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Synthesis of biphenyl through the C-H bond activation in benzene over a Pd catalyst supported on graphene oxide

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This seems a first report on the Carbon-Hydrogen (C-H) bond activation in benzene over a Palladium catalyst supported on graphene oxide (GO) leading to the formation of solely biphenyl with the yield of 78%. The reaction was performed for 12 h in the presence of acetic acid and oxygen at 80 °C. An XPS study indicated that in the initial catalyst Pd is mainly present as Pd(II) species on the GO surface. The interaction of these species with acetic acid during the reaction generates Pd acetate species. A density functional energy (DFT) study revealed that the adsorption of the first benzene molecule on the Pd acetate is weak (0.15 eV) and the energy barrier of the following C-H bond scission is high and equal to 1.67 eV. The adsorption of the second benzene molecule is relatively strong (0.40 eV), the acetic acid molecules release leaving the biphenyl Pd intermediate which gives further the biphenyl molecule formation. The presence of oxygen and acetic acid is needed for closing the catalytic cycle by regeneration of the reactive Pd acetate.

Introduction

Synthesis of biphenyl compounds has attracted enormous attention in the last ten years. Biphenyl is an important intermediate1 or constituent in wide range of agrochemicals, natural products, pharmaceuticals and many other fine chemicals. Naturally it occurs in crude oil and coal tar.² Activated halogenated substrates such as iodobenzene, chlorobenzene, bromobenzene, 4-iodotoluene, 4chloronitrobenzene, 4-bromonitrobenzene and 4-bromotoluene are the first choice of synthetic organic chemists and other fine chemicals professionals for the synthesis of biphenyl.³⁻⁷ It is due to the fact that the C-H bond cleavage in aromatic hydrocarbons such as benzene is very hard due to its high bond energy. In general, the decreasing order of bond energy⁸ (C-H > C-F > C-Cl > C-Br > C-I) clearly shows that C-H bond is very hard to break⁹ in comparison to carbon halogen bond. The synthesis of biphenyl has been carried out¹⁰ by Fujiwara et al. in 1970, where they have synthesized this compound from benzene by using olefin-palladium chloride complex in the presence of silver nitrate. The reaction was proposed to proceed via a sigma bonded benzene palladium complex. Typically, biaryl compounds are synthesized by conventional Suzuki and Heck reactions,^{11, 12} which involve the use of aryl halides as substrates. Direct use of benzene for C-C coupling reaction can minimize the use of halogenated substrates for this particular synthesis as they are not environmentally friendly. Therefore, synthesis of biphenyls from benzene presents a great opportunity for their production from nonhalogenated substrates and also opens up a gateway to probe the mechanism of the C-H bond activation.13, 14

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The C-H bond activation is one of the most popular strategies for the synthesis of organic molecules.^{15, 16} It refers to a chemical process, where the C-H bond is activated, cleaved and then replaced with carbon-X bond (X is carbon, oxygen or nitrogen).¹⁷ Mostly, transition metals are involved in the C-H bond cleavage processes.¹⁸ These metals enable the use of easily accessible feedstock for molecular synthesis that includes most of the organic substrates including aliphatic and aromatic hydrocarbons.¹⁹ Recently, metals such as palladium (Pd)^{20, 21}, rhodium (Rh)²², ruthenium (Ru)²³, copper (Cu)²⁴ and gold (Au)²⁵ have been used for the C-H bond activation. The C-H bond activation in hydrocarbon involves metal insertion in the activated [C-H] bond leading to an organometallic complex, where the hydrocarbon is coordinated to metal, either via an intermediate or a transition state, which finally undergo subsequent reaction with another substrate to produce the end product.²⁶ Yokota *et al.* have performed synthesis of biphenyl with the help of homogeneous Pd acetate catalyst and molybdovanadophosphoric acid as a co-catalyst in the presence of acetic acid and molecular oxygen.²¹ But the homogeneous catalytic pathways are not much preferred due to difficulties in recovery of expensive metal ions used in the catalytic process, therefore heterogeneous catalysts offer easy recovery and recycling of these metals used during the reaction.

Nano-carbon materials²⁷ such as GO are chemically inert and provide an opportunity to design metal based heterogeneous catalysts due to their good electrical conductivity, tuneable surface functional groups and strong interaction with metal clusters. Palladium supported on GO²⁸ was used as an efficient catalyst for the acetoxylation of 2-(o-tolyl)pyridine through the activation of C-H bond. The turnover frequency of the catalyst was higher (24.8 h⁻¹) than that of $Pd(OAc)_2$ (19.0 h⁻¹) indicating the high efficiency for the C-H bond activation. In fact, biphenyls have been synthesized by GO based metal catalysts. PdNPs on GO and functionalized graphene derivatives were used for the Suzuki-Miyaura coupling of 4-bromo-1,2-difluorobenzene with 4-methoxyphenylboronic acid leading to the formation of biphenyl.²⁹ The problem associated with the method is the use of activated halogenated substrates. The highest activity during the reaction was observed for Pd(II)-GO with TOF of 39000 h⁻¹. Also, Pd-nanoparticles supported on graphene were

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developed for the synthesis of biphenyl through C-C cross coupling of bromobenzene and phenylboronic acid with a turnover frequency of 108000 h^{-1.30} Pd nanoparticles supported on β-cyclodextrin@GO were used for the Suzuki-Miyaura cross coupling reaction of aryl halides and boronic acid.³¹ This nanocatalyst was efficient in coupling reaction for the direct formation of the biphenyl as well as benzophenone derivatives. These examples clearly show that halogenated substrates were used for synthesising biphenyl with GO supported catalysts. Therefore, we envisioned the synthesis of biphenyl through the non-halogenated substrate – benzene with the help of metal supported GO catalyst. The catalyst Pd(II)@GO had displayed good catalytic activity for the C-H bond activation of aromatic substrates particularly benzene to produce biphenyls under mild reaction conditions. It also simplifies the recovery of the metal without any further treatment and represents the first report for the use of Pd supported on GO catalyst for the C-H bond activation of aromatics for synthesis of biphenyls.

Results and discussion

Catalyst Characterization

The Pd(II)@GO catalyst was prepared by a procedure where a definite volume of a 0.069 M Pd(NO₃)₂ solution was adsorbed on the GO surface by wet impregnation method and then the material was calcined in air at 150 °C (see experimental). According to thermogravimetric analysis data³² the decomposition of Pd nitrate gives Pd oxide in the same temperature range 100-160 °C. This Pd oxide is most probably hydrated due to low temperature of calcination and contact of the sample with wet atmosphere. Partial hydrolysis of the initial Pd nitrate may take place also in the solution.^{32, 33} Inductively Coupled Plasma Mass-Spectrometry analysis (ICP-MS) was performed to quantify the amount of Pd metal present on the catalyst surface and it confirmed that 3.8 wt% of palladium was present on its surface.

The nature of Pd species and surface functional groups^{34, 35} was determined by X-ray photoelectron spectroscopy (XPS) (Figure 1 and Figure S1). The deconvoluted C *1s* spectrum exhibited the peaks at 285.1, 287.2 and 289.0 eV that were assigned to C-C species (47.5%), C-O (epoxy and hydroxyl groups) (48.3%) and COOH (carboxyl groups (4.1%)) species, respectively.^{36, 37} To check the presence of nitrate species from Pd nitrate the N *1s* spectrum was plotted (Figure S1 and S2). It showed that the sample contains nitrogen species giving the line at 402.1 eV. The peak intensity of nitrogen was significantly more intensive in comparison to pristine GO, indicating that additional nitrogen atoms have been deposited on its surface during the catalyst preparation. The peak at 402.1 eV may not be assigned to nitrate species as those should be responsible for the lines in a much higher binding energy region (>406.0 eV). Hence, the nitrogen present in the catalyst could be attached to the GO support.

The nature of Pd was probed by the Pd 3d spectrum that exhibited two pronounced peaks at 338.1 and 343.5 eV corresponding to the $3d_{5/2}$ and $3d_{3/2}$ lines assigned to Pd^{2+} ions adsorbed on the GO surface. These ions could correspond to expected hydrated Pd oxide. The atomic concentrations for C, O, N and Pd in the Pd(II)@GO sample are equal to 73.2, 25.4, 1.0 and 0.4 at%, respectively.



Figure 1. (a) C 1s and (b) Pd 3d XPS spectra of the Pd(II)@GO catalyst.

The morphology of the catalyst was determined by transmission electron microscopy (TEM). The TEM images at different resolutions are shown in Figure 2. TEM images displayed flat sheets of GO with few dark spots on it (shown under white circles). Clear-cut boundaries and nature of these particles were hard to determine, and they may probably be due to presence of small GO flakes or formed due to accumulation of palladium oxide/hydroxide particles.



Figure 2. (a), (b) and (c) TEM images of Pd(II)@GO at different resolutions (d) Small spots visible on catalyst surface are highlighted in circle.

X-ray diffraction powder analysis (XRD) was further performed in attempt to confirm the presence of Pd oxide. A comparison of XRD patterns of Pd(II)@GO and GO (Figure 3) exhibited only a small and broad peak at about 34° which could be related to (101) plane of hydrated Pd oxide.^{38,39} This line is the most intensive among the other lines of these species which are not clearly observed, but their possible positions are indicated with ticks. High dispersion of the Pd oxide could be a reason that the only one line was observed. Metallic Pd lines are not seen in accordance with the XPS data. GO is presented by two typical sharp lines at 12.7° (001, not shown) and 42.4° (100).⁴⁰

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Figure 3. XRD patterns of the Pd(II)@GO catalyst and pristine GO.



Figure 4: Comparison of FTIR spectra of Pd(II)@GO and GO

The IR spectrum of Pd(II)@GO was compared with that of pristine GO to observe the changes on the surface (Figure 4). The IR spectrum of Pd(II)@GO demonstrates the main peaks^{41, 42} at 3434 (not shown), 1782, 1720, 1570, 1386, 1232 and 1043 cm⁻¹. The peaks were assigned to -OH, -C=O, -C-OH and C-O-C linkages. The results are in agreement to the XPS results that show the presence of carboxylic, hydroxyl, aldehyde/ketone, and ether linkage on the surface of the catalyst. The peaks for the same functional groups at 3352 (not shown), 1718, 1346, 1215 and 1030 cm⁻¹ were present in the spectrum of the GO sample. The peaks at 1782 and 1386 cm⁻¹ were found to be missing. The appearance of the new peak at 1782 and 1386 cm⁻¹ in Pd(II)@GO indicated that there is formation of a new type of species with C=O/-COOH groups on its surface. These may be formed due to the interaction of Pd(II) ions present on its surface.

Thus the structural features of our sample are very much close to those of the Pearlman's catalyst (Pd(OH)₂/C). Literature reports ⁴³ demonstrate that the Pearlman's catalyst as prepared and after drying consists of carbon supported (mostly) nano-particulate hydrous palladium oxide capped with a monolayer of hydroxyls hydrogen-bonded to a few layers of water.

Once the nature of the catalyst was probed, it was further applied for the C-H activation reaction of benzene.

Catalytic Efficiency

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In a typical experiment, 200 mg benzene was dissolved in acetic acid followed by the addition of Pd(II)@GO (20 mg) catalyst. The contents were stirred at 80 °C for 12 h in presence of 1 bar of oxygen gas and the solid product was isolated in 78 % yield after the separation of catalyst (see Experimental Section for details).

The formation of biphenyl was confirmed by Nuclear Magnetic Resonance (NMR) spectroscopy. A ¹H-NMR spectrum of benzene shows a singlet⁴⁴ due to equivalent protons at δ 7.33 and if it is converted to biphenyl the singlet should convert into a multiplet showing three sets of equivalent protons in the range of δ 7-8. In fact, three peaks between δ 7.05 - 7.46 were observed (Figure S3) which indicates that the product formed is different from benzene. The physical state of the product is solid and different from benzene, which is liquid. A final confirmation was also obtained using differential scanning calorimetry (DSC), which exhibited a peak, at 66.8 °C (Figure 5b). The melting point observed for the isolated solid was 69.1 °C, which was found to be consistent with that reported in the literature.45 All these analyses confirmed the synthesis of biphenyl as the end product of this reaction (Figure 5a). The DSC analysis of crude solid clearly indicates that biphenyl is the only product formed in the reaction. Has there been any other product formed that should have been indicated by a separate peak in the DSC curve. The ¹H NMR spectrum also confirmed that the selectivity of the biphenyl product was 99%.

After the isolation and characterisation of biphenyl, we studied the effects of the reaction time, temperature, catalyst amount, acetic acid and oxygen contents on the yield of the reaction product. Thus, an increase in the yield of the product with increasing the reaction time was observed (Figure 5c). The presence of induction period may indicate the initial slow formation and accumulation of some important intermediates of the reaction. For example, unreactive hydrated Pd oxide could transform to Pd acetate due to interaction with acetic acid.

The reaction was performed at different temperatures (Table 1) and there was a decrease in the yield of biphenyl at lower temperature (70 $^{\circ}$ C) and no product was formed at 40 $^{\circ}$ C. These changes may indicate to the high apparent activation energy of the rate-determining step of the reaction. Therefore, an elevated temperature is required for benzene to show the intermolecular condensation to form biphenyl.

The catalyst loading effect was studied at 80 °C for 12 h in the presence of acetic acid and O_2 (Figure 5d). We have used 1, 3, 5 and 10 % contents of the catalyst in the reaction mixture. It was found that the yield of the product increased with the increase in the amount of the catalyst as was expected.

To understand the role of oxygen, the reaction was performed in atmospheric air instead of pure oxygen at the same other conditions. There was a significant decrease in biphenyl yield to 26% in this case (Table 1) which was provided by the decreased partial pressure of oxygen by a factor of 5. This proves that the presence of oxygen is very important for the synthesis of biphenyl. Oxygen is probably needed for oxidation of Pd atoms in the course of the reaction as was proposed earlier for aerobic homogeneous catalytic coupling reactions.^{11, 12, 21}

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Figure 5. (a) C-H bond activation reaction of benzene to biphenyl, (b) Thermal gravimetric analysis (TGA)-DSC analysis of biphenyl, (c) Yield (%) vs reaction time (h) for C-H bond activation reaction of benzene to biphenyl by using the Pd(II)@GO catalyst, (d) Plot of the catalyst performance against the loading of catalyst (%) at the same reaction conditions and (e) Stability tests using the Pd(II)@GO catalyst. Reaction condition: benzene(200 mg), 20 mg catalyst, acetic acid (1 mL), O₂ atmosphere at 80°C temperature.

To check the necessity of acetic acid, it was substituted by chloroform. It is important to note that no biphenyl formation was observed in this case (Table 1). This result indicates that acetic acid is vital for the reaction. This acid should provide the formation of some related intermediate species such as Pd acetate during the reaction from the oxidized Pd, which, as will be shown below, is the important active species for the C-H bond scission.

Table 1. Effect biphenyl	of reaction co	onditions	on the y	ield of			
Conditions	Temperature	Yield	TON	TOF			
	(°C)	(%)		(h⁻¹)			
O ₂ + CH ₃ COOH	40	0	-	-			
O ₂ + CH ₃ COOH	70	69	58.6	9.7			
O ₂ + CH ₃ COOH	80	78	66.1	11.0			
Air+CH₃COOH	80	26	22.0	3.6			
O ₂ +CHCl ₃	80	0	-	-			
Reaction conditions: benzene (200 mg), 20 mg catalyst							
(3.8 wt% of Pd), acetic acid or CHCl ₃ (1 mL), 12 h, The TON							
is defined as TON= 2 × mole (biphenyl)/mole (Pd) and TOF							
= TON/Hour.							

Finally, the stability/recyclability of Pd(II)@GO catalyst was tested through a recycling study (Figure 5e). The results have shown that there is some decrease in the product yield under identical reaction conditions observed during the first runs. Then, the activity stabilizes. The initial loss may occur due to leaching of some active metal ions into the solution or sintering of Pd species. In order to ascertain if the metal is leaching into the solution or not, we have

evaporated the filtrate and then added all the reactants (beside the catalyst) to the same flask. The contents were heated ab optimized condition for 12 h, but in this case, no product was isolated. This clearly shows that filtrate does not have any significant amount of Pd species necessary for this catalytic reaction.

The efficiency of the catalyst for the formation of other biphenyl products was checked by formation of three more derivatives by using anisole, toluene and nitrobenzene as reactants. The reactions were performed under optimised condition for 12 h and the product formation was ascertained by comparing the melting point of the product with those reported commercially (see supporting information). It is seen in Table 2 that the approach worked well for all reactants giving the highest yield with nitrobenzene (88%). This yield can be well explained due to the effect of nitro groups, which probably help the metal in the CH scission step.

Table 2.	Derivatives	study	with	different	aromatic	
compounds						
Reactants Pro		Product	(Meltir	Yield (%)		
point, °C)						
Anisole	4,4	4,4'-dimethoxy-1,1'-				
		bipheny	yl (172))		
Toluene	4,4'-d	4,4'-dimethyl-1,1'-biphenyl				
		(11	6)			
Nitrobenze	ene 4,4'-	4,4'-dinitro-1,1'-biphenyl				
		(23	88)			
Reaction conditions: Reactants (200 mg), 20 mg catalyst,						
acetic acid (1 mL), O_2 atmosphere and 80°C for 12 h.						

The performance of the catalyst was compared with some literature data (Table S1). It is found to be at par or better than those discussed in the literature. Previously, the carbon supports such as activated carbon and even GO had been used as supports for metal catalysts for the synthesis of biphenyls.^{10,46-50} The catalyst described in this work provides a better yield in comparison to earlier studied activated carbon and GO based catalysts. Moreover, the proposed system works effectively without the use of any other co-catalyst and co-solvent, and provides easy separation of the product from the reaction mixture simply by the addition of water.

DFT Calculations

DFT calculations were performed to probe the mechanism of the reaction. We have observed that the reaction proceeds well in acetic acid, but not in chloroform. The first step should involve the interaction of acetic acid with the surface Pd(II) ions (Figure 6a). Moreover, palladium acetate that preferably exists in a state⁵¹ shown in Figure 6b (1) did not show any tendency to react with benzene. Owing to the interaction of Pd(II) with the GO support the acetic acid may interact transforming it into another state where the Pd atom is attached to each acetate via a single oxygen atom [Figure 6b(2)]. Benzene molecule adsorbs on this state (2) with E_{bind}=0.154 eV. Then, the new state moves through the transition state (3), where a carbon atom of benzene is coordinated by Pd, further to the state (4). The energy barrier (E_a) for this step is high (1.666 eV). The C-H bond scission occurs with participation of the acetate oxygen atom. As a result, the C-H bond in benzene is broken, phenyl is stabilized by the Pd atom and the O-H bond in the adsorbed acetic acid molecule is formed. The state 4 has a higher energy than the state (2) by 0.904 eV. Then, the adsorption of another benzene molecule takes place. It is stronger than that of the first molecule with E_{bind} = 0.403 eV forming the state (5). When the second phenyl interacts with the Pd

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atom, two acetic acid molecules release from the complex in the form of dimer and the biphenyl Pd molecule is formed (state (6)). The energy of this step is lower by 0.113 eV. E.A. Hausman and co-workers have also reported⁵² the formation of palladium diacetate (without the formation of palladium hydroxyacetate) by hydrous palladium oxide with acetic acid. Moreover, this complex was reported to be soluble in benzene, which provides a strong evidence for existence of analogous species as reported in this work.

Hence, the DFT calculation has helped us to explain the adsorption of benzene molecules and the C-H bond scission on the Pd acetate. The obtained biphenyl Pd molecule can be an intermediate in the biphenyl molecule formation. Molecular oxygen oxidizes the Pd atom. The obtained intermediate further interacts with acetic acid present in the solution in accordance with experimental data (Table 1) providing the formation of the Pd acetate able to interact with benzene again (state (2)). This closes the catalytic cycle.



Figure 6. (a) Plausible mechanism for the C-H activation of benzene towards biphenyl formation. (b) Structures of different intermediates used during DFT calculation. The number in the parenthesis is used to designate the intermediate or transition state. The original state of palladium acetate is shown separately in a box.

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Green, red, grey, and yellow balls correspond to Pd, O, C and H atoms, respectively. DOI: 10.1039/DONJ02230F

3. Conclusion

Biphenyl has been successfully synthesized from benzene with a high yield (78%) during 12 h over a Pd catalyst supported on graphene oxide in the presence of acetic acid and molecular oxygen at 80 °C. The reaction did not involve the use of any halogenated precursor as required by Heck or Suzuki coupling. Supported Pd acetate is an important intermediate in this reaction able to break the C-H bond in benzene. It transforms to Pd biphenyl after interaction with benzene molecules. Then, releasing of biphenyl takes place, followed by oxidation of Pd by oxygen and formation of Pd acetate by interaction with acetic acid, thus, closing the catalytic cycle.

Experimental Section

Synthesis of Pd@GO catalyst

A stock solution of 0.069 M palladium nitrate in water was prepared and 628 μL of this solution was added to acetone (20 mL) to make a homogeneous mixture. Commercial GO (100 mg) with a surface area of 210 m²/g was added to it. The content was stirred for 3 h at room temperature. Afterwards, the solvent was evaporated at 55 °C under vacuum and the wet solid material obtained was heated in an oven at 150 °C in air for 10 min. The oven was allowed to cool to 40-45 °C and material was kept at this temperature for 12 h. It was unloaded and stored in a desiccator for further use.

Catalytic Test

Benzene (200 mg), acetic acid (1 mL) and Pd(II)@GO catalyst (20 mg) were placed in a round bottom flask equipped with a bottle filled with oxygen gas at 1 bar pressure. The mixture was allowed to react under stirring at 80 °C for up to 12 h. After that the reaction mixture was cooled and filtered. The filtrate was neutralized by NaOH solution (0.1 N) and extracted with ethyl acetate (10 ×3 mL). The combined organic layer was evaporated under vacuum and the residue was finally dried in hot air oven at 45°C to get the white crystalline solid. The yield was calculated by a formula (Actual yield / Theoretical yield) × 100 %]. ¹H-NMR spectroscopy confirmed the structure of synthesized biphenyl (Figure S2). ¹H-NMR spectrum of biphenyl exhibits the peaks at δ 7.05 ppm (m, 2H), δ 7.33 ppm (m, 4H), δ 7.46 ppm (m, 4H).

Recycling Test

Each catalytic run was carried out under the following reaction conditions: benzene (200 mg), catalyst loading 20 mg, acetic acid (1 mL), O_2 atmosphere and 80°C temperature for maximum of 12 h. After the completion of the reaction the catalyst was filtered and used as such without any purification.

DFT calculations

Calculations were carried out using a gradient-corrected functional of Perdew-Burke-Ernzerhof (PBE) with local and nonlocal exchange

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and correlation⁵³ within the quantum-chemical program package Jaguar (Jaguar, version 10.3, Schrödinger, LLC, New York, NY, 2019). Atomic orbitals were described by a LACVP basis set. The geometry corresponding to local energy minima was optimized by an analytical gradient method to default converged criteria. The Quadratic synchronous transit (QST) method was used to search a transition state (3) (Figure 6b). Binding energies between constituents of the model states (2) and (5) were calculated as: $E_{bind} = E_{tot}(C_6H_6) + E_{tot}(Pd-comp) - E_{tot}(model)$, where E_x is a total energy of the isolated benzene molecule, the isolated Pd compound, and the model, respectively.

Conflicts of interest

There are no conflicts to declare.

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¹ P ¹ Phylichedon 24 μmc 2020. Wownleaded hw Magnuric University on 67842020. I. 32:42 PM.

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