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Cobalt-Nanoparticles Catalyzed Efficient and Selective Hydrogenation of Aromatic Hydrocarbons

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Supporting Information

ABSTRACT: The development of inexpensive and practical catalysts for arene hydrogenations is key for future valorizations of this general feedstock. Here, we report the development of cobalt nanoparticles supported on silica as selective and general catalysts for such reactions. The specific nanoparticles were prepared by assembling cobalt-pyromellitic acid-piperazine coordination polymer on commercial silica and subsequent pyrolysis. Applying the optimal nanocatalyst, industrial bulk, substituted, and functionalized arenes as well as polycyclic aromatic hydrocarbons are selectively hydrogenated to obtain cyclohexane-based compounds under industrially viable and scalable conditions. The applicability of this hydrogenation methodology is presented for the storage of H₂ in liquid organic hydrogen carriers.



KEYWORDS: arenes, cyclohexanes, co-nanoparticles, hydrogenations, catalysis

INTRODUCTION

Aromatic hydrocarbons represent an essential feedstock for the chemical industry and their applications range from life sciences to bulk and fine chemicals as well as polymers and fuels.^{1,2} In fact, the basic substrates such as benzene, toluene, and xylene are produced on >100 million tons per annum.^{3,4} Moreover, condensed arenes are available from oil refining on large scale.⁴ Because of their importance and abundance, synthetic organic chemistry in the past century and even today focused to a large extent on their functionalization.^{1,2,5,6} In general, hydrogenations of arenes constitute green and 100% atom-efficient processes for the synthesis of cyclohexane-based products,^{1,2,7-45} which are also used in industries, drug development, material sciences, and energy sector.⁷⁻¹⁴ Because of the high stability of the benzene ring, the majority of catalysts for this transformation are based on precious metals.^{15–37} In fact, the state-of-the-art systems constitute Ru^{15-25} and Rh.^{15–19,26–35} For the advancement of sustainable arene hydrogenation, the development of more earth abundant metal catalysts is of central importance. In this respect, so far, nickel³⁸⁻⁴³ including Raney nickel,⁴⁴ as well as few other Co^{38,42-48}-based catalysts are known for the hydrogenation of benzene and other simple substrates. However, in general, these catalysts exhibit poor selectivity and low stability for recycling and have not been applied for diverse com-⁻⁴⁸ Thus, cost-efficient and chemo-, regio-, and pounds. stereo-selective hydrogenation of structurally challenging aromatic hydrocarbons in the presence of heterogeneous

base metal catalysts are highly important and continue to attract significant interest.

In recent years, supported nanostructured materials had tremendous impact on the chemical industry and the innovation of chemical processes.⁴⁹⁻⁶² Key for the implementation of these materials is the preparation of active nanoparticles on appropriate supports using inexpensive precursors and applying convenient, easy to follow up, and reproducible methods.^{49–62} In this regard, pyrolysis of (in situ generated) organometallic complexes, ${}^{51,58-62}_{52,63-67}$ metal organic frameworks (MOFs), ${}^{52,63-67}_{52,63-67}$ and coordination polymers (CPs)⁶⁷⁻⁷⁴ allows for the synthesis of unique catalytic materials. Notably, metal containing CPs can be easily engineered by variation of metal ions and organic linkers.⁶⁷⁻⁷ Following this concept, the selection of suitable linkers for the preparation of active nanoparticles with the precise size and shape is most important. Advantageously, a plethora of carboxylic acid- and nitrogen-based linkers are available to prepare different CPs. Here, we describe the preparation of cobalt-based CPs using inexpensive pyromellitic acid (PMA) and piperazine (PZ) linkers and their use as convenient precursor and structure directing template. Supporting these CPs on commercial silica (AEROSIL) and subsequent pyrolysis creates reusable cobalt nanoparticles for the hydro-

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Figure 1. Synthesis of supported cobalt nanoparticles using CPs as precursors and structure controlling templates.



Figure 2. Hydrogenation of aniline to cyclohexylamine: activity of cobalt catalysts. Reaction conditions: 1 mmol aniline, 120 mg catalyst (9 mol % Co), 50 bar H₂, 4 mL *t*-BuOH, 135 °C, 24 h, yields were determined by GC using *n*-hexadecane standard. *Catalyst was prepared using polymeric material reported in ref 74.

genation of industrially important and structurally diverse arenes.

RESULTS AND DISCUSSION

Preparation of Cobalt-Based Nanocatalysts. First, we generated different cobalt-based CPs in situ in N,N-dimethylformamide (DMF) combining $Co(NO_3)_2$ ·6H₂O with different carboxylic acids such as terephthalic acid (TPA; 1,4-benzenedicarboxylic acid; 1), trimesic acid (1,3,5-benzenetricarboxylic acid; TMA; 2), PMA (1,2,4,5-benzenete-tracarboxylic acid; PMA; 3), and nitrogen linker, for example, 1,4-diazabicyclo[2.2.2]octane (triethylendiamine; DABCO; 4) and PZ (diethylenediamine; PZ; 5) (Figure 1).

The resulting materials were assembled on different supports $(SiO_2, Al_2O_3, ZSM-5 TiO_2, carbon, and MgO)$ and then pyrolyzed under argon to obtain the respective nanomaterials (see the Experimental Section for detailed preparation). Hereafter, these materials are labeled as Co-acid linker-amine linker@support-x, where x denotes the pyrolysis temperature.

Initially, all of the prepared materials were tested for the hydrogenation of industrially important aniline to cyclohexylamine as a benchmark reaction (Figure 2). Cyclohexylamine is used as a valuable intermediate for pharmaceuticals (e.g., mucolytics, analgesics, bronchodilators) and herbicides. Furthermore, it is the precursor for accelerators for vulcanization and an effective corrosion inhibitor. First, we tested Co-TPA-DBCO@SiO2-800 material prepared using TPA and DABCO linkers, which were used previously for the preparation of cobalt-based MOFs and nanocatalysts.^{52,66} Interestingly, this catalyst showed some activity (13%). Variation of the nitrogen linker from DABCO to PZ gave Co-TPA-PZ@SiO₂-800 with increased product yield (20%). Further preparation of CPs using different benzene carboxylic acid linkers and PZ resulted in more active materials. Among these, Co-CPs based on PMA and piparazine (PZ) linkers produced the best catalyst (Co-PMA-PZ@SiO₂-800), which led to 90% cyclohexylamine. The reported cobalt-CP⁷⁴ using CoCl₂·6H₂O, PMA and PZ linkers with a molar ratio of 1:1:3 was also prepared and immobilized on SiO₂. Pyrolysis of this material at 800 °C under argon produced a much less active catalyst for the formation of cyclohexylamine (5%). To produce an active catalyst, 3 equivalents of each of PMA and PZ linkers with respect to cobalt are required. The X-ray powder diffraction (XRD) pattern of cobalt-PMA-PZ CP is given in Figure S1. Comparison with materials made from single linkers, Co-PMA@SiO2-800 and Co-PZ@SiO2-800, showed activity (52%) for the former one, whereas the latter is almost inactive. Similarly, cobalt nitrate@SiO2-800, the nonpyrolyzed Co-PMA-PZ@SiO2 and corresponding Co-PMA-PZ CP were not active too. In addition to the different linkers, the effect of the pyrolysis temperature was also studied. The material pyrolyzed at 400 °C (Co-PMA-PZ@SiO₂-400) again is completely inactive, whereas pyrolysis at 600 °C and 1000 °C (Co-PMA-PZ@SiO₂-600; Co-PMA-PZ@SiO₂-1000) showed little activity (25 and 8%, respectively). Further, to know the effect of supports, different supported materials prepared using Co-PMA-PZ CP were also tested. Among these Al₂O₃, TiO₂, and zeolite-supported catalysts showed some activity (10-28%). However, carbon- and MgO-supported ones are completely inactive.

Catalysis and Synthetic Applications. Hydrogenation of Bulk and Functionalized Arenes. With the successful catalyst Co-PMA-PZ@SiO₂-800 for the benchmark process of aniline to cyclohexylamine in hand, we carried out its general applicability for the hydrogenation of various aromatic hydrocarbons. As shown in Schemes 1-4, this catalyst allows

Scheme 1. Co-PMA-PZ@SiO₂-800 Catalyzed Hydrogenation of Bulk and Functionalized Arenes to Obtain Value-Added Cyclohexanes^a



^{*a*}Reaction conditions: 1 mmol substrate, 120 mg catalyst (9 mol % Co), 50 bar H₂, 4 mL *t*-BuOH, 135 °C, 24 h, yields were determined by gas chromatography (GC) using *n*-hexadecane standard. ^{*b*}Nitrobenzene was used as substrate to obtain cyclohexylamine. ^{*c*}At 150 °C for 48 h. ^{*d*}At 150 °C for 34 h. ^{*e*}For 40 h and isolated yields.

for the selective hydrogenation of diverse functionalized and substituted arenes, including annulated compounds to cyclic aliphatic hydrocarbons. Several bulk chemicals including benzene, toluene, and phenol were hydrogenated to produce industrially important products in excellent yields (Scheme 1 products 8–11). As an example, cyclohexane is used for the production of KA oil (mixture of cyclohexanone and cyclohexanol), adipic acid, and caprolactam. This product, which is currently produced (>5 million tons/annum) using either Ni or Pt catalysts at >160 $^{\circ}C_{,}^{75,76}$ is conveniently formed in 95% yield at 135 °C and 50 bar H₂ (Scheme 1; product 8). Similarly, methylcyclohexane used as energy fuel is obtained in 95% (product 10). Apart starting from aniline, cyclohexylamine can be prepared directly from nitrobenzene in 82% yield (Scheme 1; product 7). It is worthwhile to mention here that cyclohexylamine is industrially produced by the hydrogenation of aniline (see benchmark reaction), which is obtained from nitrobenzene. In this respect, the production of cyclohexylamine directly from nitrobenzene has obvious advantages with respect to step- and cost-economy. The preference of this catalyst for chemoselective arene hydrogenation is showcased using functionalized substrates containing amine, ether, amide, ester, and pyrazole groups (Scheme 1; products 13-22). In all these cases, the benzene ring was selectively reduced by tolerating these functional groups.

Hydrogenation of Multiring Aromatic Hydrocarbons. In case of aromatic hydrocarbons with multiple rings, the reduction of one in the presence of others is generally more challenging and most of the known catalysts are less selective for such substrates.^{15–48} However, using Co-PMA-PZ@SiO2-800 catalyst regioselective hydrogenation of one ring in case of naphthalenes, biphenyl, diphenyl methane, fluorine and xanthene molecules took place at 135 °C (Scheme 2; products





^{*a*}Reaction conditions: 1 mmol substrate, 120 mg catalyst (9 mol % Co), 50 bar H₂, 4 mL *t*-BuOH, 135 °C, isolated yields. ^{*b*}In 4 mL *i*-PrOH and GC yield using *n*-hexadecane. ^{*c*}In 4 mL *t*-BuOH and 100 μ L H₂O. ^{*d*}150 °C.

23–35). Notably, some of these partially hydrogenated derivatives are of increasing interest as intermediates for energy technologies. As an example, cyclohexylbenzene (CHB; product 26) is used as electrolyte additive in lithium ion batteries. Interestingly, at slightly elevated temperature (150 $^{\circ}$ C) we achieved full hydrogenation in selected molecules. As a

Scheme 3. Diastereoselective Hydrogenation of Substituted Phenols and Arenes^a



^{*a*}Reaction conditions: 1 mmol substrate, 120 mg catalyst (9 mol % Co), 50 bar H₂, 4 mL *t*-BuOH, 135 °C, 24 h, isolated yields. Cis-trans isomers selectivity was determined by NMR spectral analysis. ^{*b*}At 150 °C. ^{*c*}In 4 mL *i*-PrOH. ^{*d*}1 g substrate, 9 mol % catalyst, 15 mL *t*-BuOH, 150 °C, 48 h, isolated yields. Isomeric ratio in case of 2-isopropyl-5-methylcyclohexanol was determined by GC.

result, 9 bicyclic aliphatic hydrocarbons were obtained in up to 92% yields (Scheme 2; products 36–44).

Diastereoselective Hydrogenation Process. A major challenge for any new arene hydrogenation catalyst to be implemented in synthetic chemistry is the diastereoselective hydrogenation of multiple substituted derivatives.^{20,23,26,35,77} In general, such reactions offer a unique possibility to synthesize platform molecules for new pharmaceuticals, agrochemicals, and fine chemical applications. Unfortunately, relatively, a few catalysts have been applied for such transformations.^{20,23,26,37,77} Among these, notable works are based on Rh²⁶ and Ru²⁰ for the preparation fluorinated cycloalkanes and substituted cyclohexanols, respectively.

To evaluate the potential of our Co-PMA-PZ@SiO₂-800 system in this context, the hydrogenation of a series of substituted phenols for the preparation of cyclohexanols was performed. Apart from being interesting intermediates, the present hydroxyl group can be easily further functionalized. As shown in Scheme 3, various di- and trisubstituted phenols underwent hydrogenation to give the corresponding diastereoisomers in good to excellent yields (Scheme 3). 1,2-Disubstituted phenols with methyl, cyclohexyl, and benzyl groups lead preferentially to the thermodynamically more stable trans products in up to 95% selectivity (Scheme 3; products 29, 38,40). On the other hand, 2-tert-butylphenol gave the corresponding cis product with 93% selectivity (Scheme 3; product 46). To understand this observation, isomerization experiments of both cis- and trans-2-methylcyclohexanol were performed under the typical hydrogenation conditions. However, no isomerization occurred. Similar to the 1,2-disubstituted phenols, the related 1,4-derivatives yield preferentially the thermodynamically more stable trans isomers (Scheme 3; products 30, 44, 49-54). An exception is the formation of 27, which is explained by the stronger coordination of the second arene ring to the catalyst surface, which leads to the cis-product. In case of 1,3-disubstituted phenols, the cis products were preferentially formed, which is also explained by their increased thermodynamic stability (Scheme 3; products 47-48). To showcase the selective hydrogenation of disubstituted anilines and biaryls, N-phenyltoluidine and 4,4'-dimethylbiphenyl, respectively, were also reduced in high yields (Scheme 3; products 44 and 27). As an example for the reduction of trisubstituted arenes, the hydrogenation of thymol (2-isopropyl-5-methylphenol; 55) was investigated, which is industrially important for the synthesis of menthol isomers.⁷⁸ At 150 °C, full conversion of thymol was observed using our novel base metal catalyst yielding 71% of (\pm) -isomenthol.⁷⁸

Scheme 4. Application of Cobalt-Catalyzed Hydrogenation Process for the Storage of H₂ in LOHCs^a



^aReaction conditions: 2 mmol substrate, 240 mg catalyst (9 mol % Co), 50 bar H₂, 8 mL *t*-BuOH, 150 °C, 48 h. ^bAt 135 °C, 24 h.





"Reaction conditions: 1–25 g substrate, 4.5 mol % catalyst, *t*-BuOH solvent (10 v for each 1 g substrate), 135 °C. *With 9 mol % catalyst. [†]In *i*-PrOH solvent.

Applicability of Cobalt Nanoparticles for the Storage of H_2 in LOHC. Catalytic hydrogenation reactions constitute a key element for the transformation of renewable energy (wind, PV, etc.) into chemical energy carriers. In this context, the storage of hydrogen in liquid organic hydrogen carriers (LOHCs) has attracted significant interest in recent years.⁷⁹⁻⁸¹ In general, different arenes such as benzene, methylbenzene, diphenylmethane, bipyridine, and dibenzyltoluene are considered as LOHCs. For example, the latter compound is readily available and technically applied as heat transfer oil (MARLOTHERM SH, MSH).7 Regarding the known catalysts for this transformation, commercially available Ru/Al₂O₃ was used for the hydrogenation of MSH (45% storage of hydrogen at 150 °C).⁸¹ Using our cobalt catalyst at 150 °C, hydrogenation of MSH yielded three different isomers with overall hydrogen storage of 65% (Scheme 4). In addition, other selected molecules reacted smoothly and resulted in up to 99% hydrogen storage (Scheme 4).

Synthetic Utility Co-Catalyzed Arenes Hydrogenation Protocol. After having demonstrated several applications of this novel Co-PMA-PZ@SiO₂-800 material, reaction upscaling and catalyst recycling were showcased. Consequently, several arenes were hydrogenated to obtain corresponding cyclohexanes in up to 25 g (Scheme 5). Notably, all of these reactions were carried out using lower catalyst loading (4.5 mol % Co).

Recycling and reusability of the catalyst was performed using phenol hydrogenation. It was recycled up to 4 times without significant loss of activity and in all cases, the yield of cyclohexanol was >90% (Figure 3). In addition to recycling, we also tested the stability of the Co-PMA-PZ@SiO₂-800 catalyst by performing recycling of the catalyst at reduced reaction time (Figure S22). At 10 h of reaction time, the yield of cyclohexanol in each run was rapidly decreased (Figure S22). These studies showed that the catalyst is not stable and deactivation occurred. Hence, 24 h of the reaction time is



Figure 3. Catalyst recycling for the hydrogenation of phenol to cyclohexanol. Reaction conditions: 10 g phenol (106 mmol), 6.35 g catalyst (4.5 mol %), 100 mL t-BuOH, 135 $^{\circ}$ C, 24 h.

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required to obtain >90% cyclohexanol in up to 5th run (Figure 3)

Characterization of Co-Based Nanocatalysts. In order to identify the structural features and to understand the varying catalytic activities of these novel cobalt-based materials, we characterized the active catalyst (Co-PMA-PZ@SiO₂-800), less active (Co-TPA-PZ@SiO₂-800, Co-PMA@SiO₂-800), and completely inactive materials (Co-PZ@SiO₂-800) using X-ray powder diffraction (XRD), Brunauer-Emmett-Teller (BET), scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), and energy-dispersive X-ray spectroscopy (EDXS) and X-ray photoelectron spectroscopy-(XPS). XRD analysis revealed that the most active catalyst contains metallic cobalt particles along with some Co₃O₄ (Figure S2). In case of less active materials, a mixture of metallic Co and oxidic cobalt (Co₃O₄ and CoO) particles were present (Figures S3 and S4). However, in case of the inactive material, the presence of mainly Co_3O_4 particles was observed (Figure S5). Another nonactive material, cobalt nitrate@SiO₂-800 also contained mainly metal oxide particles (Figure S6). BET measurements revealed the importance of the surface area for the catalyst activity which increased in the order of 42 (Co-PZ@SiO₂-800), 77 (Co-PMA@SiO₂-800) to 155 m²/g (Co-PMA-PZ@SiO₂-800) (Figures S8-S10).

The STEM analysis of the most active material revealed the formation of cobalt nanoparticles with sizes between 5 and 20 nm of different compositions. Contrast in high-angle annular dark field (HAADF) micrographs shows the presence of probably metallic Co particles tightly covered in graphitic carbon and particles of Co oxide (Figure 4A) more loosely attached to carbon and the support. Unfortunately, during EDXS and EELS measurements, the morphology of the Cocontaining particles changed somewhat under the extended influence of the electron beam and formation of particles similar to such Co oxide crystallites was observed. Therefore, EELS data cannot be used to determine the exact nature of the Co species, for example, by fingerprinting the fine structure of the Co-L edge in the EELS data (Figures S12 and S13A).⁸² Additionally, there is a carbon phase containing N attached to the SiO₂ support as seen in the EELS elemental maps. Highresolution HAADF images of a free hanging carbon structure indicate the presence of even heavier atoms in this phase; however, the density was too low for EDXS or EELS analysis (Figure S14). In case of the less active material prepared using TPA and PZ linkers (Co-TPA-PZ@SiO₂-800), metallic cobalt particles are surrounded by graphitic shells and Co oxide particles show little contact to carbon structures when attached to the silica support (Figures 4B and S13B). The Co-PMA@ SiO₂-800 material contained generally small (<15 nm) with a few large polycrystalline particles as exceptions (Figures 4C and S13C). Some of these particles are encapsulated within large well-ordered graphitic carbon others without carbon shell and probably of a Co oxide variant are also located directly on silica. In case of the inactive sample (Co-PZ@SiO₂-800), large particles up to 85 nm, which are completely encapsulated with in graphitic shells, are found (Figures 4D and S13D). In addition, some Co/Co₃O₄ particles in core shell structures were also observed, however, with no clear connection to carbon structures.

Further XPS analysis for Co-PMA-PZ@SiO₂-800, Co-PMA@SiO₂-800, and Co-PZ@SiO₂-800 samples has been conducted to understand in more detail the states of cobalt and nitrogen at the surface of the catalysts (Figure S15). In the

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Figure 4. STEM-HAADF and -ABF images of silica supported cobalt catalysts. Left column shows HAADF images of the general structure, the middle column shows details of Co oxide particles with ABF images as an inset to highlight possible carbon structures, and the right column shows ABF images with details of Co particles, with tightly packed graphitic covering of metallic Co particles where these metallic particles are present, (a) Co-PMA-PZ@SiO₂-800, (b) Co-TPA-PZ@SiO₂-800, (c) Co-PMA@SiO₂-800, and (d) Co-PZ@SiO₂-800.

most active catalyst, (Co-PMA-PZ@SiO₂-800) the deconvolution of Co 2p peaks shows the presence of two types of Cospecies (Figure S15a; left image). The peak at 778.55 eV represents metallic cobalt (Co $2p_{3/2}$), while the peak at 780.51 eV denotes $Co^{2+}(2p_{3/2})$ species (Figure S15a; left image). The corresponding Co $2p_{1/2}\ peaks$ are observed at 794.43 and 796.45 eV. Co $2p_{3/2}$ and Co $2p_{1/2}$ peak energy splitting was found to be 15.88 eV for Co(0) and 15.90 eV for $Co^{2+,83}$ The catalyst Co-PMA@SiO2-800 also contains mixed oxidation states for Co-species (Figure S15b; left image). A peak at 778.49 eV represents the presence of Co $2p_{3/2}$ in the metallic state, whereas a peak at 779.92 eV can be assigned to Co²⁺ species. Although, a peak for Co³⁺ could not be deconvoluted, however, the presence of strong satellite peaks at 786.43 and 802.20 eV are indicative for multiple oxidized Co species, as satellite peaks arise due to spin-spin interactions of different Co species.^{83,84} The Co-PZ@SiO₂-800 material also shows the presence of two cobalt species (Figure S15c; left image); however, the absence of a peak around 778.5 eV indicates that metallic Co is not present.⁸⁵ The peaks present at 779.91 and 781.52 eV can be assigned to $2p_{3/2}$ Co²⁺ and Co³⁺ species. The corresponding 2p_{1/2} peaks are present at 793.52 and 795.45 eV for both these species (Figure S15c; left image). In these three catalysts, surface concentration and states of N vary due to the use of different ligands in the pyrolysis process. Clearly, the presence of different linkers affects the graphitization process and the occurrence of N at the surface.⁸⁶ Nevertheless, in all these samples, N 1s spectra are complicated due to the low concentrations of N on the surface and also its interaction with cobalt, carbon, and SiO₂.⁸⁶⁻⁸⁸ For Co-PMA-PZ@SiO₂-800, which was prepared using $Co(NO_3)_2$, PMA, and PZ, N 1s spectra could be deconvoluted to three N 1s peaks within the catalyst structure (Figure S15a; right image). The binding energies centered at 399.35, 401.36, and 403.88 eV can be assigned to pyridinic N, pyrrolic N, and graphitic N, respectively.^{86,87} In contrast, the sample Co-PMA@SiO₂-800, which was prepared form $Co(NO_3)_2$, PMA, contains only two types of N (Figure S15b; right image). Deconvolution results fitting of two N-peaks centered at binding energies of 399.4 and 400.1 eV. Compared to Co-PMA-PZ@SiO₂-800, in this case, graphitic N is absent at the surface. The presence of N in this sample obviously comes from cobalt nitrate. The material Co-PZ@SiO₂-800 prepared by $Co(NO_3)_2$ and PZ also contains two types of N 1s peaks centered at 401.21 and 404.05 eV (Figure S15c; right image). In this case, pyridinic N is absent. Further to know the phases of cobalt, in situ XRD analysis has been performed (Figures S16-S21). If the catalyst is decomposed, the formation of CoO has to be observed at 800 °C under a helium (He) flow of 10 mL/min. However, the catalyst cooled down, and the product of the thermal treatment was investigated ex situ and observed only Co₃O₄. According to this result, the experiments were performed by flushing with He (10 mL/min) for approximately 25 min. Then, the gas flow was stopped, and the temperature program was started. After heating to 800 °C (25 °C/min heating rate), the diffraction data were collected over a period of 2 h (each 10 min) and the cooling of the sample were monitored by the collection of diffraction data each 100 °C step. In this experiment, the formation of metallic Co can be stated. Then, the metallic Co is oxidized to Co₃O₄ during the cooling process. An additional experiment was also carried out to check the amount of O2 during heating, isothermal, and cooling procedure by the analysis of the gas passed through an empty capillary. The value of the O₂ concentration was constant over the whole experiment (heating to 800 °C, 30 min isothermal, cooling to 25 °C, heating rate: 25 °C/min).

All of these characterization studies revealed that in the most active material (Co-PMA-PZ@SiO₂-800) different types cobalt nanoparticles are present. Metallic Co particles tend to be covered in graphitic shells possibly isolating them, whereas a large fraction of Co oxide particles connects to the carbon matrix containing nitrogen and possibly highly disperse Co. The nitrogen content indicates that PMA with PZ as the linker forms these structures which in accordance with the BET results seems to enhance the active surface area of the catalyst strongly when compared to the pure support.

CONCLUSIONS

In conclusion, we have developed efficient cobalt-based nanocatalysts for general and selective hydrogenation of aromatic hydrocarbons to produce the corresponding aliphatic products, which serve as essential compounds in chemical and life science industries as well as for energy and material sciences. Key to success for this hydrogenating process is the graphitic shell-encapsulated cobalt nanoparticles prepared by the template synthesis of cobalt–PMA–PZ CP on commercial silica and subsequent pyrolysis under an inert atmosphere. This cobalt-based protocol proceeds for the hydrogenation of industrial bulk, substituted, and functionalized arenes as well as polycyclic aromatic hydrocarbons under industrially viable and scalable conditions. In addition, this catalyst system has been applied for the diastereoselective hydrogenation of multiple substituted phenols and arenes. The utility and applicability of this hydrogenation methodology is demonstrated by catalyst recycling and gram-scale synthesis as well as for the storage of $\rm H_2$ in LOHC.

EXPERIMENTAL SECTION

General Consideration. All substrates were obtained commercially from various chemical companies. Cobalt(II) nitrate hexahydrate (cat no. 139267-100G), PZ (ReagentPlus, >99%: cat no. P45907) 1.4-diazabicvclo[2.2.2]octane (DABCO; ReagentPlus, ≥99%; cat no. D27802-25G), TPA (cat no. 185361; 98%), and titanium(IV) oxide (TiO_2 ; cat no. 718467; ≥99.5%) were obtained from Sigma-Aldrich. PMA (cat no. B23099; 96%), 1,3,5-benzenetricarboxylic acid (TMA; cat no. A15947; 98%), zeolite ZSM-5 ammonium (ZSM-5; cat no. 45879), and magnesium oxide (MgO; cat no. 43196; 99.95%) were obtained from Alfa Aesar. t-Butanol (t-buOH, code-390690025; 99.8%) was obtained from Across chemicals. Silica (AEROSIL OX 50) was obtained from Evonik. Carbon powder, VULCAN XC72R with code XVC72R and CAS no. 1333-86-4 was obtained from Cabot Corporation Prod. The pyrolysis experiments were carried out in a Nytech Qex oven. Before using, the purity of the substrate has been checked.

STEM measurements were performed at 200 kV with aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS). The microscope was equipped with a JED-2300 (JEOL) energy-dispersive X-ray-spectrometer and Enfinium ER (GATAN) electron energy-loss spectrometer with dual EELS for chemical analysis. HAADF and annular bright field (ABF) detectors were used for general imaging; the annular dark field detector was used for position control for EELS acquisition. Dual EELS was done at a camera length of 4 cm, an illumination semi angle of 27.8 mrad, and a filter entrance aperture semi angle of 41.3 mrad using the low loss region for compensation of energy shifts during acquisition. The solid samples were deposed without any pretreatment on a holey carbon supported Cu-grid (mesh 300) and transferred to the microscope.

XRD powder pattern were recorded on a PANalytical X'Pert diffractometer equipped with a XCelerator detector using automatic divergence slits and Cu K α 1/ α 2 radiation (40 kV, 40 mA; $\lambda = 0.15406$, 0.154443 nm). Cu β -radiation was excluded using a nickel filter foil. The measurements were performed in 0.0167° steps and 100 s of data collecting time per step. The samples were mounted on silicon zero background holders. The obtained intensities were converted from automatic to fixed divergence slits (0.25°) for further analysis. Peak positions and the profile were fitted with Pseudo-Voigt function using the HighScore Plus software package (PANalytical). Phase identification was done by using the PDF-2 database of the International Center of Diffraction Data (ICDD).

BET surface areas of the catalysts were determined on a NOVA 4200e instrument by N₂-physisorption at -196 °C. Prior to the measurements, the known amount of the catalyst was evacuated for 2 h at 220 °C to remove physically adsorbed water.

In situ XRD studies were preformed on a Stoe Stadi P equipped with a Stoe ht2-in situ oven and a Mythen 1K detector in Debye–Scherrer geometry using a Mo-X-ray tube [50 kV, 40 mA, $K\alpha$ 1: 0.70930 Å, Ge(111)]. Temperature correction was applied by measurement of well-known phase transitions of standard materials (AgNO₃, KClO₄, Ag₂SO₄, SiO₂, K₂SO₄, K₂CrO₄, WO₃, BaCO₃). Gas dosage was done via

a Bronkhorst mass flow controller. The sample to investigate was grinded, pressed to pellets by a pressure of 10 tons, crushed, and sieved to fraction of 100–150 μ m. The fraction was filled to a quartz glass capillary (approx. 2 mm outer diameter, 1 mm inner diameter, opened on both sides) to a height of approx. 8 mm and fixed by quartz glass wool at both sides. The loading of the catalyst precursor was increased to 20 wt % to obtain data of reliable guality after the decomposition of the precursor. The capillary was mounted into the in situ chamber, and the capillary was flushed with He (10 mL min⁻¹) for 20 min. The gas flow was switched off before starting the heating. The sample was heated to 800 °C (25 °C min⁻¹), and the temperature was kept constant for 2 h while recording diffraction data every 10 min (stationary measurement, 300 s of acquisition time). The cooling process (25 °C min⁻¹) was monitored each 100 °C step.

All catalytic experiments were carried out in 300 and 100 mL autoclaves (PARR Instrument Company). In order to avoid unspecific reactions, all catalytic reactions were carried out either in glass vials, which were placed inside the autoclave or glass/Teflon vessel-fitted autoclaves.

GC and GC-mass spectrometry (MS) were recorded on Agilent 6890N instrument. GC conversion and yields were determined by GC-FID, HP6890 with a FID detector, column HP530 m \times 250 mm \times 0.25 μ m.

¹H and ¹³C NMR data were recorded on Bruker ARX 300 and Bruker ARX 400 spectrometers using DMSO-*d*₆, CD₃OD and CDCl₃ solvents.

HRMS data were recorded on a mass spectrometer MAT 95 XP (Thermo Electron), 70 eV.

Procedure for the Catalyst Preparation. Preparation of Co-PMA-PZ@SiO₂ Template (3 g Preparation) and Pyrolysis To Obtain Nanomaterial. In a 50 mL round-bottom flask, cobalt(II) nitrate hexahydrate (444.5 mg; 1.5 mmol) and PZ (395.2 mg; 4.5 mmol) were stirred for 5 min in 15 mL of DMF at 150 °C. To this mixture, the already dissolved (by heating) PMA (1.16 g; 4.5 mmol) in 10 mL of DMF was added. Then, the round-bottom flask containing the reaction mixture was placed into an aluminum block preheated at 150 °C and stirred for 20-30 min after fixing a reflux condenser to the roundbottom flask. Then, 1.2 g of silica (AEROSIL OX 50) was added followed by the addition of 15 mL of DMF, and the reaction mixture was stirred again at 150 °C for 4-5 h. Then, the reflux condenser was removed, and the round-bottom flask containing the reaction product was allowed to stand without stirring and closing for 20 h at 150 °C in order to slowly evaporate DMF and to grow the cobalt-CP template on carbon. After the evaporation of the solvent and ensuring the complete drying, the material was cooled to room temperature and grinded to give a fine powder. The powdered material was pyrolyzed at the defined temperature (400, 600, 800, or 1000 °C) for 2 h under an argon atmosphere and then cooled to room temperature after pyrolysis.

Elemental analysis (wt %): Co-PMA-PZ@SiO₂-800: Co = 4.6%, C = 16.98%, H = 0.10%, Si = 32.59% N = 0.81%.

The same procedure has been applied for the preparation of other supported materials.

Preparation of Co-PMA-PZ CP. In a 50 mL round-bottom flask, cobalt(II) nitrate hexahydrate (444.5 mg) and PZ (395.2 mg) were stirred for 5 min in 15 mL DMF at 150 °C, and to this mixture the already dissolved PMA (by heating) (1.16 g) in 10 mL DMF was added. Then, the round-bottom flask containing a reaction mixture was placed into an aluminum

block preheated at 150 °C and stirred for 1 h after fixing a reflux condenser to the round-bottom flask. Then, the reflux condenser was removed, and the reaction mixture was allowed to stand without stirring for 1–2 h at 150 °C. A pink colored cobalt-CP was formed and filtered through filter paper and washed 3–4 times with hot DMF (15–20 mL each time). The washed material was dried at 140–150 °C in an oven for 15 h and then finally dried under high vacuum at room temperature for 4–5 h.

General Procedure for the Hydrogenation of Arenes. A magnetic stirring bar and 1.0 mmol of the corresponding arene were transferred to a glass vial (8 mL), and 3 mL of the solvent (t-BuOH) was added. Then, 120 mg of the catalyst (Co-PMA-PZ@SiO₂-800; 9 mol % Co) was added, and the vial was fitted with a septum, cap, and needle. The reaction vials (eight vials with different substrates at a time) were placed into a 300 mL autoclave. The autoclave was flushed with 30 bar hydrogen twice, and then, it was pressurized with 50 bar of hydrogen. The autoclave was placed into an aluminum block preheated at 145 °C (placed 30 min before counting the reaction time in order to attain reaction temperature), and the reactions were stirred for the required time. During the reaction, the inside temperature of the autoclave was measured to be 135 °C, and this temperature was used as the reaction temperature. After completion of the reactions, the autoclave was cooled to room temperature. The remaining hydrogen was discharged, and the vials containing the reaction products were removed from the autoclave. The solid catalyst was filtered off and washed thoroughly with ethyl acetate. The reaction products were analyzed by GC-MS. The corresponding products were purified by column chromatography (silica; nhexane-ethyl acetate mixture) and characterized by NMR and GC-MS analysis.

Procedure for the Yields Determined by GC for Selected Compounds. After completion of the reactions, *n*-hexadecane (100 μ L) was added as the standard to the reaction vials, and the reaction products were diluted with ethyl acetate followed by filtration using plug of silica and then analyzed by GC.

Procedure for Gram Scale Reactions. To a Teflon or glass fitted 300 mL or 1.0 L autoclave, a magnetic stirring bar and the corresponding arene were transferred and 20-250 mL of t-BuOH was added. After adding the required amount of catalyst (Co-PMA-PZ@SiO₂-800; 4.5 mol % Co; 60 mg for each 1.0 mmol substrate), the autoclave was flushed with 40 bar hydrogen twice, and then, it was pressurized with 40 bar hydrogen. The autoclave was placed into an aluminum block preheated at 145 °C (placed 30 min before counting the reaction time in ordered to attain reaction temperature), and the reaction was stirred for the required time. During the reaction, the inside temperature of the autoclave was measured to be 135 °C, and this temperature was used as the reaction temperature. After completion of the reaction, the autoclave was cooled to room temperature. The remaining hydrogen was discharged, and the reaction products were removed from the autoclave. The solid catalyst was filtered off and washed thoroughly with ethyl acetate. The reaction products were analyzed by GC-MS, and the corresponding products were purified by column chromatography (silica; n-hexane-ethyl acetate mixture) and characterized by NMR and GC-MS spectral analysis.

Procedure for Catalyst Recycling. A magnetic stirring bar and 106 mmol of phenol were transferred to a 300 mL autoclave, and then, 70 mL *t*-BuOH was added. After adding

6.3 g of catalyst (Co-PMA-PZ@SiO₂-800; 4.5 mol % Co), the autoclave was flushed with 40 bar hydrogen, and then, it was pressurized with 50 bar hydrogen. The autoclave was placed into the heating system, and reactions were allowed to progress at 135 °C (temperature inside the autoclave) by stirring for the required time. After the completion of the reaction, the autoclave was cooled and the remaining hydrogen was discharged. To the reaction mixture, 250 μ L *n*-hexadecane as standard was added. The catalyst was separated by centrifugation and the filtrate was subjected to GC analysis for determining the yield of cyclohexanol. The separated catalyst was washed with ethyl acetate, dried under vacuum, and used without further purification or reactivation for the next run.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b02193.

Additional materials characterization data and NMR data and spectra (PDF)

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Notes

The authors declare no competing financial interest.

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