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A New Route to Cyclohexanone using H_2CO_3 as a Molecular Catalytic Ligand to Boost the Thorough Hydrogenation of Nitroarenes over Pd Nanocatalysts

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Dedication ((optional))

Abstract: Carbon dioxide has been important in green chemistry, especially in catalytic and chemical engineering applications. While exploring CO_2 to produce cyclohexanone for nylon or nylon 66 that is currently produced with low yields using harsh catalytic methods, we made the exciting discovery that carbonic acid, generated from dissolved CO_2 in water, was utilized as molecular catalytic ligand to produce cyclohexanone via the hydrogenation of nitrobenzene in aqueous solution that uses Pd catalysts with a total yield higher than 90%. Importantly, the gaseous nature of catalytic ligand H_2CO_3 profoundly simplifies post-catalysis cleanup unlike liquid or solid catalysts. This new green catalysis strategy demonstrated the universality for hydrogenation of aromatic compounds like aniline and N-methylaniline and could be broadly applicable in other catalytic field like artificial photosynthesis and electrocatalytic organic synthesis.

Introduction

Waste gas-carbon dioxide (CO_2) reutilization has for some time been understood as an important and desirable part of green chemistry. [1] There are numerous "trash-to-treasure" examples of CO_2 catalytic and chemical engineering applications, and there has been recently been renewed interest in energy storage via reduction of CO_2 [2] and in the chemical fixation of CO_2 [3] into high-valuable chemicals. However, until now, H_2CO_3, generated from dissolved CO_2 in water, has not been employed as a gas-ligand additive for catalytic and chemical engineering applications. Whereas traditional organic ligands or other additives [4-7] that are typically used to activate heterogeneous nanocatalysts incur additional costs from the need for separation and purification of the target products, the reutilization of gaseous state CO_2 not only facilitates fast separations following reactions, but also efficiently reduced CO_2 emission in the atmosphere which human activity contributes about 35 GT per year. [1]

Our research group has been exploring the industrially important synthesis of cyclohexanone, an important intermediate for the production of the caprolactame and adipic acid that is needed to manufacture nylon 6 and nylon 66. [8,9] The production of cyclohexanone at an industrial scale is typically achieved via the oxidation of cyclohexane [10-13] (Figure 1a) or the hydrogenation of phenol [14-23] (Figure 1b). Benzene can be hydrogenated into cyclohexane (Figure 1a) under harsh and high energy conditions, but the oxidation of cyclohexane to cyclohexanone is inefficient, even when using hydrogen peroxide as the oxidant. [10, 11] The conversion rates of phenol from benzene are low (Figure 1b) via cumene peroxidation or via direct hydroxylation of benzene even by the aid of noble metal-based catalysts under harsh conditions. [14-23]

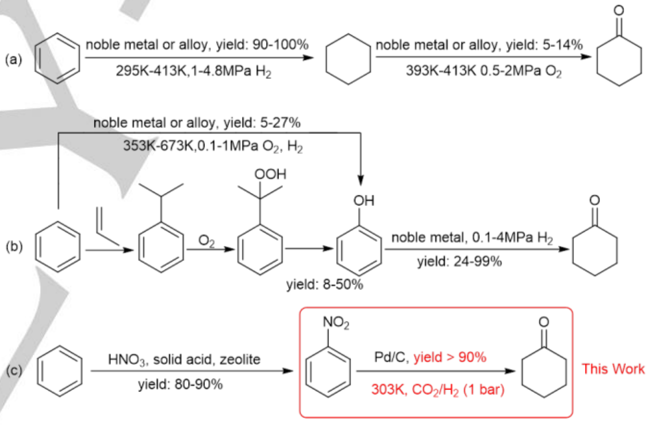

Figure 1. Oxidation of cyclohexane (a), hydrogenation of phenol (b), and the hydrogenation of nitrobenzene featured in the present study (c).

Here, we describe the use of carbonic acid, generated from dissolved CO_2 in water, as unique catalytic "binder" ligands to boost a mild and efficient synthetic process for transforming benzene via nitrobenzene to cyclohexanone in high yields (Figure 1c). As compared to other substrates (cyclohexane and phenol), the synthesis of nitrobenzene from the complete nitrification of benzene is only usually prepared using zeolite or solid acid under relatively mild conditions with much lower energy consumption (Figure 1a and 1b).[24-27] Besides, H_2CO_3 can activate the supported Pd nanocatalysts and thereby boost the formation of cyclohexanone as the main product from the hydrogenation of nitrobenzene in water at room temperature, yielding cyclohexanone in excess of 90%; note that cyclohexanone is usually the minor byproduct under pure H_2 atmosphere.[28-30] Beyond being a new trash-to-treasure application for it in green chemistry, this new highly efficient catalytic system marked facilitates the separation process after the reaction compared to systems that use a liquid or solid catalyst. Moreover, our demonstration that H_2CO_3 can be used

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similarly as a catalytic ligand for the synthesis of many other intermediates such as cyclohexanecarboxylic acid, substituted methylcyclohexanone, tetrahydro-1-naphthylamine, tetrahydronaphthalene, and tetrahydroquinoline, the conceptual door to a truly vast domain of potential applications in synthetic chemistry and chemical engineering.

Results and Discussion

Heterogeneous Pd catalysts, especially Pd carbon supported (Pd/C) catalysts (The characterizations of Pd/C were presented as Figure S1 and S2), are currently preferred in industry for cyclohexanone production due to their excellent universality for hydrogenation of nitrobenzene with aniline as the main product (Figure 2a-b).[31] In the absence of CO_2, we found that only 6% of nitrobenzene was transformed into cyclohexanone (Figure 2b), with aniline being the main product. Strikingly, unexpectedly high selectivity (Figure 2b) to cyclohexanone was achieved when a mixed gas of CO_2 and H_2 was used to replace pure H_2 gas: 90% yields were achieved within 6 h when we optimized the molar ratios of CO_2 and H_2 (CO_2/H_2) to 1:3 and utilized water as the solvent (Figure 2c).

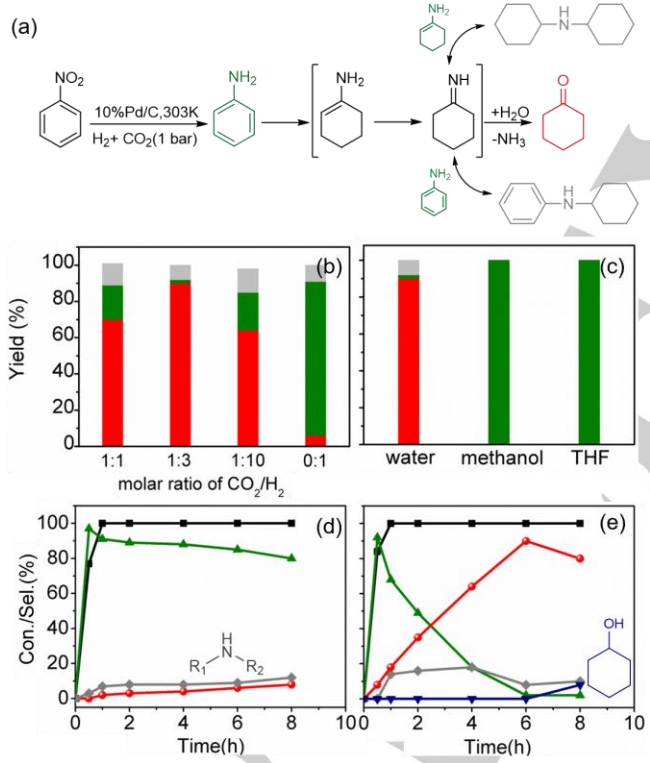

Figure 2. Proposed reaction routes (a) for the hydrogenation of nitrobenzene into cyclohexanone in the presence of CO_2 gas. Screening molar ratios of CO_2 and H_2 (b), solvents (c). Typical time courses of nitrobenzene hydrogenation to cyclohexanone over Pd/C under pure H_2 (d) or H_2/CO_2 (e) atmosphere. Reaction conditions: 0.25 mmol nitrobenzene, 10 mg of catalyst, 5 mL of H_2O, pressure (1 bar), 6 h, room temperature. (black, green, red and gray lines represent nitrobenzene, aniline, cyclohexanone and diamines, respectively).

Water is essential for the hydration of enamine and also essential following the deamination process to yield cyclohexanone[32] (Figure 2a), as cyclohexanone was not detected when the water was replaced with anhydrous methanol or tetrahydrofuran (THF) as the solvent (Figure 2c and Table S1).

Monitoring the hydrogenation of nitrobenzene over Pd/C in CO_2-H_2 atmosphere throughout a time course (Figure 2e) revealed a gradual increase in the yield of cyclohexanone, from 6% to 90%, dramatically outpacing the yield of the same reaction with a pure H_2 atmosphere (Figure 2d and 2e) by more than 14 times.

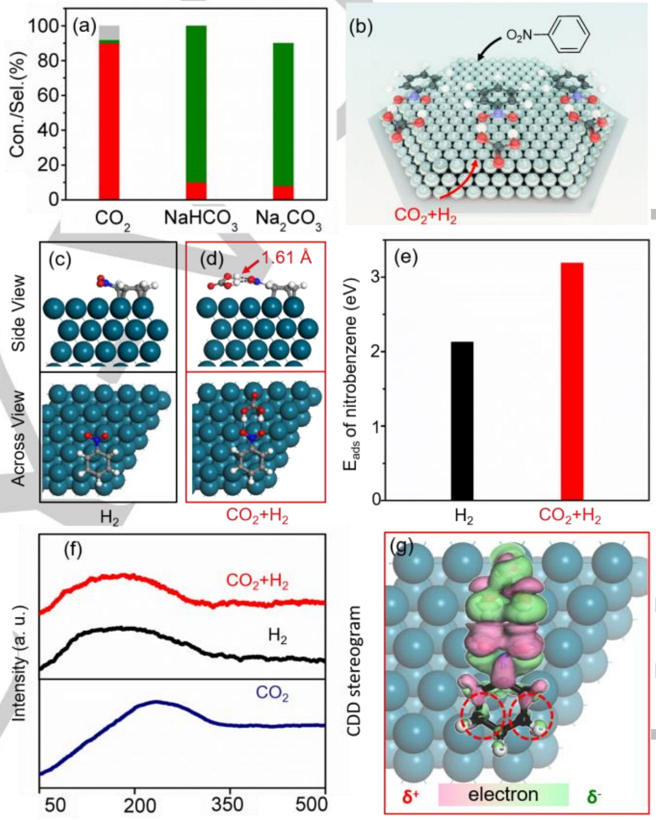

Figure 3. CO_2-related additives (carbonates) (a) for optimized yields of cyclohexanone (the molar ratios of carbonates (e.g. $NaHCO_3$, Na_2CO_3) and nitrobenzene were 10:1). Proposed structure of as-formed H_2CO_3 (b) from the dissolved CO_2 in water on the Pd surface for the proposed activation of nitrobenzene. Optimized structures of nitrobenzene (c) and H_2CO_3-coupled nitrobenzene in the presence of CO_2 (d) on the Pd surface, and the corresponding adsorption energies (e). Temperature Programmed Desorption profiles of CO_2/H_2 (red line), H_2 (black line), and CO_2 (navy blue line) over 10% Pd/C catalyst (f). Charge density difference stereogram of H_2CO_3-coupled nitrobenzene on the Pd surface (g).

The role of H_2CO_3 molecules in promoting the observed selectivity to cyclohexanone over Pd nanocatalysts was further examined via both experimental and theoretical methods. The promoting effect of HCO_3^- or CO_3^{2-} on the formation of cyclohexanone was negligible, yielding cyclohexanone at only 10% and 8%, respectively (Figure 3a and Table S2). Density-functional-theory (DFT) calculations (The (111) plane of Pd was chose in DFT calculation)[35,36] were performed to elucidate the possible states of the nitrobenzene in the presence of CO_2-based complexes, including H_2CO_3, HCO_3^- CO_3^{2-}, and CO_2 (Figure 3c-d, Figure S3 and Table S3), on the surface of a Pd nanocatalyst.[33-35] Uniquely among these carbonates, the simulations indicated that only H_2CO_3 can function to significantly promote the adsorption of nitrobenzene on the Pd surface; this results from its ability to form two hydrogen bonds (1.61 Å and 1.67 Å) that increase nitrobenzene's adsorption energy on Pd from 2.13 to 3.19 eV. We noted only slight changes in the adsorption energies of nitrobenzene when using HCO_3^- , CO_3^{2-}, or CO_2 species as possible ligands (Figure S3 and Table S3), underscoring their relatively weak interactions with nitrobenzene molecules. Beyond elucidating the energetics of the mechanism through which nitrobenzene binds to the Pd catalyst, the specific functional role for H_2CO_3 that was revealed by these theoretical simulations underscores the important fact that water—which facilitates H_2CO_3 formation from CO_2—is an essential reaction component for the use of H_2CO_3 as a catalytic ligand (Figure 3a and 3b). Similarly, the simulations revealed that H_2CO_3 can also function to promote intermediate hydrogenation product-aniline adsorpted on the Pd surface by one hydrogen bonds (1.73 Å) that increase aniline's adsorption energy on Pd from 2.62 to 3.93 eV (Figure S4).

The promoting effect of H_2CO_3 for nitrobenzene was further confirmed via Diffuse reflectance FT-IR spectroscopy (DRIFT) analysis (Figure S9).[42-43] Typical weakened vibration signals of -NO_2 group of nitrobenzen-H_2CO_3 complex was observed as compared to pure nitrobenzene sample, directly indicating the adsorption and stablization of nitrobenzene by H_2CO_3. Most importantly, a blue shift of the -NO_2 DRIFT peaks from 1518 and 1344 cm^{-1} for the pure nitrobenzen to 1526 and 1347 cm^{-1} respectively for the nitrobenzen-H_2CO_3 complex further confirmed the interaction between nitrobenzen and H_2CO_3 with hydrogen bond.

Importantly, the binding effect of the absorbed CO_2 molecules doesn't disturb the absorbance of H_2 to supported Pd for further reactions. Temperature programmed desorption (TPD) analysis results (Figure 3f and Figure S10) indicate that CO_2 showed no obvious influence on the adsorption uptakes of H_2 with approximated desorption peak location and desorption volume over 10% Pd/C in H_2+CO_2 (red line) and pure H_2 (black line) atmospheres even though a significant amount of CO_2 could also be adsorbed on Pd (Figure 3f bottom). Again, water is essential to transform CO_2 into H_2CO_3 to enhance the preferred adsorption and further activation of nitrobenzene.

The DFT simulations revealed and confirmatory experiments then confirmed the coupling effect of nitrobenzene with H_2CO_3 on the formation a divergent electron distribution of its benzene ring (Figure 3g). The prediction that the hydrogenation of the benzene ring becomes more favorable via the addition of the first H radical to electron-deficient *meta* carbons (marked by red rings in Figure 3g) was confirmed by a series of control reactions (Figure 4a-d).

The substrate with all of its *meta* carbons blocked by methyl groups (3,5-dimethylnitrobenzene) could only give a trace yield (0.5%) of 3,5-dimethylcyclohexanone (Figure 4a), even with higher loading of the catalysts and with longer reaction times. The 4-nitrobenzotrifluoride-with its strong electron withdrawing group (-CF_3) adjacent to the *meta* carbons (Figure 4b) could also completely quench the hydrogenation reaction of the benzene ring; the p-nitroaniline was only hydrogenated into 1,4-diaminobenzene, which could couple with two H_2CO_3 molecules and thus destroy the divergent electron distribution of the benzene ring, preventing any further hydrogenation (Figure 4c). Similarly, the hydrogenation of benzene ring in methylbenzene or styrene with weak coupling effect with the H_2CO_3 molecule was not observed under fixed conditions (Table S4 and Figure 4d). Collectively, these results experimentally confirm the essential contribution of the H_2CO_3 ligand to promoting the hydrogenation of the *meta* carbons of the benzene ring.

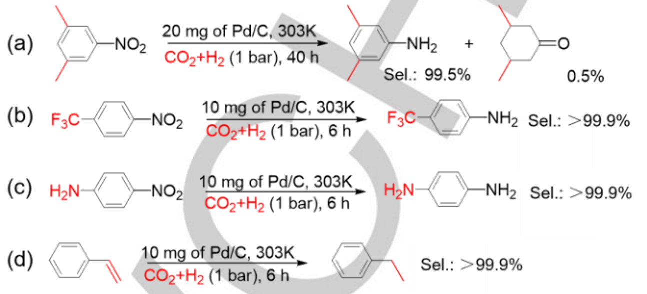

Figure 4. Control experiments using substituted nitrobenzene (a-c) and styrene (d) as the substrates.

Moving beyond nitrobenzene, we excitingly found that the enhancing effect of the H_2CO_3 catalytic ligand is also general for the hydrogenation of various nitroarenes that possess at least one exposed exposable *meta* carbon and lack strong electron-attraction groups at their *para* position; we even observed the enhancing effect when using Pd nanocatalysts immobilized on other supports (Figure 5a-b). Indeed, the yields (94-97%) of cyclohexanone over variously supported Pd nanoparticles (Pd/TiO_2, Pd/g-C_3N_4, Pd/γ-Al_2O_3 and Pd/C) were increased by 14–45.5 times with the assistance of H_2CO_3 as a molecular catalytic ligand (Figure 5a). Further expanding the reaction scope, in addition to H_2CO_3's ability to promote hydrogenation of various nitroarenes (Figure 5b) into their corresponding cyclohexanone compounds, coupling of H_2CO_3 with the functional groups of other aromatic compounds also boosted hydrogenation of benzene rings (e.g., anisole, benzoic acid, aniline, N-methylaniline, N, N-dimethylaniline, and 1-nitronaphthalene). Indeed, the simple addition of the CO_2 gas elevated the turnover frequency (TOF) values of the Pd nanocatlysts for the hydrogenation of the benzene rings of these aromatic substrates by 4-29 times (Figure 5b-c and Table S4). Given this impressive catalytic performance, and considering the well-appreciated reusability of Pd nanocatalysts, it is clear that the use of molecular H_2CO_3 catalytic ligands can be viewed as a highly attractive green catalytic system for the hydrogenation of various aromatic compounds into high-value-added product.

We here described a new and mild synthetic process for the high efficiency hydrogenation of nitrobenzene to cyclohexanone. Mechanistically, it demonstrated that CO_2 dissolved in water generates H_2CO_3 which couples with and thus activates the nitrobenzene molecules adsorbed on the Pd surface, giving high yields of cyclohexanone (90-97%). An important point to consider relates to the post-catalysis purification of gaseous-H_2CO_3-catalyzed reaction products like cyclohexanone: unlike a liquid or solid ligand (e.g. triethanolamine, ethylenediamine, (R,R)-2,3-Bis(t-butylmethylphosphino)quinoxaline, 4,4′ di-(3-pentyl)-2,2′ -dipyridyl, or 2,2′ -bipyridine-4,4′ -dicarboxylic acid chloride),[4-7] gaseous CO_2 can be easily sequestered upon completion of a reaction, dramatically simplifying any required clean-up steps.

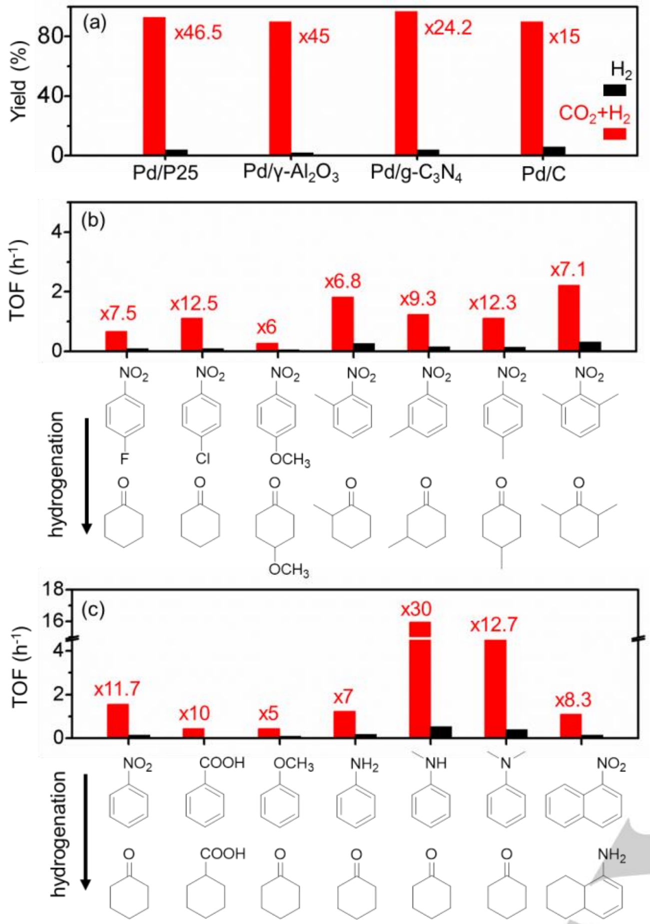

Figure 5. (a) Yields of cyclohexanone from nitrobenzene over Pd nanocatalyts on different supports in CO_2/H_2 (red bars) or pure H_2 atmosphere (black bars). (b-c) Turnover frequency (TOF) values for the hydrogenation of conjugated aromatic compounds over Pd/C. All reactions were conducted under the conditions described in Figure 2. The reaction time was 6 h for all catalysts in (a), excepting the Pd/CN catalyst for which the time was prolonged to 16 h. The time number represent TOF enhancement which was calculated on the basis of conversions between 2-50%, as listed in Table S4.

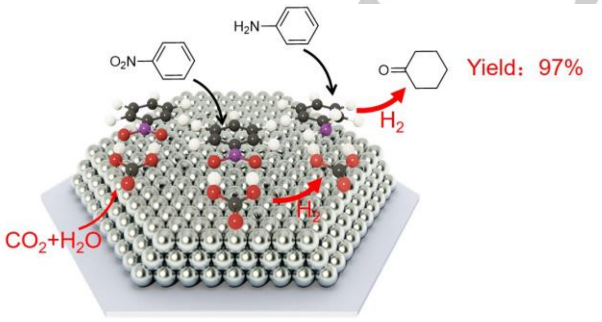

Figure 6. Proposed reaction pathway for the high selectivity to cyclohexanone from nitrobenzene over Pd catalyst with promotion effect H_2CO_3.

In order to verifying the promotion effect, other Bronsted acid-type additives (Table S7), including HNO_3, HCl, H_3PO_4 and H_3BO_3, were tested instead of CO_2, till offering a poor selecivity to cyclohexanone. Again, the carbonic acid molecule, generated from dissolved CO_2 in water, can function as a unique catalytic "binder" ligand to significantly promote the adsorption of nitrobenzene and following aniline on the Pd surface mainly by forming hydrogen bonds (Figure 6) rather than providing protons.

Unlike the typical role of supercritical CO_2 as a unique solvent in promoting the kinetic issues for specific catalytic reactions[32], the H_2CO_3 in water could however induce the pre-adsorption of the substrate on the Pd surface via relatively strong inter-molecule interactions and thus largely depress the activation barrier to boost an innovative route for highly selective production of cyclohexanone from nitrobenzene hydrogenation.

Conclusions

In summary, expanding beyond cyclohexanone, we demonstrated a broader application scope for this new green catalysis system with the successful hydrogenation of the benzene rings of a large variety of aromatic compounds. It is easy to imagine the use of similar approaches for other applications such as transfer hydrogenation, C-C or C-N coupling, and even selective oxidation, and one can imagine possible extensions of the technology for applications like artificial photosynthesis and electrocatalytic organic synthesis. Indeed, given its ability to potentiate the absorption of substrates onto catalytic surfaces, our study shows the way forward for a green strategy that is in theory applicable for all heterogeneous catalytic process involving the adsorption and activation of reactant molecules.

Experimental Section

Synthesis of 10 wt. % Pd/P25: 135 mg P25 was dispersed into 40 mL distilled water under sonication for 2 h, and 2.5 mL $PdCl_2$ solution (6 mg/mL) was added and stirred overnight. 4 M NaOH solution was used to adjust PH to 13. Then, the aqueous solution containing 60 mg $NaBH_4$ was dropped quickly into as-preparation solution to reduce Pd^{2+} to Pd^0. Until no H_2 was released, the catalyst was centrifuged and washed by water twice and ethanol once which was finally dried at 333 K overnight.

Synthesis of 10 wt% Pd/γ-Al_2O_3: 135 mg γ-Al_2O_3 was dispersed into 40 mL distilled water under sonication for 2 h, and 2.5 mL $PdCl_2$ solution (6 mg/mL) was added and stirred overnight. 4 M NaOH solution was used to adjust PH to 13. Then, the aqueous solution containing 60 mg $NaBH_4$ was dropped quickly into as-preparation solution to reduce Pd^{2+} to Pd^0. Until no H_2 was released, the catalyst was centrifuged and washed by water twice and ethanol once which was finally dried at 333 K overnight.

Synthesis of 10 wt% Pd/g-C_3N_4: 135 mg g-C_3N_4 was dispersed into 40 mL distilled water under sonication for 2 h, and 2.5 mL $PdCl_2$ solution (6 mg/mL) was added and stirred overnight. 4 M NaOH solution was used to adjust PH to 13. Then, the aqueous solution containing 60 mg $NaBH_4$ was dropped quickly into as-preparation solution to reduce Pd^{2+} to Pd^0. Until no H_2 was released, the catalyst was centrifuged and washed by water twice and ethanol once which was finally dried at 333 K overnight.

Temperature Programmed Desorption (TPD) test

The TPD measurements were conducted with AutoChem-Disvovery 2920 equipped with TCD signal. Firstly, 250 mg Pd/C catalyst was pretreated under N_2 atmosphere at 393 K for 120 min to remove H_2O and O_2. After pre-treatment, object gas adsorption was performed under 298 K for 2 h (50 mL/min). Then catalyst was purged with N_2 for 60 min to remove physical absorption gas. Furtherly, the process of desorption was set up from 298 K to 550 K with the heat rate 15 K/min. Due to the similar thermal conductivity between N_2 (0.024 W/(m*C)) and CO_2 (0.0146 W/(m*C), CO_2 showed slight signal even though a significant amount of CO_2 could also be adsorbed on Pd surface.

Density functional theory (DFT) calculations

All the DFT calculations were performed with PerdewBurke-Ernzerh (PBE) generalized gradient approximation (GGA) exchange-correlation functional using DMol3 program. Valence orbitals were described with the double numerical plus polarization (DNP) basis and TS dispersion correction was used. The orbital cutoff is 4.5 Å. Density functional semicore pseudopotentials (DSPPs) was utilized to describe metals. In this work, Pd (111) was chosen and p(4x4x4) supercell was established with 3x3x1 Monkhorst-Pack k-point sampling for describing Brillouin zone. During the optimization steps, the bottom two layers were fixed in the slab and top two layers were relax. The vacuum layer thickness was set to be 19.2 Å. Structural optimization was obtained on the basis of convergence criterion that SCF tolerance was 10^{-5} Ha, and convergence tolerances of energy, maximum force, and maximum displacement applied during geometry optimization were $2x10^{-5}$ Ha, 0.004 Ha/Å, and 0.005 Å, respectively. In order to accelerate convergence, smearing was used with the value of 0.005. The adsorption energy was defined as: $E_{ad}=E_{Pd+sub}-E_{Pd}-E_{sub}$. E_{ad}, E_{Pd+sub}, E_{Pd}, E_{sub} represents the adsorption energy, total energies of palladium- organic molecular complex, pure Pd and organic molecular respectively.

Acknowledgements ((optional))

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Keywords: nitroarenes • cyclohexanone • hydrogenation • H_2CO_3 • palladium nanocatalysts

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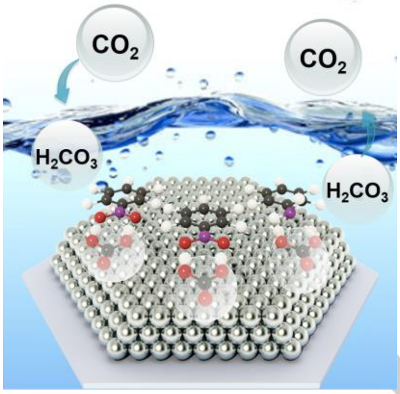
Molecular catalytic ligand CO_2, generating carbonic acid (H_2CO_3) in water, is applied to accelerated the adsorption and following hydrogenation of nitrobenzene on Pd surface by forming two hydrogen bonds. Such an enhanced pre-adsorption of nitrobenzene boosts the yield of cyclohexanone excess of 90% on Pd nanocatalysts, promising a new, mild and highly efficient route for the cyclohexanone production than other routes in industrial scale using a reusable molecular ligand for facile separation.



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A New Route to Cyclohexanone using H_2CO_3 as a Molecular Catalytic Ligand to Boost the Thorough Hydrogenation of Nitroarenes over Pd Nanocatalysts