Supplementary Information

Visible light mediated and water-assisted selective hydrodeoxygenation of lignin derived guaiacol to cyclohexanol

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**Chemicals and characterization.** Chitosan, sodium borohydride, Pd(NO$_3$)$_2$, AgNO$_3$, HAuCl$_4$, CuSO$_4$, CoCl$_2$.6H$_2$O, PtCl$_2$, FeSO$_4$, Formic acid (>99%), and all organic solvents and guaiacol were received from Sigma-Aldrich chemicals. For each experiment, deionized water (18.2 mS conductivity) was used. Analytical thin-layer chromatography (TLC) was performed using analytical chromatography silica gel 60 F254 pre-coated plates (0.25 mm). A theta-theta diffractometer (PANalytical X’Pert Pro, PANalytical B.V.; The Netherlands) with a copper X-ray tube was used to identify crystalline phases of the synthesized solids. The XRD tube was operated at 45 keV and 40 mA for the analyses. Scans were performed over a 2-theta range between 2° to 90° with a step of 0.02° and a one-second count time at each step. Pattern analysis was performed following ASTM procedures using computer software (Materials Data, Incorporated. Jade+ v.5-8 XRD Processing Software; Livermore, California) with reference to the 2002 ICDD PDF-2 data files (International Center for Diffraction Data, Incorporated; Newtown Square, PA). The amorphous morphology and crystallinity of experimentally developed solid samples were investigated using A JEOL (JEM-2010F) high resolution-transmittance electron microscope (HR-TEM) with field transmission of 200 kV. To prepare the samples for HR-TEM, the copper solid samples were suspended in water and sonicated for 30 min, then fixed on a Lacy Carbon-Copper grid (LC300-Cu, EMS) by the drop-casting method. The TEM sample was prepared by dispersing dry powder of catalyst in water. For scanning electron microscopy (SEM), gold sputter coating was carried out on desired samples at a pressure ranging in between 1 and 0.1 Pa. The Sample was loaded in the chamber of Philip XL30 SEM and recorded by operating at 10-2 to 10-3 Pa with EHT 15.00 kV with 300 V collector bias. Sonication (Power Sonic 405) and centrifugation (Gyrogen 1236 MG) were used for re-dispersing and separating of the catalysts, respectively. X-ray photoelectron spectroscopy (XPS) was used to identify the oxidation states of metals. GC-MS analysis was conducted using an Shimadzu technology GCMS-QP2010 instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard) and an in-built MS 5975C VL MSD system with triple axis detector (Heater=290C, Pressure (He)= 7.02 psi, Total Flow= 23.6 mL/min; injection volume=0.5ul, syringe size= 5.0 uL).
1. Synthesis of materials

a) Synthesis of CN$_X$

The nitrogen enriched carbon nitride (CN$_X$) was synthesized by the calcination of chitosan (5.0 g, 4 h) with heating rate of 50 °C/min in a dynamic nitrogen flow of 20 mL/min using silica crucible in a furnace (KSL-1100X) operating at 600 °C.

b) Synthesis of AgPd/Fe@CN$_X$ catalyst

1.0 g CNx support was first dispersed in 1000 ml water and sonicated for 3 h. Then the solution of FeSO$_4$ (500 mg in 100 ml) was added dropwise at room temperature (RT). Aqueous solution of AgNO$_3$ (0.5 mM, in 25 ml water) was added to colloidal solution and stirring for 10 min. Then aqueous solution of Pd(NO$_3$)$_2$ (0.5 mM, in 25 ml water) was added to the dispersed solution at RT and reaction mixture was further stirring for 3 h. 1.0g Sodium borohydride (NaBH$_4$) was added, in portions, at 50 °C to reduce the iron sulfate, Ag (I) and Pd (II) to magnetic ferrites, Ag(0) and Pd(0), respectively. This reaction mixture was stirred for next 12 h. The ensuing black colored solid was isolated as AgPd/Fe@CN$_X$ using an external magnet, washed with water and methanol; finally dried at 60 °C in vacuum. The obtained AgPd/Fe@CN$_X$ composite powder was further analyzed by various instrumental techniques such as X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray

![Figure S1: Pictorial representation of the synthesis of AgPd/Fe@CN$_X$](image)
photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) surface area analysis and Inductive coupled plasma atomic emission spectroscopy (ICP-AES).

c) Screening of AgPd/Fe@CN_x catalyst for upgrading of guaiacol

Guaiacol (1.0 mmol), catalyst (20 mg), H_2O (1.0 mL), formic acid (5.0 mmol) and internal standard n-hexadecane (5.0 mmol) were placed in a reaction tube (10 mL) which was sealed with rubber septa. The reaction mixture was exposed to visible light using 20 W domestic bulb at ambient temperature and pressure. During the reaction, the temperature was monitored carefully to ensure that a 30 °C temperature was maintained. Reaction was monitored by TLC (ethyl acetate: hexane = 10:90; R_f = 0.40). After completion of reaction, 10 mL dichloromethane (DCM) was added and the catalyst was separated using an external magnet. DCM and water layer were separated with the help of separating funnel. DCM solvent was evaporated from the extracted solution and analyzed by GC-MS and NMR.

Figure S2. Pictorial representation of the experimental set-up for transformation of guaiacol
Figure S3. XRD analysis of AgPd/Fe@CN$_X$ as compared with JCPDS standards
Figure S4. XPS full spectrum of carbon nitride (CNx)
Figure S5. XPS full spectrum of AgPd/Fe@CNx.
Figure S6. Detailed XPS analysis for carbon nitride (CN$_x$) catalyst. a) C1s spectra. b) N1s spectra.
Figure S7. Detailed XPS analysis for AgPd/Fe@CN_X catalyst. a) C1s spectra. b) N1s spectra.
Figure S8. Detailed XPS analysis for AgPd/Fe@CNₓ catalyst. c) O1s spectra. d) Ag3d spectra
9. Recycling of AgPd/Fe@CNX catalyst:
After each reaction, the catalyst AgPd/Fe@CNX was recovered using an external magnet, washed with water followed by methanol and dried under vacuum at 60 °C. The recovered catalyst was then used for a new reaction using a fresh substrate. It was observed that the catalyst remained active after the reaction; could be recycled and reused over 6 times without much loss in activity.

Figure S10: Recycling of AgPd/Fe@CNX catalyst
Figure S10. FT-IR of CN$_X$ and AgPd/Fe@CN$_X$ catalyst
GC-MS monitoring results

GC-MS Result after 2 hours of reaction

n-hexadecane (Internal standard)
GC-MS Result after 4 hours of reaction

n-hexadecane
(Internal standard)
GC Result after 6 hours of reaction

- n-hexadecane
  (Internal standard)

R_f = 4.531
Molar mass = 82
$R_t = 4.582$

Molar mass = 98
$^1$NMR and $^{13}$CNMR

![NMR Spectrum Image]