A Cobalt Tandem Catalyst Supported on a Compressible Microporous Polymer Monolith

Do Yeon Kim, Tae Jin Choi, Jong Gil Kim, and Ji Young Chang*

Department of Materials Science and Engineering, College of Engineering, Seoul National University, Seoul 08826, Korea

ABSTRACT: A compressible microporous polymer monolith (MPM) was prepared by performing the Sonogashira–Hagihara reaction between 1,4-diodobenzene and 1,3,5-triethynylbenzene in a gel state without stirring. MPM was functionalized via the click reaction with 1,3,5-tris(azidomethyl)-2,4,6-trimethylbenzene and 2,6-diethynylpyridine. MPM showed superhydrophobicity but became hydrophilic after the click reaction. The functionalized MPM (F-MPM) had polar triazole groups generated by the click reaction, which were used as coordination sites for Co(II) ions. Cobalt nanoparticles were loaded to F-MPM through in situ reduction of coordinated Co(II) ions to produce a monolithic Co heterogeneous catalyst (Co-MPM). The microscopic study showed that MPM, F-MPM, and Co-MPM consisted of fiber bundles, together with spherical particles on the micrometer scale. Co-MPM was used for tandem catalysis. Co-MPM promoted the reaction of dehydrogenation of ammonia borane and hydrogenation of nitro compounds in one pot to give amine products. The reactions with the compression and release process were much faster compared with the reactions performed under the stirring conditions, suggesting that the repeated compression and release facilitated interfacial contact between the reactants and active sites in Co-MPM.

1. INTRODUCTION

Microporous organic polymers (MOPs) have been considerably studied as catalyst supports in recent years. As supporting materials, MOPs have advantages associated with the flexibility in their structural design compared with other porous solids such as porous carbon and oxides. MOPs with highly cross-linked structures are generally prepared by step-reactions of multifunctional monomers. Because a variety of synthetic methods are available for the preparation of MOPs including the transition metal-mediated coupling reactions and other condensation reactions, MOPs have a wide range of chemical and physical properties. They can be further modified by postreactions to have tuned functionalities. The suitably adjusted interactions between catalytically active species and the supports have a significant influence in enhancing the stability and performance of the heterogeneous catalysts.

Herein, we present the synthesis of a cobalt heterogeneous catalyst supported on a compressible and hydrophilic microporous polymer monolith (MPM). The Co heterogeneous catalyst sequentially promoted the dehydrogenation of ammonia borane and the reduction of nitro compounds in an aqueous environment. Ammonia borane with a high hydrogen density is an attractive chemical hydrogen storage material. The catalytic dehydrogenation of ammonia borane has been considered as a promising hydrogen generation process under mild conditions. Various metal nanoparticles including Pt, Rh, Ru, Pd, and Co exhibited catalytic activity in the hydrogen release.

The monolithic microporous polymer support was prepared via the Sonogashira–Hagihara cross-coupling reaction of triethynyl benzene and diiodobenzene. A series of microporous polymers were previously reported by the reaction of triethynyl benzene with aromatic halides, but they were usually isolated as precipitated solids. We were able to obtain the monolithic microporous polymer by performing the reaction in a gel state without stirring. The post-click reaction of the polymer monolith provided hydrophilicity as well as coordination sites for Co(II) ions. Cobalt nanoparticles (Co NPs) were incorporated into the polymer monolith by an in situ reduction method.

2. RESULTS AND DISCUSSION

Scheme 1 shows the synthetic processes of a MPM, functionalized MPM by the post-click reaction (F-MPM), and Co NP-incorporated MPM (Co-MPM). MPM was
prepared via the Sonogashira–Hagihara coupling reaction of 1,4-diiodobenzene and 1,3,5-triethynyl benzene in a 20 mL vial. The molar ratio between the halogen and the ethynyl groups was set to be 1:1.5, so that MPM had enough terminal alkynes for the click reaction. The reaction was carried out at room temperature without stirring. The reaction mixture became a viscous gel in 5 min (Figure S1). The cross-linked polymer was isolated as a monolith after 24 h. MPM was functionalized by the click reaction with 1,3,5-tris(azidomethyl)-2,4,6-trimethylbenzene and 2,6-diethynylpyridine. The click reaction generated triazole groups, which had good ability to complex with metal ions. The incorporation of Co NPs into F-MPM proceeded in two steps. At first, an aqueous solution of cobalt chloride hexahydrate was absorbed to F-MPM, and then the monolith was allowed to contact an aqueous sodium borohydride solution through the compression and release process. The click reaction also greatly improved the water wettability of the monolith. MPM consisted only of hydrocarbons and showed a superhydrophobic property with a water contact angle (WCA) of 151°. After the click reaction, the surface of the monolith became hydrophilic, showing WCAs of 0° because of the presence of triazole groups (Figure S2). We previously used a fluorinated MOP monolith as a catalyst support, but the poor water wettability was a problem for its application in an aqueous reaction. The polymer monoliths, MPM, F-MPM, and Co-MPM had cylindrical shapes which were complementary to the shape of the reactor (Figure S2).

The structures of the polymer monoliths were characterized by Fourier transform infrared (FT-IR) and solid-state 13C CP/TOSS NMR spectroscopy. MPM showed the absorption bands at 2207 and 3298 cm⁻¹, corresponding to the stretching vibration of C−C triple bonds and the C−H stretching vibration of terminal alkynes, respectively (Figure 1a). In the spectrum of F-MPM, the characteristic band of triazole rings showed up around 1450 and 1600 cm⁻¹. There still appeared the bands corresponding to terminal alkynes at 3298 cm⁻¹ and azido groups at 2093 cm⁻¹, suggesting that some functional groups did not participate in the click reaction. The solid-state 13C NMR spectrum of MPM showed aromatic carbon peaks at 131 and 123 ppm and an acetylene carbon peak at 90 ppm (Figure 1b). The spectrum of F-MPM exhibited an additional peak at 146 ppm, corresponding to triazole ring carbons. The energy-dispersive X-ray spectroscopy (EDS) spectrum of Co-MPM showed the presence of Co along with nitrogen, which was not observed in the spectrum of MPM (Figure S3).

The formation of Co NPs was further confirmed by X-ray diffraction (XRD) analysis. The XRD patterns of MPM and F-MPM showed no discernible peaks, indicating their amorphous structures (Figure S4a). In contrast, there appeared sharp peaks at 2θ = 20.3° and 32.9° in the XRD pattern of Co-MPM, which corresponded to the (111) and (220) planes of fcc Co, respectively. The thermogravimetric analysis (TGA) data (Figure S4b) demonstrated that the monoliths had good thermal stability. The initial degradation temperature of MPM was around 350 °C. After the postmodifications, the thermal resistance was enhanced to give a higher char yield.

The polymer monoliths had hierarchically porous structures. Micropores and mesopores were originated from the highly cross-linked structures, and macropores were produced by the solvent removal from the cross-linked gels. Hierarchically porous structures have benefits in catalysis applications because micropores and mesopores supply large surface areas while macropores improve mass transport. The porosities of the monoliths were investigated by N₂ adsorption−desorption measurements at 77 K (Figure 2a). The polymer monoliths showed type I adsorption isotherms with a high N₂ uptake in the low relative pressure region (P/P₀ < 0.01), implying the existence of micropores. Type IV adsorption isotherms were observed with hysteresis loops in the high pressure region (P/P₀ > 0.4), indicating the presence of mesopores.
relative pressure region, indicating the existence of mesopores.\textsuperscript{39,40} The pore size distributions of the polymer monoliths were determined by the nonlocal density functional theory (NLDFT), which showed the existence of micropores and mesopores. The total pore volumes of MPM, F-PM, and Co-PM were 0.63, 0.54, and 0.41 cm\textsuperscript{3} g\textsuperscript{−1} and their Brunauer–Emmett–Teller surface areas were 882, 708, and 523 m\textsuperscript{2} g\textsuperscript{−1}, respectively. After the postmodification reaction and the incorporation of Co NPs, the surface areas of the monoliths decreased compared to that of MPM mainly because of the increase in the weight per unit volume.\textsuperscript{41}

The scanning electron microscopy (SEM) images of MPM, F-PM, and Co-PM showed fiber bundles, together with spherical particles on the micrometer scale (Figure 3a–c). In the transmission electron microscopy (TEM) images, individual fibers with diameters of hundreds nanometers could be observed (Figure 3d–f). Overall, MPM showed a less well-defined fibrous structure than the fluorinated MPM that was previously synthesized by the Sonogashira–Hagihara coupling reaction between 1,4-diiodotetrafluorobenzene and 1,3,5-triethynylbenzene.\textsuperscript{20} This result was attributable to the differences in the solubility and the reactivity of the fluorinated and nonflorinated monomers. The TEM image of Co-PM (Figures 3f and S5) exhibited that the Co NPs were well-distributed in the polymer fibers and the average size of Co NPs was 10.9 nm (Figure S5). When a solution of cobalt
chloride hexahydrate in methanol was absorbed to unfunctionalized MPM and reduced to Co NPs, most Co NPs were removed during the purification process (Figure S6).

MPM showed good mechanical stability against compressive stress. When MPM was compressed to a strain of 40%, it rapidly recovered its original shape upon the release of the stress (Figure S7). The maximum stress slightly decreased after 10 loading-unloading cycles to a strain of 40%, but the deformation was still reversible (Figure 4). Co-MPM showed a higher compressive strength than MPM, suggesting the reinforcement effect of Co NPs.

Co is one of the earth abundant transition metals. Co NPs have been increasingly used as catalysts in diverse reactions including hydrogenation, oxidation, and water splitting. In recent years, more attention has been paid to the high catalytic activity of Co NPs to promote hydrogen production from hydrogen sources because hydrogen has been considered as a clean energy carrier. We successfully used Co-MPM as a tandem catalyst in the sequential dehydrogenation of ammonia borane and hydrogenation of nitro compounds (Scheme 2). A nitro compound was dissolved in a cosolvent of water and methanol (3:2, v/v), and then, the solution was diluted to 0.05–0.1 mM with water for the UV measurement. A piece of Co-MPM with a cylindrical shape (150 mg) was immersed in the diluted nitro compound solution with an excess amount of ammonia borane. Co-MPM was manually compressed and released at a rate of 2 s per cycle using a glass rod. The UV–vis absorption of the solution was measured every 30 cycles (1 min) to monitor the progress of the reaction. For comparison, the reactions with stirring and without stirring were also carried out under the same conditions except that the sponge was not compressed.

Figure 5a shows UV–vis spectra of the 4-nitrophenol (4-NP) solution measured during the reaction with the compression and release process. The reaction solution showed an absorption maximum at 400 nm because of the formation of 4-nitrophenolate. The absorption intensity at 400 nm decreased rapidly with the concomitant increase of the peak corresponding to the presence of 4-aminophenol at 296 nm, indicating that Co-MPM catalyzed the tandem dehydrogenation of ammonia borane and hydrogenation of 4-NP. The reaction was 5.5 times faster compared with the reaction performed under the stirring conditions and 7.5 times faster than the reaction under the static conditions when determined based on the UV absorption change at 400 nm (Figures 5b,c and S8). Apparently, the repeated compression and release facilitated interfacial contact between the reactants and active sites in Co-MPM. Co-MPM maintained the catalytic activity even after 5 times run without any significant loss (Figure S9).

Nitrobenzene and nitroaniline were also reduced to the corresponding amines by the tandem reaction catalyzed by Co-MPM. Figure S10 shows UV–vis spectral changes measured during the reactions, where the absorption peak intensity of a nitro compound decreases and a new amine peak appears as the reaction proceeds. As observed in the reaction of 4-NP, the reactions of nitrobenzene and nitroaniline with the compression and release process were much faster than the reactions performed under the stirring and static conditions.

Scheme 2. Schematic Illustration of the Tandem Dehydrogenation of Ammonia Borane and Hydrogenation of Nitro Compounds

Figure 5. UV–vis spectral changes of the 4-NP solution (initial concentration = 0.1 mM) with reaction time: (a) reaction with the compression and release process, (b) reaction with stirring, and (c) reaction without stirring.
3. CONCLUSIONS

A compressible MPM was prepared by performing the Sonogashira–Hagihara reaction in a gel state without stirring. The superhydrophobic surface of the monolith was functionalized via the alkyne–azide cycloaddition click reaction, which provided hydrophilic coordination sites for Co(II) ions. The Co NP-incorporated polymer monolith was prepared by an in situ reduction method and was applied to the tandem dehydrogenation of ammonia borane and hydrogenation of nitro compounds. The rate of the tandem reaction was significantly accelerated when the catalyst was compressed and released during the reaction. Because a solid support can prevent direct contact between active sites, catalytic metal NPs supported on monolithic MOPs can be promising candidates for use in tandem catalysis.

4. EXPERIMENTAL SECTION

4.1. Materials. 1,3,5-Tris(azidomethyl)-2,4,6-trimethylbenzene and 2,6-diethynylpyridine were synthesized according to the literature methods.47,48 1,3,5-triethylbenzene, 1,4-diiodobenzene, and bis(triphenylphosphine)palladium(II) dichloride were purchased from TCI. Copper iodide was purchased from Sigma-Aldrich. All chemicals were used without any further purification.

4.2. Measurements. 1H NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (300 MHz). Solid-state 13C NMR spectra were obtained with a Bruker AVANCE II spectrometer (500 MHz) equipped with a CP-MAS probe. FT-IR measurements were made on a Thermo Scientific Nicolet 6700 using KBr pellets. SEM images were obtained by using a JEOL JSM-6330F microscope. TEM images were obtained by using a JEOL JEM-2010 microscope at 200 keV. UV–vis spectra were recorded by using a Shimadzu UV-3600 spectrometer. EDS elemental maps were acquired using an Oxford instrument X-Max detector and analyzed with an AZtecEnergy EDS analyzer. XRD measurements were performed on a Smart lab equipped with a Mo Kα X-ray source. TEM images were obtained by using a JEOL JEM-2010 microscope at 200 keV. UV–vis spectra were recorded by using a Shimadzu UV-3600 spectrometer. EDS elemental maps were acquired using an Oxford instrument X-Max detector and analyzed with an AZtecEnergy EDS analyzer. XRD measurements were performed on a Smart lab equipped with a Mo Kα X-ray source.

4.3. Preparation of MPM. 1,4-Diodobenzene (330 mg, 1 mmol), 1,3,5-triethylbenzene (150 mg, 1 mmol), and PdCl2(PPh3)2 (35 mg, 0.05 mmol) were dissolved in a cosolvent of toluene and tetraethylammonium (TEA) (9 mL, 2:1, v/v). The solution was transferred to a 20 mL vial and then degassed by bubbling with nitrogen. A solution of Cul (9 mg, 0.05 mmol) in a cosolvent of toluene and TEA (1 mL, 2:1, v/v) was added to the solution mixture. The reaction was carried out at 65 °C for 24 h. The polymer monolith was washed with methanol and acetone and Soxhlet extracted with tetrahydrofuran. After drying in vacuo at 70 °C, F-PM is obtained as a yellowish monolith.

4.4. Preparation of F-PM. 1,3,5-Tris(azidomethyl)-2,4,6-trimethylbenzene (57 mg, 0.2 mmol), and 2,6-diethynylpyridine (50 mg, 0.4 mmol) were dissolved in a cosolvent of toluene and TEA (9 mL, 2:1, v/v). MPM (240 mg) was then a solution of Cul (9 mg, 0.05 mmol) in a cosolvent of toluene and TEA (1 mL, 2:1, v/v) was added to the reaction mixture. The reaction was carried out at 65 °C for 24 h. The polymer monolith was washed with methanol and acetone and Soxhlet extracted with tetrahydrofuran. After drying in vacuo at 70 °C, F-PM is obtained as a black monolith.

4.5. Preparation of Co-PM. Cobalt chloride hexahydrate (70 mg, 0.54 mmol) was dissolved in 9 mL of deionized water, and then, the solution was added to F-PM (325 mg). An excess amount of an aqueous sodium borohydride solution (50 mM, 40 mL) was added to the mixture of F-PM. After 1 h at room temperature, the polymer monolith was isolated and washed with methanol and deionized water. After Soxhlet extraction with methanol and drying in vacuo at 70 °C, Co-PM was obtained as a black monolith.

4.6. COMPRESSION TEST. The compression tests were carried out with a KES-FB3 automatic compression tester. Strain–stress curves were measured at a strain rate of 5 mm/min. Ten cycles of compression-release tests were recorded at a strain rate of 50 mm/min.

4.7. CATALYTIC PERFORMANCE TEST. Typically, a nitro compound (nitrobenzene: 0.01 mmol, 4-NP and 4-nitroaniline: 0.02 mmol) was dissolved in deionized water and methanol (20 mL, 3:2, v/v), and the solution was 10 times diluted with deionized water. Co-PM was cut into a cylindrical shape (150 mg) and immerse; and released at a rate of 2 s per cycle. The UV–vis spectra of the solution were recorded every 30 cycles (1 min). For comparison, the reactions with stirring and without stirring (static condition) were also carried out under the same conditions except that the sponge was not compressed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01416.

Characterization data of MPM, F-PM, and Co-PM; recyclability of Co-PM; catalytic activity evaluation data of Co-PM in the tandem reactions of dehydrogenation of ammonia borane; photographs of MPMs; and hydrogenation of 4-NP, nitrobenzene, and 4-nitroaniline.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jichang@snu.ac.kr.

ORCID

Ji Young Chang: 0000-0003-2695-1210

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (no. 2015R1A2A2A01006585).

REFERENCES

(1) Li, H.; Xu, B.; Liu, X.; Sigen, A.; He, C.; Xia, H.; Mu, Y. A Metallosalen-Based Microporous Organic Polymer as a Heteroge-
The Importance of Reaction Solvent Choice.

Yamashita, H. Phenylamine-Functionalized Mesoporous Silica (3) Zhang, Y.; Riduan, S. N. Functional Porous Organic Polymers and Copolymer Networks.

dimension and Surface Area in Conjugated Microporous Polymer and Copolymer Networks. J. Am. Chem. Soc. 2008, 130, 7710–7720.

elication of Mercury Cations from Aqueous Media. J. Mater. Chem. A 2017, 5, 7803–7810.

Nunes, S.; Hong, P.-Y. Antibiofilm Effect Enhanced by Click-Based Porous Organic Polymers. Sci. Rep. 2016, 6, 352–364.

Cheng, H.; Xie, Y.; Villalobos, L. F.; Song, L.; Peinemann, K.-V.; Nunes, S.; Hong, P.-Y. Antibiofilm Effect Enhanced by Modification of 1,2,3-Triazole and Palladium Nanoparticles on Polysulfone Membranes. Sci. Rep. 2016, 6, 24289.

Gómez-Valdemoro, A.; San-José, N.; García, F. C.; De La Peña, J. L.; Serna, F.; García, J. M. Novel Aromatic Polyamides with Main Chain and Pendant 1,2,4-Triazole Moieties and Their Application to the Extraction/elimination of Mercury Cations from Aqueous Media. Polym. Chem. 2010, 1, 1291–1301.

Dawson, R.; Laybourn, A.; Khimyak, Y. Z.; Cooper, A. I. Functionalized Conjugated Microporous Polymers. Macromolecules 2009, 42, 8809–8816.

Li, H.; Zheng, Q.; Han, C. Click Synthesis of Podand Triazole-Linked Gold Nanoparticles as Highly Selective and Sensitive Colorimetric Probes for lead(II) Ions. Analyst 2010, 135, 1360–1364.

Pandey, P.; Farha, O. K.; Spokoyny, A. M.; Mirkin, C. A.; Kanatidis, M. G.; Hupp, J. T.; Nguyen, S. T. A “click-based” porous organic polymer from tetrahedral building blocks. J. Mater. Chem. 2011, 21, 1700–1703.

Li, L.; Zhou, C.; Zhao, H.; Wang, R. Spatial Control of Palladium Nanoparticles in Flexible Click-Based Porous Organic Polymers for Hydrogenation of Olefins and Nitrobenzene. Nano Res. 2015, 8, 709–721.

Wang, X.; Hassan, Y. S.; Parida, M. R.; Murali, B.; Mohammed, O. F.; Pellecha, P. J.; Fontecave, M.; Alkordi, M. H. Porous-Hybrid Polymers as Platforms for Heterogeneous Photochemical Catalysis. ACS Appl. Mater. Interfaces 2016, 8, 19994–20002.

Cu-Catalyzed Alkyne-Azide “Click” Cycloadditions from a Mechanistic and Synthetic Perspective. Eur. J. Org. Chem. 2006, 2006, 51–68.

Aromí, G.; Barrios, L. A.; Roubeau, O.; Gamez, P. Triazoles and Tetrazoles: Prime Ligands to Generate Remarkable Coordination Materials. Coord. Chem. Rev. 2011, 255, 485–546.

Zhong, H.; Gong, Y.; Zhang, F.; Li, L.; Wang, R. Click-Based Porous Organic Framework Containing Chelating Terdentate Units and Its Application in Hydrogenation of Olefins. J. Mater. Chem. A 2014, 2, 7502–7508.

Li, L.; Zhao, H.; Wang, J.; Wang, R. Facile Fabrication of Ultrafine Palladium Nanoparticles with Size- and Location-Control in Click-Based Porous Organic Polymers. ACS Nano 2014, 8, 5352–5364.

Cheng, H.; Xie, Y.; Villalobos, L. F.; Song, L.; Peinemann, K.-V.; Nunes, S.; Hong, P.-Y. Antibiofilm Effect Enhanced by Modification of 1,2,3-Triazole and Palladium Nanoparticles on Polysulfone Membranes. Sci. Rep. 2016, 6, 24289.

Gómez-Valdemoro, A.; San-José, N.; García, F. C.; De La Peña, J. L.; Serna, F.; García, J. M. Novel Aromatic Polyamides with Main Chain and Pendant 1,2,4-Triazole Moieties and Their Application to the Extraction/elimination of Mercury Cations from Aqueous Media. Polym. Chem. 2010, 1, 1291–1301.

Dawson, R.; Laybourn, A.; Clowes, R.; Khimyak, Y. Z.; Cooper, A. I. Functionalized Conjugated Microporous Polymers. Macromolecules 2009, 42, 8809–8816.

Li, H.; Zheng, Q.; Han, C. Click Synthesis of Podand Triazole-Linked Gold Nanoparticles as Highly Selective and Sensitive Colorimetric Probes for lead(II) Ions. Analyst 2010, 135, 1360–1364.

Pandey, P.; Farha, O. K.; Spokoyny, A. M.; Mirkin, C. A.; Kanatidis, M. G.; Hupp, J. T.; Nguyen, S. T. A “click-based” porous organic polymer from tetrahedral building blocks. J. Mater. Chem. 2011, 21, 1700–1703.

Li, L.; Zhou, C.; Zhao, H.; Wang, R. Spatial Control of Palladium Nanoparticles in Flexible Click-Based Porous Organic Polymers for Hydrogenation of Olefins and Nitrobenzene. Nano Res. 2015, 8, 709–721.

Wen, S.; Zhao, X.; Liu, Y.; Cheng, J.; Li, H. Synthesis of Hierarchical Sword-like Cobalt Particles and Their Microwave Absorption Properties. RSC Adv. 2014, 4, 40456–40463.

Li, L.; Zhou, C.; Zhao, H.; Wang, R. Spatial Control of Palladium Nanoparticles in Flexible Click-Based Porous Organic Polymers for Hydrogenation of Olefins and Nitrobenzene. Nano Res. 2015, 8, 709–721.

Wen, S.; Zhao, X.; Liu, Y.; Cheng, J.; Li, H. Synthesis of Hierarchical Sword-like Cobalt Particles and Their Microwave Absorption Properties. RSC Adv. 2014, 4, 40456–40463.

Li, L.; Zhou, C.; Zhao, H.; Wang, R. Spatial Control of Palladium Nanoparticles in Flexible Click-Based Porous Organic Polymers for Hydrogenation of Olefins and Nitrobenzene. Nano Res. 2015, 8, 709–721.

Wen, S.; Zhao, X.; Liu, Y.; Cheng, J.; Li, H. Synthesis of Hierarchical Sword-like Cobalt Particles and Their Microwave Absorption Properties. RSC Adv. 2014, 4, 40456–40463.
(37) Seo, M.; Kim, S.; Oh, J.; Kim, S.-J.; Hillmyer, M. A. Hierarchically Porous Polymers from Hyper-Cross-Linked Block Polymer Precursors. J. Am. Chem. Soc. 2015, 137, 600–603.

(38) Saba, S. A.; Mousavi, M. P. S.; Buhlmann, P.; Hillmyer, M. A. Hierarchically Porous Polymer Monoliths by Combining Controlled Macro- and Microphase Separation. J. Am. Chem. Soc. 2015, 137, 8896–8899.

(39) Du, R.; Zhang, N.; Xu, H.; Mao, N.; Duan, W.; Wang, J.; Zhao, Q.; Liu, Z.; Zhang, J. CMP Aerogels: Ultrahigh-Surface-Area Carbon-Based Monolithic Materials with Superb Sorption Performance. Adv. Mater. 2014, 26, 8053–8058.

(40) Chakraborty, S.; Colón, Y. J.; Snurr, R. Q.; Nguyen, S. T. Hierarchically Porous Organic Polymers: Highly Enhanced Gas Uptake and Transport through Templated Synthesis. Chem. Sci. 2015, 6, 384–389.

(41) Wang, Z. J.; Ghasimi, S.; Landfester, K.; Zhang, K. A. I. Photocatalytic Suzuki Coupling Reaction Using Conjugated Microporous Polymer with Immobilized Palladium Nanoparticles under Visible Light. Chem. Mater. 2015, 27, 1921–1924.

(42) Wang, D.; Astruc, D. The recent development of efficient Earth-abundant transition-metal nanocatalysts. Chem. Soc. Rev. 2017, 46, 816–854.

(43) Rakap, M.; Özkar, S. Hydrogen Generation from the Hydrolysis of Ammonia-Borane Using Intrazeolite cobalt(0) Nanoclusters Catalyst. Int. J. Hydrogen Energy 2010, 35, 3341–3346.

(44) Arthur, E. E.; Li, F.; Momade, F. W. Y.; Kim, H. Catalytic Hydrolysis of Ammonia Borane for Hydrogen Generation Using Cobalt Nanocluster Catalyst Supported on Polydopamine Functionalized Multiwalled Carbon Nanotube. Energy 2014, 76, 822–829.

(45) Wu, W.; Liu, G.; Xie, Q.; Liang, S.; Zheng, H.; Yuan, R.; Su, W.; Wu, L. A Simple and Highly Efficient Route for the Preparation of P-Phenylenediamine by Reducing 4-Nitroaniline over Commercial CdS Visible Light-Driven Photocatalyst in Water. Green Chem. 2012, 14, 1705–1709.

(46) Yang, X.-J.; Chen, B.; Zheng, L.-Q.; Wu, L.-Z.; Tung, C.-H. Highly Efficient and Selective Photocatalytic Hydrogenation of Functionalized Nitrobenzenes. Green Chem. 2014, 16, 1082–1086.

(47) Leininger, S.; Schmitz, M.; Stang, P. J. Molecular Architecture via Coordination: Self-Assembly of Pseudoheptagonal A23X23-Macrocycles. Org. Lett. 1999, 1, 1921–1923.

(48) Tian, J.; Wan, L.; Huang, J.; Hu, Y.; Huang, F.; Du, L. Synthesis and Characterization of a Novel Polyyiazole Resin with Low-Temperature Curing Character. Polym. Adv. Technol. 2007, 18, 556–561.