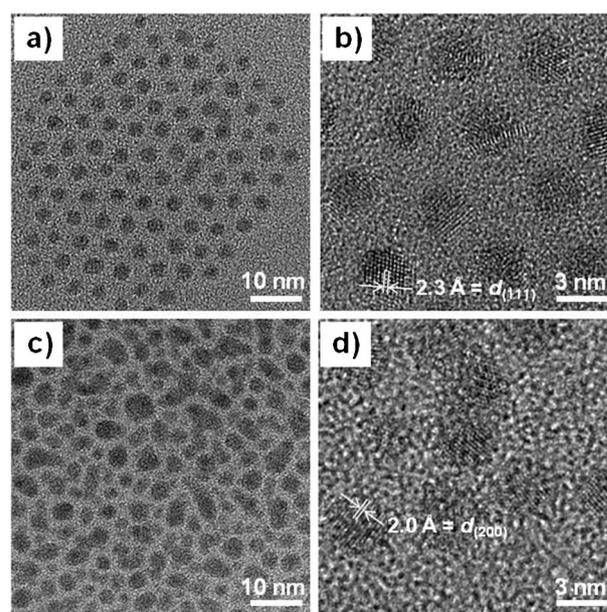


Figure 1. a, c) TEM and b, d) HRTEM images of OA-Pd NPs (a, b) and TOP-Pd NPs (c, d).

talline phases. Closer observation of the single-crystalline Pd NPs showed lattice fringes with a spacing of 2.3 Å, which corresponded to the (111) plane of face-centered-cubic (fcc) Pd. The TOP-Pd NPs (Figure 1c) were also monodisperse with an average size of $3.2(\pm 0.4)$ nm (for the particle size distribution, see the Supporting Information, Figure S1 b), which is slightly larger than that of the OA-Pd NPs. A HRTEM image of the TOP-Pd NPs (Figure 1d) indicated the existence of both single-crystalline and polycrystalline phases, similar to the case of the OA-Pd NPs. Single-crystalline TOP-Pd NPs also showed lattice fringes on the fcc phase of Pd metal.

Preparation and structural characterization of the Pd/CMK-3 nanocatalysts

Hexagonally ordered mesoporous carbon material CMK-3 was chosen as a support for the preparation of Pd/CMK-3 nanocatalysts. CMK-3 was synthesized by a nanocasting route by using SBA-15 silica, which had a hexagonal mesostructure, uniform mesopores (5.5 nm), and high surface area ($1230 \text{ m}^2 \text{ g}^{-1}$, Table 1). The Pd/CMK-3 nanocatalysts were prepared by incor-

Sample	Pd content [wt%]	Surface area [$\text{m}^2 \text{ g}^{-1}$]	Pore volume [$\text{cm}^3 \text{ g}^{-1}$]	Pore diameter [nm]
CMK-3		1228	1.37	5.5
OA-Pd/CMK-3	3.33	1229	1.32	5.5
OA-Pd/CMK-3-A	3.25	1224	1.27	5.5
TOP-Pd/CMK-3	1.77	1203	1.31	5.5

[a] Surface areas and pore diameters were calculated by using the BET and BJH methods, respectively.

porating the above-synthesized Pd NPs into the pores of the CMK-3 mesoporous support by using a sonication-induced capillary-inclusion method. It has previously been demonstrated that the sonication of an aqueous slurry that contain mesoporous silica and pre-synthesized colloidal NPs is effective for achieving the uniform inclusion of the NPs throughout the mesoporous silica pores.^[12] By using this scheme, model 3D OA-Pd/CMK-3 and TOP-Pd/CMK-3 nanocatalysts were prepared from OA-Pd NPs and TOP-Pd NPs, respectively. In addition, in an attempt to fully remove the organic capping agent, OA-Pd/CMK-3 was further treated with acetic acid to yield the OA-Pd/CMK-3-A nanocatalyst, by following a literature procedure.^[42]

TEM and HRTEM images of the Pd/CMK-3 catalysts, shown in Figure 2, indicate that the Pd NPs were well-incorporated into the mesopores of the CMK-3 mesoporous carbon material. Detailed analysis of the particle size distributions of the three catalysts revealed that the size of the original Pd NPs was preserved (see the Supporting Information, Figure S2). HRTEM images (Figure 2, inset) of the three catalysts showed that the crystalline nature was maintained during the sonication and post-treatment with acetic acid. The mesostructure of the Pd/CMK-3 catalysts was analyzed by using small-angle X-ray dif-

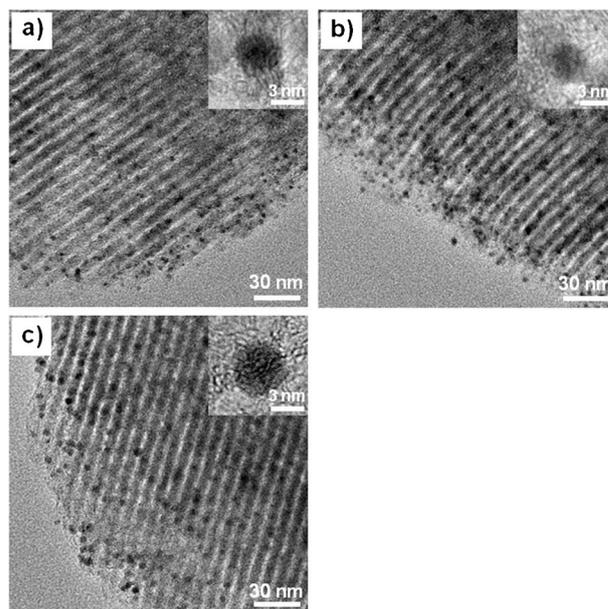


Figure 2. TEM images of a) OA-Pd/CMK-3, b) OA-Pd/CMK-3-A, and c) TOP-Pd/CMK-3. Insets: corresponding HRTEM images.

fraction (XRD) analysis (Figure 3a). Three characteristic peaks were present in the XRD patterns of pristine CMK-3, as well as in all of the Pd/CMK-3 catalysts, which could be indexed to the (100), (110), and (200) planes of the 2D $p6mm$ hexagonal mesostructure, thus indicating that the original hexagonal structure

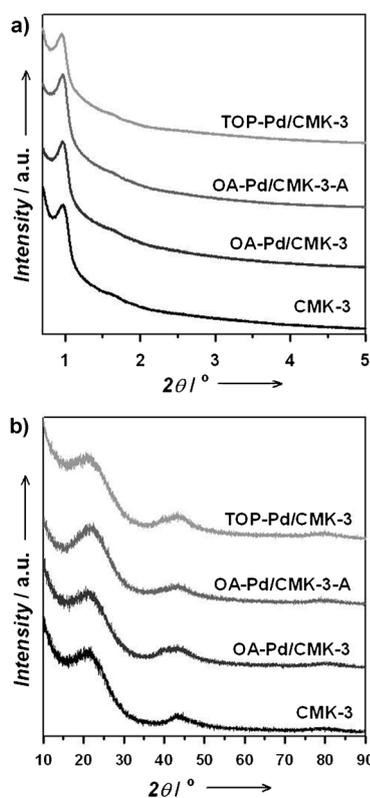


Figure 3. a) Small-angle and b) wide-angle XRD patterns of SBA-15 and Pd/CMK-3.

of the pristine CMK-3 support was unaltered after incorporation of the Pd NPs. In their wide-angle XRD patterns, CMK-3, as well as the Pd/CMK-3 samples, exhibited broad peaks at around 22–25° and 40–45°, which originated from amorphous, glassy carbon layers. In the XRD patterns of the Pd/CMK-3 catalysts, a peak at around 39–40° was detected, which could be indexed to the (111) plane of the face-centered-cubic structure of palladium. However, the peak intensity was very weak because of the multicrystalline nature of the Pd NPs. Nitrogen-adsorption isotherms were measured to evaluate the porous structure of the Pd/CMK-3 catalysts (Figure 4). Type-IV isotherms were obtained for CMK-3, as well as the Pd/CMK-3 catalysts, which indicated that the inclusion of Pd NPs into CMK-3 did not disrupt the porous structure of the pristine CMK-3. A pore size of 5.5 nm was determined for all of the catalysts based on the Barrett–Joyner–Halenda (BJH) pore-size distribution that was deduced from the adsorption branches of the isotherms; the pore size of the catalysts was the same as that of the CMK-3 support. The Brunauer–Emmett–Teller (BET) surface areas and pore volumes of the Pd/CMK-3 catalysts (Table 1) were similar to (1200–1230 m²g⁻¹ and 1.27–1.32 cm³g⁻¹, respectively), or slightly lower than, those of CMK-3 (1230 m²g⁻¹ and 1.37 cm³g⁻¹). Overall, the Pd NPs with various capping agents were successfully incorporated into the mesopores of the CMK-3 support whilst preserving the mesostructure of the pristine CMK-3 carbon framework. The as-prepared CMK-3 supported catalysts incorporated the Pd NPs with similar particle size and crystallinity; the only difference was in the type of surface-capping agents. Thus, with this series of catalysts, the effect of surface capping could be independently studied without the intervention of other structural factors.

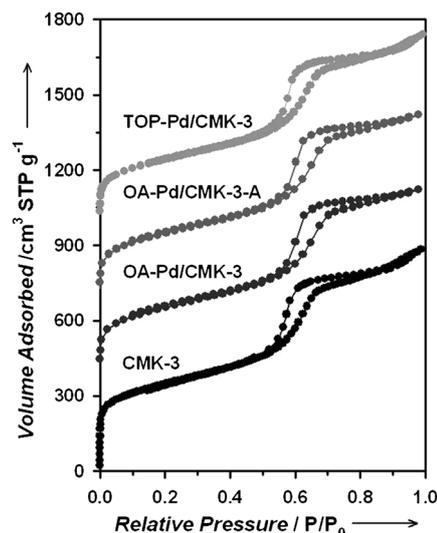
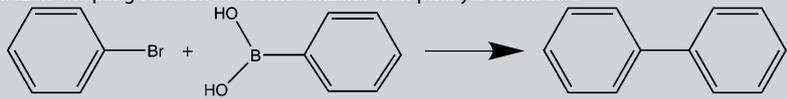


Figure 4. Nitrogen-adsorption/desorption isotherms of CMK-3 and Pd/CMK-3; for clarity, the isotherms of OA-Pd/CMK-3, OA-Pd/CMK-3-A, and TOP-Pd/CMK-3 were shifted upwards by 300, 600, and 900 cm³g⁻¹, respectively.

amount of water in the mixed DMF/H₂O solvent increased by changing the ratio from 20:1 to 5:1, the conversion increased significantly from 18% to 50% (Table 2, entry 5). Complete conversion was achieved by increasing the quantity of the TOP-Pd/CMK-3 catalyst to 0.09 mol% whilst lowering the reaction temperature to 150 °C (Table 2, entry 6). The complete conversion that was achieved with this catalyst suggests that, even though the surface of the Pd NPs is capped with TOP sur-

Suzuki coupling reactions over Pd/CMK-3 catalysts

These Pd/CMK-3 catalysts were employed in the Suzuki coupling reactions of bromobenzene and phenylboronic acid (Table 2). To optimize the reaction conditions, a series of reactions was performed by varying the solvent, base, reaction temperature, and reaction time with the TOP-Pd/CMK-3 catalyst (Table 2, entries 1–6). At a temperature of 200 °C, the conversion approached 99% for a reaction time of 60 min in the presence of 0.02 mol% TOP-Pd/CMK-3 catalyst, regardless of the type of base that was used (Table 2, entries 1 and 2). As expected, lowering the reaction temperature and time effectively decreased the conversion (Table 2, entries 3 and 4). Interestingly, when the

Table 2. Suzuki coupling reaction of bromobenzene with phenylboronic acid.						
						
Entry	Catalyst [mol%]	T [°C]	t [min]	Base	Solvent	Conversion ^[a] [%]
1	TOP-Pd/CMK-3 (0.02)	200	60	Cs ₂ CO ₃	DMF/H ₂ O (20:1)	99
2	TOP-Pd/CMK-3 (0.02)	200	60	K ₂ CO ₃	DMF/H ₂ O (20:1)	99
3	TOP-Pd/CMK-3 (0.02)	150	60	K ₂ CO ₃	DMF/H ₂ O (20:1)	27
4	TOP-Pd/CMK-3 (0.02)	200	30	K ₂ CO ₃	DMF/H ₂ O (20:1)	18
5	TOP-Pd/CMK-3 (0.02)	200	30	K ₂ CO ₃	DMF/H ₂ O (5:1)	50
6	TOP-Pd/CMK-3 (0.09)	150	30	K ₂ CO ₃	DMF/H ₂ O (5:1)	> 99
7	TOP-Pd/CMK-3 (0.09)	150	20	K ₂ CO ₃	DMF/H ₂ O (5:1)	48
8	TOP-Pd/CMK-3-A (0.09)	150	20	K ₂ CO ₃	DMF/H ₂ O (5:1)	99
9	OA-Pd/CMK-3 (0.09)	150	20	K ₂ CO ₃	DMF/H ₂ O (5:1)	99
10	OA-Pd (0.09)	150	20	K ₂ CO ₃	DMF/H ₂ O (5:1)	52
11	Pd/AC (0.09)	150	20	K ₂ CO ₃	DMF/H ₂ O (5:1)	44
12	OA-Pd/CMK-3 (0.02)	150	10	K ₂ CO ₃	DMF/H ₂ O (5:1)	32
13	OA-Pd/CMK-3-A (0.02)	150	3	K ₂ CO ₃	DMF/H ₂ O (5:1)	17
14	OA-Pd/CMK-3-A (0.02)	150	5	K ₂ CO ₃	DMF/H ₂ O (5:1)	62
15	OA-Pd/CMK-3-A (0.02)	150	10	K ₂ CO ₃	DMF/H ₂ O (5:1)	> 99
16	recovered from #15	150	10	K ₂ CO ₃	DMF/H ₂ O (5:1)	> 99
17	recovered from #16	150	10	K ₂ CO ₃	DMF/H ₂ O (5:1)	> 99
18	recovered from #17	150	10	K ₂ CO ₃	DMF/H ₂ O (5:1)	> 99
19	recovered from #18	150	10	K ₂ CO ₃	DMF/H ₂ O (5:1)	> 99
20	recovered from #19	150	10	K ₂ CO ₃	DMF/H ₂ O (5:1)	> 99

[a] Determined by using ¹H NMR spectroscopy.

factants, the TOP-Pd/CMK-3 catalyst exhibits sufficient catalytic activity for use in Suzuki coupling reactions.

Next, the catalytic activity of TOP-Pd/CMK-3 was compared with that of OA-Pd/CMK-3, colloidal OA-Pd NPs, and a commercially available activated carbon supported Pd (Pd/AC) catalyst at a reaction temperature of 150 °C, a reaction time of 20 min, and a catalyst loading of 0.09 mol% (Table 2, entries 7 and 9–11). Based on the conversions that were obtained with each of these four catalysts, the Pd/CMK-3 nanocatalysts reported herein clearly exhibited higher activity than the other catalysts tested. The difference in catalytic activity of mesoporous carbon supported catalysts and the activated carbon supported catalyst may be correlated with the porous nature of each support. The Pd particles in the Pd/AC catalyst are embedded or encapsulated within the microporous carbon layers, which diminishes the active surface area of the Pd particles. On the other hand, in the Pd/CMK-3 catalysts, the Pd NPs are dispersed in the open mesopores, as shown in the TEM images (Figure 2). Therefore, the Pd/CMK-3 catalysts exhibited superior catalytic activity to the Pd/AC catalyst, even in the presence of surface-capping agents. Comparison of the two Pd/CMK-3 nanocatalysts shows that higher activity is exhibited by the OA-Pd/CMK-3 catalyst than by the TOP-Pd/CMK-3 catalyst. Previous studies have shown that the OA surfactants were less strongly coordinated to the surfaces of the NPs than to the TOP surfactants.^[41] Thus, the reactants could access the OA-Pd NPs more easily than the TOP-Pd NPs, with consequently higher activity of the OA-Pd/CMK-3 catalyst. The effect of heterogenization of the colloidal Pd NPs with a mesoporous carbon support was examined by comparing the activities of OA-Pd/CMK-3 and colloidal OA-Pd NPs (Table 2, entries 9 and 10). Supported catalyst OA-Pd/CMK-3 showed higher activity than the unsupported OA-Pd catalyst, thus suggesting the beneficial effect of the solid porous support in the stabilization of colloidal catalyst. Further comparison of the activity of the OA-Pd/CMK-3 catalyst versus the OA-Pd/CMK-3-A catalyst at 150 °C for 10 min by using 0.02 mol% catalyst (Table 2, entries 12 and 15) showed that complete conversion was achieved with the OA-Pd/CMK-3-A catalyst, whereas the OA-Pd/CMK-3 catalyst showed substantially lower conversion (32%). A similar tendency was observed with the TOP-Pd/CMK-3 and the TOP-Pd/CMK-3-A catalysts (Table 2, entries 7 and 8). This result indicates that sufficient removal of the OA and TOP surfactants was achieved by treatment with acetic acid, which induced an increase in the density of the exposed NP surfaces and higher activity. Overall, the catalytic activity of the Suzuki coupling reaction between bromobenzene and phenylboronic acid was in the following order: OA-Pd/CMK-3-A > OA-Pd/CMK-3 ≈ TOP-Pd/CMK-3-A > OA-Pd > TOP-Pd/CMK-3 > Pd/AC. Notably, the OA-Pd/CMK-3-A catalyst that exhibited the highest activity could be reused five times under the conditions given in Table 2, entry 15 without any loss in catalytic activity (Table 2, entries 16–20).

The stability of the NPs in the supported catalysts represents an important issue for their sustainable use. To access the stability of our catalysts, OA-Pd/CMK-3-A was separated by hot filtration after the reaction and the Suzuki reaction was per-

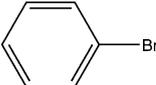
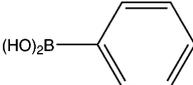
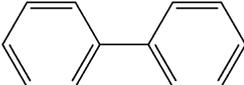
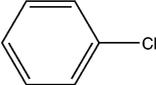
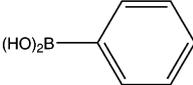
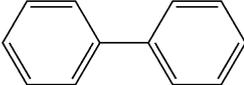
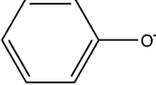
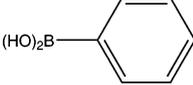
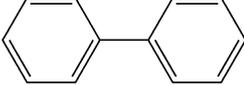
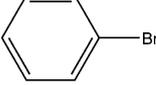
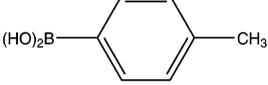
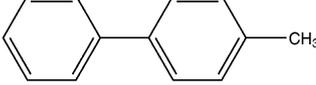
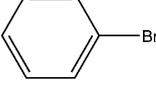
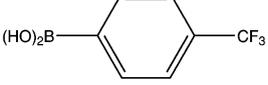
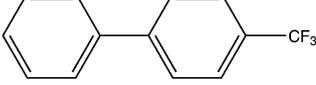
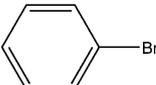
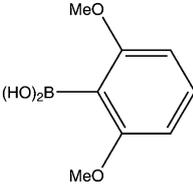
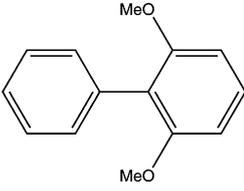
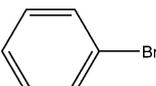
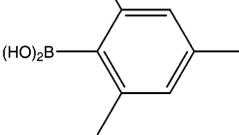
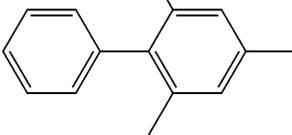
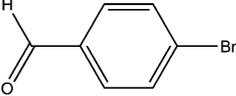
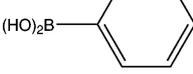
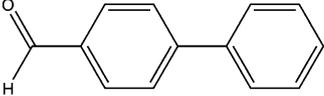
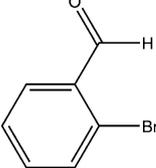
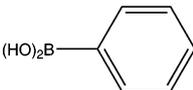
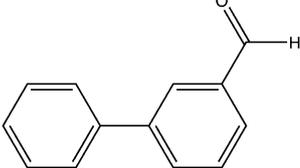
formed with the hot filtrate. No coupling reaction occurred in the filtrate, thus demonstrating the absence of any dissolved Pd species in the reaction mixture. ICP analysis revealed that a negligible amount of Pd was detected in the filtrate. TEM images and the particle size distribution of the OA-Pd/CMK-3-A catalyst after the Suzuki coupling reaction (see the Supporting Information, Figure S3) showed that the Pd NPs were uniformly dispersed throughout the mesopores of CMK-3 and that the Pd NP size was almost the same as that of the OA-Pd/CMK-3-A catalyst before the reaction.

The versatility of our nanocatalysts was tested by performing the Suzuki coupling reactions of various substrates under the optimized reaction conditions with the OA-Pd/CMK-3-A catalyst (Table 3). Clearly, this reaction can be extended to a wide variety of substituted aryl halides and arylboronic acids. The OA-Pd/CMK-3-A catalyst promotes the complete conversion of substrates with C–Br, C–Cl, and C–OTf bonds (Table 3, entries 1–3). In addition, both electron-rich- and electron-deficient substituents, as well as sterically hindered arylboronic acids, were readily coupled with bromobenzene with complete conversion (Table 3, entries 4–7). Furthermore, the reactions of various aryl bromides, including electron-deficient substrates, proceeded readily and various functional groups were tolerated in the reaction with high reactivity and complete conversion in some cases (Table 3, entries 8 and 9).

Role of organic capping agents in catalysis

Narayanan and El-Sayed have previously investigated the effect of organic capping agents on Suzuki coupling reactions by using colloidal Pd NP based pseudo-heterogeneous catalysts.^[16] They comparatively studied the effect of the catalytic reaction on the growth behavior of the Pd NPs that were stabilized by either dendrimers or polyvinyl pyrrolidone (PVP). They found that more strongly encapsulating dendrimers could suppress the growth of Pd NPs more effectively than the PVP polymers. Herein, we generated model supported catalysts from Pd NPs and found that the capping agents can profoundly affect their catalytic activity. Many of the previous works that were related to the catalytic application of colloidal NPs focused on the removal of the organic capping agents with the aim of fully exploiting the catalytically active surfaces.^[45–47] However, in view of modulating the catalytic activity, the capping agents could potentially play a significant role; likewise, the role of certain types of supports can alter the activity through strong metal–support interactions.^[48] In particular, for chemoselective or regioselective reactions, the presence of capping agents can alter reaction selectivity. For instance, Wu et al. have recently shown that long-chain amine-capped Pt₃Co NPs can be used as effective catalysts for the highly selective hydrogenation of α,β -unsaturated aldehydes to afford α,β -unsaturated alcohols, which, in the absence of the capping agent, are typically obtained in low yields.^[49]

Table 3. Suzuki coupling reaction of various aryl halides with arylboronic acids catalyzed by OA-Pd/CMK-3-A.^[a]

Entry	Aryl halides	Arylboronic acid	Product	Conversion ^[b] [%]
1				> 99
2				> 99
3				> 99
4				> 99
5				> 99
6				> 99
7				> 99
8				> 99
9				> 99

[a] Reaction conditions: halobenzene (0.10 mL, 0.95 mmol), arylboronic acid (0.14 g, 1.10 mol), OA-Pd/CMK-3-A (1.0 mg, 0.02 mol%), and DMF/water (10 mL:2.0 mL) were placed in a 25 mL stainless-steel reactor at 150 °C for 10 min. [b] Determined by using ¹H NMR spectroscopy.

Conclusions

High-surface-area 3D model Pd/CMK-3 nanocatalysts were prepared from the combination of colloidally synthesized 3 nm Pd NPs and mesoporous CMK-3 carbon supports. The Pd NPs were uniformly dispersed throughout the mesopores of the CMK-3 supports whilst preserving the particle size and crystallinity of the NPs, as well as the structural integrity of the CMK-3 support. An investigation of the effect of various capping agents for the Pd NPs on the catalytic activity for Suzuki coupling reactions revealed that all of the Pd/CMK-3 nanocatalysts exhibited higher activity than the commercial Pd/AC catalyst. We also found that the presence and type of the surfactants had a significant effect on the catalytic activity for Suzuki coupling reactions: OA-Pd/CMK-3-A exhibited the highest activity

followed by OA-Pd/CMK-3 and TOP-Pd/CMK-3. The OA-Pd/CMK-3-A catalyst also showed high activity for a wide range of substrates and demonstrated good recyclability for Suzuki coupling reactions.

Experimental Section

Chemicals

Pluronic P123 ($M_w = 5800$), tetraethyl orthosilicate (TEOS, 98%), palladium(II) acetate (98%), palladium acetylacetonate ($[\text{Pd}(\text{acac})_2]$, 99%) oleylamine (OA, 70%), oleic acid (OAc, 90%), tetrabutylammonium borohydride (TBAB, 98%), and trioctylphosphine (TOP, 90%) were purchased from Sigma Aldrich. Sucrose, hydrochloric acid (HCl, 35 wt%), sulfuric acid (H_2SO_4 , 95%), EtOH (94.5%), and

CHCl_3 (99.5%) were purchased from Samchun Pure Chemical Co. Ltd.

Synthesis of SBA-15 mesoporous silica and CMK-3 mesoporous carbon

For the synthesis of the SBA-15 mesoporous silica template,^[43] Pluronic P123 (8.0 g), deionized water (251.4 g), and HCl (48.6 g) were added into a 500 mL polypropylene bottle and the mixture was stirred at 35 °C. After complete dissolution of P123, TEOS (17.0 g) was added into the solution, which was stirred for 5 min and aged for 24 h at 35 °C without stirring. The reaction mixture was then transferred into a Teflon-lined autoclave and heated at 150 °C for 24 h. The white precipitates were filtered, washed twice with deionized water, and then dried in an oven at 60 °C for 1 day. Finally, the samples were calcined in air at 550 °C for 5 h. The CMK-3 mesoporous carbon support was replicated from a SBA-15 mesoporous silica template by using sucrose as a carbon source.^[44] Briefly, a precursor solution was obtained by dissolving sucrose (4.13 g) and H_2SO_4 (0.47 g) in H_2O (15 g). SBA-15 mesoporous silica (3 g) was added to this solution that was homogeneously mixed. The mixture was placed in a drying oven for 6 h at 100 °C. The oven temperature was subsequently increased to 160 °C and maintained at this temperature for 2 h. After the addition of sucrose (2.48 g), H_2SO_4 (0.28 g), and H_2O (15 g), the silica-polymerized-sucrose composite was again treated at 100 and 160 °C. The sample was carbonized by heating to 900 °C and maintained at that temperature for 2 h under an Ar flow. Finally, the carbon-silica composite was washed with 4 M hydrofluoric acid at RT to remove the silica template. The thus-obtained template-free carbon product was filtered, washed with EtOH, and dried at 100 °C.

Synthesis of Pd NPs

Pd NPs with two different capping agents were prepared herein. OA-capped Pd NPs (OA-Pd NPs) were prepared according to a literature procedure.^[40] Palladium(II) acetate (112 mg) and OA (3.3 mL) were mixed at 50 °C in a 50 mL three-neck, round-bottomed flask that was equipped with a gas-inlet adapter to produce a clear, colorless solution. OAc (3.2 mL) was added into the solution, which was stirred at 50 °C for 1 h to form a clear, pale-yellow solution. A solution of TBAB (386 mg, 1.5 mmol) in CHCl_3 (2 mL) was quickly injected into the reaction mixture with vigorous stirring. The resulting dark-brown solution was stirred at 50 °C for 1 h and then cooled to RT. Next, the reaction solution was mixed with EtOH (30 mL) and the precipitated OA-Pd NPs were recovered by centrifugation at 6000 rpm for 10 min, followed by decantation of the supernatant solvent. Finally, the OA-Pd NPs were redispersed in CHCl_3 for further use. Trioctylphosphine (TOP)-capped Pd NPs (TOP-Pd NPs) were synthesized by a heating-up process.^[41] In a typical synthesis, the TOP-Pd complex was prepared by dissolving $[\text{Pd}(\text{acac})_2]$ (0.1 g) in trioctylphosphine (1 mL) under an Ar atmosphere. The resulting solution of the metal-surfactant complex was injected into TOP (9 mL) at RT, which was slowly heated to 300 °C and aged at the same temperature for 30 min, thereby generating a black colloidal NP solution. A black precipitate was obtained by adding EtOH (50 mL) into the colloidal solution and the mixture was centrifuged at 5000 rpm for 10 min. The precipitate that was obtained after decanting the supernatant was redispersed in CHCl_3 for further use.

Preparation of Pd/CMK-3 catalysts

Three kinds of Pd/CMK-3 catalysts were prepared by incorporating the Pd NPs into the pores of the CMK-3 mesoporous carbon supports by using a sonication-induced capillary-inclusion method. Given amounts of Pd NPs that were dispersed in CHCl_3 and CMK-3 (1 g) were added into CHCl_3 (50 mL) in a 100 mL Erlenmeyer flask. The slurry was stirred at RT for 1 h and sonicated for 3 h at RT by using an ultrasound cleaner (Branson, 1510R-MT, 70 W, 42 kHz). The precipitates were separated by centrifugation at 4000 rpm for 10 min, washed thoroughly with CHCl_3 , and dried in an oven at 60 °C. The final catalysts that were prepared from the OA-Pd NPs and TOP-Pd NPs were referred to as OA-Pd/CMK-3 and TOP-Pd/CMK-3, respectively. The OA-Pd/CMK-3 and TOP-Pd/CMK-3 catalysts was further treated with acetic acid at 80 °C to remove any residual OA surfactant.^[42] The obtained catalysts were designated as OA-Pd/CMK-3-A and TOP-Pd/CMK-3-A.

General procedure for Suzuki coupling reactions

Under the optimized reaction conditions, the OA-Pd/CMK-3-A nanocatalyst (1.0 mg, 0.02 mol%), aryl halide (0.10 mL, 0.95 mmol), phenylboronic acid (0.14 g, 1.10 mmol), DMF (10 mL), water (2.0 mL), and K_2CO_3 (0.26 g, 1.9 mmol) were added into a 25 mL stainless-steel reactor. The mixture was stirred at 423 K for 10 min. After the reaction, the OA-Pd/CMK-3-A catalyst was separated from the clear solution by centrifugation.

Characterization methods

The morphology of the samples was analyzed by SEM on a FEI Quanta 200 microscope operating at 15 kV. The size and shape of the Pd NPs, as well the Pt/CMK-3 catalysts, were analyzed by TEM on a JEOL JEM-2100F microscope at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns of the samples were obtained on a Rigaku D/Max 2500 V/PC X-ray diffractometer that was equipped with a CuK_α source at 40 kV and 200 mA. The porous structure of the CMK-3 and Pd/CMK-3 catalysts was analyzed by acquiring nitrogen-adsorption isotherms at -196 °C on a BEL Bel-sorp-Max machine. Prior to the N_2 -adsorption measurements, the samples were degassed under a vacuum at 300 °C for 12 h. The surface area and pore-size distribution of the samples were calculated by using the BET equation and the BJH method, respectively. The palladium content of the Pd/CMK-3 catalysts was measured by inductively coupled plasma optical emission spectrometry on a Varian 720-ES instrument.

Acknowledgements

This work was supported by the Basic Science Research Program through the National Research Foundation (NRF) of Korea, funded by the Ministry of Education, Science and Technology (Grant Nos. 2012-0003813, 2009-0070926, and 2010-0002834). S.H.J. and K.H.P. are supported by the TJ Park Junior Faculty Fellowship.

Keywords: capping agents · cross-coupling · mesoporous materials · nanoparticles · palladium

[1] G. A. Somorjai, H. Frei, J. Y. Park, *J. Am. Chem. Soc.* **2009**, *131*, 16589–16605.

- [2] V. Polshettiwar, R. J. Varma, *Green Chem.* **2010**, *12*, 743–754.
- [3] G. A. Somorjai, J. Y. Park, *Angew. Chem.* **2008**, *120*, 9352–9368; *Angew. Chem. Int. Ed.* **2008**, *47*, 9212–9228.
- [4] R. Narayanan, M. A. El-Sayed, *Top. Catal.* **2008**, *47*, 15–21.
- [5] G. A. Somorjai, J. Y. Park, *Top. Catal.* **2008**, *49*, 126–135.
- [6] C.-J. Jia, F. Schüth, *Phys. Chem. Chem. Phys.* **2011**, *13*, 2457–2487.
- [7] N. Semagina, L. Kiwi-Minsker, *Catal. Rev.* **2009**, *51*, 147–217.
- [8] A. R. Tao, S. Habas, P. Yang, *Small* **2008**, *4*, 310–325.
- [9] Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem.* **2009**, *121*, 62–108; *Angew. Chem. Int. Ed.* **2009**, *48*, 60–103.
- [10] A. Corma, *Chem. Rev.* **1997**, *97*, 2373–2419.
- [11] F. Schüth, *Angew. Chem.* **2003**, *115*, 3730–3750; *Angew. Chem. Int. Ed.* **2003**, *42*, 3604–3622.
- [12] R. M. Rioux, H. Song, J. D. Hoefelmeyer, P. Yang, G. A. Somorjai, *J. Phys. Chem. B* **2005**, *109*, 2192–2202.
- [13] M. E. Grass, S. H. Joo, Y. Zhang, G. A. Somorjai, *J. Phys. Chem. C* **2009**, *113*, 8616–8623.
- [14] R. M. Rioux, H. Song, M. Grass, S. Habas, K. Niesz, J. D. Hoefelmeyer, P. Yang, G. A. Somorjai, *Top. Catal.* **2006**, *39*, 167–174.
- [15] I. Lee, F. Delbecq, R. Morales, M. A. Albiter, F. Zaera, *Nat. Mater.* **2009**, *8*, 132–138.
- [16] R. Narayanan, M. A. El-Sayed, *J. Phys. Chem. B* **2004**, *108*, 8572–8580.
- [17] J. N. Kuhn, C.-K. Tsung, W. Huang, G. A. Somorjai, *J. Catal.* **2009**, *265*, 209–215.
- [18] J. Y. Park, C. Aliaga, J. R. Renzas, H. Lee, G. A. Somorjai, *Catal. Lett.* **2009**, *129*, 1–6.
- [19] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483.
- [20] A. Balanta, C. Godard, C. Claver, *Chem. Soc. Rev.* **2011**, *40*, 4973–4985.
- [21] A. Fihri, M. Bouhrara, B. Nekouishahraki, J.-M. Basset, V. Polshettiwar, *Chem. Soc. Rev.* **2011**, *40*, 5181–5203.
- [22] M. Pérez-Lorenzo, *J. Phys. Chem. Lett.* **2012**, *3*, 167–174.
- [23] M. Choi, D.-H. Lee, K. Na, B.-W. Yu, R. Ryoo, *Angew. Chem.* **2009**, *121*, 3727–3730; *Angew. Chem. Int. Ed.* **2009**, *48*, 3673–3676.
- [24] C. M. Crudden, M. Sateesh, R. Lewis, *J. Am. Chem. Soc.* **2005**, *127*, 10045–10050.
- [25] R. B. Bedford, U. G. Singh, R. I. Walton, R. T. Williams, S. A. Davis, *Chem. Mater.* **2005**, *17*, 701–707.
- [26] S. Jana, B. Dutta, R. Bera, S. Koner, *Inorg. Chem.* **2008**, *47*, 5512–5520.
- [27] J. C. Park, E. Heo, A. Kim, M. Kim, K. H. Park, H. Song, *J. Phys. Chem. C* **2011**, *115*, 15772–15777.
- [28] B. M. Choudary, S. Madhi, N. S. Chowdari, M. L. Kantam, B. Sreedhar, *J. Am. Chem. Soc.* **2002**, *124*, 14127–14136.
- [29] Y. Kitamura, S. Sako, T. Udzu, A. Tsutsui, T. Maegawa, Y. Monguchi, H. Sajiki, *Chem. Commun.* **2007**, 5069–5071.
- [30] G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mülhaupt, *J. Am. Chem. Soc.* **2009**, *131*, 8262–8270.
- [31] X. Chen, Y. Hou, H. Wang, Y. Cao, J. He, *J. Phys. Chem. C* **2008**, *112*, 8172–8176.
- [32] R. Ryoo, S. H. Joo, M. Kruk, M. Jaroniec, *Adv. Mater.* **2001**, *13*, 677–680.
- [33] J. Lee, J. Kim, T. Hyeon, *Adv. Mater.* **2006**, *18*, 2073–2094.
- [34] R. Ryoo, S. H. Joo, S. Jun, *J. Phys. Chem. B* **1999**, *103*, 7743–7746.
- [35] S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, *Nature* **2001**, *412*, 169–172.
- [36] Y. Wan, H. Wang, Q. Zhao, M. Klingstedt, O. Terasaki, D. Zhao, *J. Am. Chem. Soc.* **2009**, *131*, 4541–4550.
- [37] H. Wang, Y. Wan, *J. Mater. Sci.* **2009**, *44*, 6553–6562.
- [38] Y. S. Ahn, K. I. Min, Y. M. Chung, H. K. Rhee, S. H. Joo, R. Ryoo, *Stud. Surf. Sci. Catal.* **2001**, *135*, 313.
- [39] J. Park, J. Joo, S. G. Kwon, Y. Jang, T. Hyeon, *Angew. Chem.* **2007**, *119*, 4714–4745; *Angew. Chem. Int. Ed.* **2007**, *46*, 4630–4660.
- [40] R. Sato, M. Kanehara, T. Teranishi, *Small* **2011**, *7*, 469–473.
- [41] S.-W. Kim, J. Park, Y. Jang, Y. Chung, S. Hwang, T. Hyeon, *Nano Lett.* **2003**, *3*, 1289–1291.
- [42] V. Mazumder, S. Sun, *J. Am. Chem. Soc.* **2009**, *131*, 4588–4589.
- [43] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548–552.
- [44] S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* **2000**, *122*, 10712–10713.
- [45] N. F. Zheng, G. D. Stucky, *J. Am. Chem. Soc.* **2006**, *128*, 14278–14280.
- [46] C. Aliaga, J. Y. Park, Y. Yamada, H. S. Lee, C.-K. Tsung, P. Yang, G. A. Somorjai, *J. Phys. Chem. C* **2009**, *113*, 6150–6155.
- [47] S. H. Joo, J. Y. Park, C.-K. Tsung, Y. Yamada, P. Yang, G. A. Somorjai, *Nat. Mater.* **2009**, *8*, 126–131.
- [48] S. J. Tauster, S. C. Fung, R. T. K. Baker, J. A. Horsley, *Science* **1981**, *211*, 1121–1125.
- [49] B. Wu, H. Huang, J. Yang, N. Zheng, G. Fu, *Angew. Chem.* **2012**, *124*, 3496–3499; *Angew. Chem. Int. Ed.* **2012**, *51*, 3440–3443.

Received: April 8, 2012

Revised: May 31, 2012

Published online on July 16, 2012