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Selective hydrodeoxygenation of lignin-derived phenols to cyclohexanols or cyclohexanes over magnetic CoN_x@NC catalysts under mild conditions

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ABSTRACT: The hydrodeoxygenation (HDO) of lignin-derived phenols is important to produce the renewable biofuels. Herein, we reported a simple method to prepare magnetic nitrogen-doped carbon supported cobalt nitrides catalysts (CoN_x@NC) by co-pyrolysis of cellulose and cobalt nitrate under ammonia atmosphere. The catalysts were prepared at different temperatures and characterized by elemental analysis, AAS, BET, XRD, XPS, TEM

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4 and TPR. The CoNx@NC-650 (pyrolyzed at 650 °C) exhibited the best HDO activity for
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6 eugenol conversion among a series of Co-based catalysts. The yield of propylcyclohexanol
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8 from eugenol was greater than 99.9% under 2 MPa H₂, 200 °C for 2 h. Moreover, high yield
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10 of propylcyclohexane (99.1%) could be achieved when the solid acid HZSM-5 was added to
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12 the reaction system. Other lignin-derived phenolic compounds were also investigated and the
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14 yield of alkanes was greater than 90%. Based on the mechanism investigation, the catalyst
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16 demonstrated a high selectivity to cleave C_{aryl}-OR bond under mild conditions.
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22 **KEYWORDS:** Cobalt nitrides; nitrogen-doped carbon; biomass; hydrodeoxygenation;
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24 phenols conversion;
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30 INTRODUCTION

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32 Biofuels derived from lignocelluloses as substitutes for the traditional fossil fuels have
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34 aroused wide attention around the world.^{1,2,3,4} Lignin as an important part of lignocelluloses
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36 with 40% of biomass energy has a great potential for producing fuels and bulk chemicals.^{5,6}
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38 However, due to the high oxygen content, lignin depolymerized components (mainly
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40 phenolic mixtures) are difficult to use directly.^{7,8,9} In order to address this issue,
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42 hydrodeoxygenation (HDO) has been proposed to transform these compounds to chemicals
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44 and liquid fuels¹⁰. Previous research found that the catalysts used for hydrodesulfurization in
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46 petroleum refinery industry such as sulfide NiMo and CoMo also showed good activities for
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48 phenolic HDO.^{11,12,13,14} However, these catalysts are deactivated easily and may cause the
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50 sulfur pollution of the products.^{15,16,17}
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4 In recent years, non-sulfurized catalysts have been studied for phenolic HDO reaction.
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6 These catalysts are mainly focused on the noble metals like Pd,^{18,19,20,21,22} Pt^{23,24} and
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8 Ru,^{25,26,27,28,29,30} etc.. For examples, Pd/C-H₃PO₄/H₂O system was first employed by Zhao et
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10 al. to catalyze phenolic bio-oil to cycloalkanes under 5 MPa H₂, 250 °C.¹⁹ Later Ohta et al.
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12 using Pt/AC to catalyze phenols to cyclohexanes under 4 MPa H₂, 280 °C, and found that Pt
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14 could catalyze not only hydrogenation of phenols, but also hydrogenolysis of
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16 cyclohexanols.²³ They further developed the Pt/HZSM-5 catalyst which could catalyze
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18 various phenols to cyclohexanes even at 110 °C under ambient H₂ pressure,²⁴ which is the
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20 mildest condition having been reported. Because Ru has high hydrogenation and hydrolysis
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22 activity, it has also been employed for phenols HDO. Nakagawa et al. using Ru/C and bases
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24 (MgO, NaOH) as catalysts, and found that the presence of base is advantageous to the
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26 cleavage of C_{aryl}-OCH₃ bond.²⁷ Recently, Ishikawa et al used Ru-MnO_x/C to catalyze HDO
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28 of guaiacol and found that the addition of MnO_x slowed down the reaction rate of full
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30 saturation of aromatic ring. Increasing the relative rate of the cleavage of methoxy group to
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32 full saturation of aromatic ring can make HDO fulfilled under milder conditions.³⁰
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41 Considering the cost of the noble metal catalysts, non-noble metal catalysts were also
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43 applied to catalyze this type of reaction.^{31,32,33,34} RANEY Ni -Nafion/SiO₂ system was used
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45 by Zhao et al. to catalyze phenols to cycloalkane with 95% conversion of dihydroeugenol and
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47 75.7% total yields of cycloalkanes at 300 °C, 4 MPa H₂.³¹ Ni/HZSM-5 was also used by the
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49 same research group to catalyze phenols to cycloalkanes at 250 °C and 5 MPa H₂.³² Although
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51 these non-noble catalysts have shown high hydrogenation activity, the reaction condition is
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3 still harsh. Therefore, the development of new type of non-noble catalyst is still necessary to
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6 convert lignin-derived phenols under mild condition.
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9 Transition metal nitrides and carbides have been proposed for hydrogenation process³⁵.
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11 Especially molybdenum nitride and carbide can absorb and activate hydrogen and then
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13 transfer it to the reactant molecules.^{36,37} For cobalt nitride, Milad et al. reported that Co₄N
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15 had higher pyridine hydrodenitrogenation (HDN) activity than other bulk metal nitride
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17 catalysts (group IV–VIII, Co₄N > Fe₃N > Mo₂N > W₂N > VN ≈ NbN ≈ CrN > TiN).³⁸ In the
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19 meantime, carbon materials, especially for nitrogen-doped carbons (NC) have received
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21 increasing attention in recent years.^{39,40,41,42} The doping of nitrogen into the carbon
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23 architecture can significantly change the physical and chemical properties of the carbon
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25 materials like basicity⁴³ and catalytic activity,^{44,45} which makes NC have good performance
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27 in various applications, such as supercapacitors,⁴⁶ oxygen reduction catalyst⁴⁷ and catalyst
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29 supports,^{48,49} etc. More recently, metal particles surrounded by NC as redox reaction catalysts
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31 showed good activities. Xu et al. used 3-methyl-1-butylpyridine dicyanamide (ionic liquid) as
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33 precursor, nano-SiO₂ as hard template agent to prepare high nitrogen-content (12 wt%) NC
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35 material. This material showed excellent property in stabilizing Pd nanoparticles and the
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37 prepared Pd@NC catalyst was highly efficient in HDO of vanillin.⁵⁰ In addition, some
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39 researchers prepared such kind of catalysts by one-step pyrolysis at high temperatures under
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41 inert gas atmospheres.^{51,52,53,54} Jagadeesh et al. prepared Fe₂O₃/NGr@C catalyst by pyrolysis
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43 of Fe(OAc)₂-phenanthroline complex on carbon supports at 800 °C under argon atmosphere.
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45 The catalysts could convert various nitroarenes to anilines with high selectivity.⁵⁵ Bai et al.
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47 used cobalt-containing MOFs as precursors to prepare Co/N-C catalysts by pyrolysis method
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4 for selective oxidation of alcohols.⁵⁶ Although these materials showed good performance in
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6 catalysis, the precursors acting as nitrogen and/or carbon sources were expensive. Moreover,
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8 the preparation processes of the precursors were complicated.
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11 To solve the aforementioned challenges, we developed a simple method to prepare
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13 magnetic CoN_x@NC catalyst by co-pyrolysis of wide-available cellulose and Co(NO₃)₂
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15 under ammonia atmosphere. In this study, the catalysts with different preparation
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17 temperatures were characterized and tested by the HDO of eugenol. Different acids, reaction
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19 temperatures were characterized and tested by the HDO of eugenol. Different acids, reaction
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21 temperature and H₂ pressure were employed to explore the influence of various parameters
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23 and the optimal reaction conditions. The possible reaction pathway was proposed based on a
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25 kinetic study. Besides eugenol, the HDO of other phenolic compounds were studied. The
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27 stability of the catalyst was also investigated.
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32 **EXPERIMENTAL SECTION**

33 **Reagents**

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35 α -Cellulose (particle size: 50 μ m), eugenol, phenol, guaiacol, 3-methoxy phenol,
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37 2,6-dimethoxy phenol, catechol, 4-isopropylphenol, diphenyl ether, 4,4'-Dihydroxydiphenyl
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39 ether, 4-propyl phenol, 4-propylcyclohexanol and 5% Pd/C were purchased from Aladdin
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41 Chemistry Co. Ltd. 3-isopropylphenol was purchased from TCI; Co(NO₃)₂·6H₂O, acetone
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43 and ethyl acetate were purchased from Sinopharm Chemical Reagent Co. Ltd.
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49 Dihydroeugenol was prepared according to a previous reported method.⁷
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51 2-methoxy-4-propylcyclohexanol was synthesized as follows: eugenol (1g), Pd/C (100 mg)
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53 and H₂O (15 ml) were added to the Parr reactor and reacted at 200 °C, 5 MPa H₂ for 30 h
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4 with magnetic stirring. After reaction, the water was removed and the target product was
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6 separated by a silica gel column chromatography.
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8 **Catalysts Preparation**

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10 All of the CoN_x@NC catalysts were prepared by the in situ co-pyrolysis methods. The
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12 catalysts were labeled as CoN_x@NC-T (T is the pyrolysis temperature, 500 °C, 600 °C,
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14 650 °C, 700 °C or 800 °C, respectively). The preparing procedure of CoN_x@NC-650, for
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16 example, is described as follows: 10 g of α-cellulose was added into 300 g of acetone in a
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18 round-bottom flask and stirred at 45 °C. 1 g of Co(NO₃)₂·6H₂O was dissolved in acetone (15
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20 g) and then added to the above α-Cellulose/acetone suspension. The mixture was stirred at
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22 45 °C for 24 h. The solvent was then removed using rotary evaporation and dried at 105 °C
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24 for 10 h. After drying, the powder was added into a feed pipe and purged with NH₃ for 1 h.
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26 Then the powder was added into a quartz tube heated by a furnace slowly at 300 °C in the
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28 NH₃ flow. After feeding, the temperature was held at 300 °C for 30 min and then raised to a
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30 certain pyrolysis temperature (e.g. 650 °C) with a heating rate of 1°C/min. The temperature
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32 was then kept at 650 °C for 2 h before cooling to room temperature in NH₃ flow. The
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34 material was then purged with N₂ for 2 h.
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43 The procedure for preparing NC-650 was same as that of CoN_x@NC-650, but no
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45 Co(NO₃)₂·6H₂O was impregnated in the cellulose. The procedure for preparation of
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47 Co@C-650 was also same as that of CoN_x@NC-650, but NH₃ was substituted by N₂.
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51 The procedure for preparation of Co/NC is described as follows: 0.7 g of NC-650 was
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53 added into a 250 ml round-bottom flask with 100 g of acetone and stirred at 45 °C. 127 mg of
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55 Co(NO₃)₂·6H₂O was dissolved in acetone (15 g) and then added to the above suspension. The
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4 mixture was stirring at 45 °C for 24 h. The solvent was then removed using rotary
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6 evaporation and dried at 105 °C for 10 h. After drying, the powder was reduced by H₂ in a
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8 quartz tube furnace at 650 °C for 2 h with a heating rate of 1 °C/min. After cooling to the
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10 room temperature, the catalyst was purged with N₂ for 2 h.

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13 All of the catalysts were stored in a glove box before used for reaction.

14 15 16 **Catalyst Characterization**

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18 The nitrogen adsorption/desorption isotherms were measured by Micromeritics TriStar II
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20 (TriStar II 3020 V1.03). The surface area was determined through the Barrett–Emmet–Taller
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22 (BET) method. The average pore volume and pore size were measured by
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24 Barret–Joyner–Halenda method.
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29 X-ray power diffraction (XRD) patterns were conducted on an X'pert (PANalytical)
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31 diffractometer, using Cu_{Kα} radiation at 40 kV and 40 mA, 2θ ranges were 20°-80°. The
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33 crystal size was calculated by Scherrer equation through the Co(111) diffraction peak:
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35 $\langle L \rangle = \frac{K\lambda}{\beta \cos \theta}$, where K is a constant and equal to 0.89, λ is the X-ray wavelength and equal to
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37 0.154056 nm, β is the full width at half maximum (rad) and θ is the diffraction angle (rad).
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42 The transmission electron microscopy (TEM) images were taken by a JEOL JEM-2010
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44 LaB6 transmission electron microscope. The X-ray photoelectron spectroscopy (XPS) spectra
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46 were taken by an X-ray photoelectron spectrometer (ESCALAB250). The elemental analysis
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48 was measured by an Elementar vario EL cube. The combustion tube temperature was
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50 950 °C and the reducing tube temperature was 550 °C. The atomic absorption spectroscopy
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52 (AAS) was performed on a Perkin-Elmer Corporation Analyst 800 instrument. The sample
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54 handling process is as follows: 10 mg of catalyst was added into a 10 ml round-bottom flask
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3 with 4 ml of aqua regia and stirred at 80 °C for 24 h. After that, the mixture was diluted to 25
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5 ml in a volumetric flask.
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9 The temperature-programmed reduction (TPR) was carried out in a home-built reactor
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11 system coupled to a gas chromatograph. Before TPR tests, the samples were pretreated in Ar
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13 flow at 500 °C for 1 h. The TPR was carried out in a 5% H₂/Ar mixture gas flow from 40 °C
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15 with a heating rate of 10 °C/min. The liquid nitrogen/ethanol cooling bath was used to
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17 remove the moisture from the effluent stream before the stream entered a thermal
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19 conductivity detector (TCD).
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24 The reaction rate computation formula is as follows:

$$\text{Reaction rate} = \frac{\text{mole of propylcyclohexane}}{\text{mole of Co metal} * t(\text{h})}$$

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35 **Catalyst Test**

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37 All of the phenolic HDO reactions were performed in a 25 ml Parr reactor. In a typical
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39 experiment, 164 mg of eugenol, certain amount of catalyst and solvent (10 ml of *n*-dodecane)
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41 were added into the reactor. After purging with hydrogen for 5 times, the reactor was
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43 pressured with 2 MPa H₂ at ambient temperature. The reactions were conducted at certain
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45 temperature for certain time with magnetic stirring. After the reaction, the products were
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47 separated from the catalyst by an external magnet (shown in Figure S7), and then diluted with
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49 ethyl acetate and identified by a gas chromatograph–mass spectrometer combination (GC-MS,
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51 Agilent 5975C) and quantified by a gas chromatograph (Kexiao 1690) with HP-INNOWAX
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53 capillary column (30 m×0.250 mm×0.25 μm). The GC detecting conditions were as follows:
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4 nitrogen as carrier gas; injection port temperature: 280 °C; detector (FID) temperature:
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6 280 °C; column temperature: 40 °C, heating up to 250 °C with a heating rate of 10 °C/min.
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9 Bicyclohexane was used as internal standard to quantify the products.

10 11 **Catalyst Recycle**

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14 After reaction, the catalyst was separated from solution with an external magnet and
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16 washed three times with dodecane. After that, the catalyst was used for the next run directly.
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20 21 **RESULTS AND DISCUSSION**

22 23 **Characterization of the Catalysts**

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26 In order to explore the characteristics of the catalysts, a series of tests were carried out. As
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28 shown in Table 1, the surface area of the catalyst was increased with the pyrolysis
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30 temperature except at 700 °C. The reason for the decrease of the surface area of
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32 CoN_x@NC-700 might be due to the morphology transformation of the carbon support from
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34 600 °C to 800°C, which could be observed by TEM and XRD results. The N contents
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36 decreased from 14.89% to 6.12% when the temperature increased from 500 °C to 800 °C. The
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38 Co contents of the catalysts were about 5-10 wt%. Compare with NC-650, the
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40 CoN_x@NC-650 had higher surface area, pore volume and size, indicating that the presence
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42 of cobalt could promote the carbon material to form pores and significantly change the
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44 carbon structure.
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Table 1. Characteristics of CoN_x@NC_x Catalysts

Sample	S _{BET} (m ² /g)	Pore volume(cm ³ /g)	Pore size (nm)	Content (wt%)					Particle size(nm)	Crystal size(nm) ^c
				C ^a	N ^a	H ^a	O	Co ^b	TEM	XRD
CoN _x @NC-500	74	0.05	22.8	63.21	14.89	3.06	12.47	6.37	6.4	--
CoN _x @NC-600	272	0.04	6.1	64.26	11.94	2.81	15.62	5.37	11.3	5.4
CoN _x @NC-650	417	0.12	8.5	67.29	11.32	2.6	12.26	6.53	13.1	6.9
CoN _x @NC-700	290	0.18	13.0	65.36	9.22	2.42	18.83	9.17	14.1	10.1
CoN _x @NC-800	425	0.18	41.5	70.81	6.12	1.74	12.72	8.61	46.4	9.4
NC-650	301	0.02	5.1	75.11	11.99	2.48	10.42	--	--	--

[a] Measured by elemental analysis. [b] Measured by AAS. [c] The crystal size was calculated by Scherrer equation through the Co(111) diffraction peak.

The morphologies and metal dispersions of the catalysts were characterized by TEM. As shown in Figure 1, the Co particles were well dispersed on the N-doped carbon when the pyrolysis temperature was below 700 °C. The size of Co particle prepared at 500 °C was around 6.4 nm (Table 1). At 600 °C, the size of the particles increased to 11.3 nm. Further raising the temperature to 700 °C, the particle size increased slightly. However, a serious aggregation happened when the temperature rose to 800 °C. The average particle size was 46.4 nm and the morphology of the support transformed to nanotubes. Therefore, the pyrolysis temperature had a significant influence on the morphology and particle size of the catalysts.

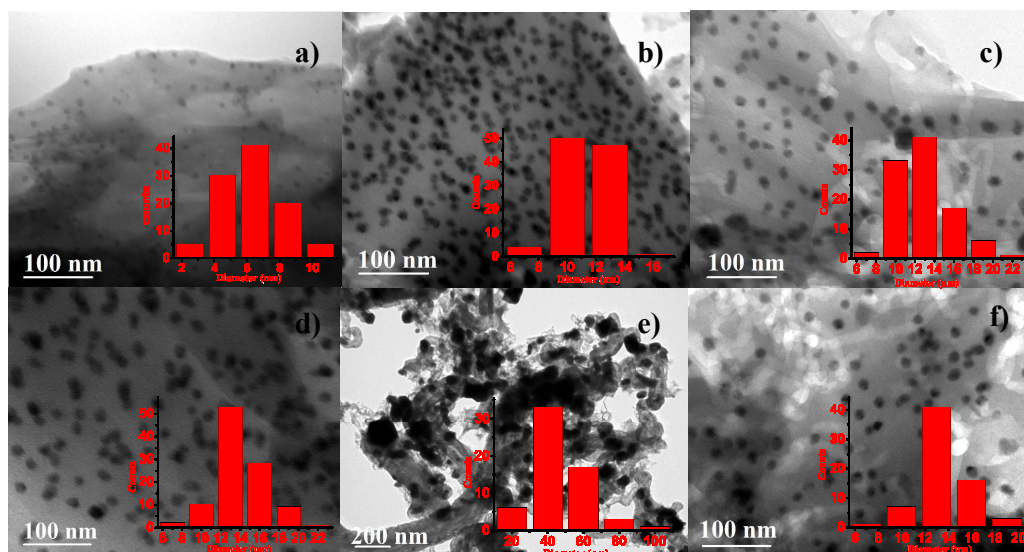


Figure 1. TEM images of (a) CoN_x@NC-500, (b) CoN_x@NC-600, (c) CoN_x@NC-650, (d) CoN_x@NC-700, (e) CoN_x@NC-800, (f) CoN_x@NC-650 after 4 runs

In order to investigate the crystal structure of the catalysts, XRD analysis was carried out. Figure 2 shows the XRD patterns of the CoN_x@NC catalysts. For NC-650, only a broad peak at 24° was detected, which was the diffraction peak of amorphous carbon. For CoN_x@NC catalysts, when the pyrolysis temperature was 500 °C, no diffraction peak of cobalt was found from the XRD patterns, indicating that the cobalt species were amorphous at this pyrolysis temperature. For CoN_x@NC-650, the diffraction peaks at 43.9°, 51.0° and 75.3° which are closed to the (111), (200) and (220) planes of both Co⁰ (JCPDS 15-0806) and Co₄N (JCPDS 41-0943) (Figure S2). It is difficult to identify the Co⁰ and Co₄N superficially from XRD patterns because of their similar lattice structure and parameters (Table S1).^{57, 58, 59, 60} To verify the component of the catalyst, partial XRD analyses of CoN_x@NC-650, Co/NC (reduced by H₂) and Co@C-650 from 41° to 54° were carried out (Figure 3). According to the Co/NC and Co@C patterns, the diffraction peak at 44.5° could

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4 be the (111) plane of Co^0 . From the standard PDF cards of Co_4N and Co^0 , the diffraction
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6 peak (111) of Co_4N was about 0.5° lower than the Co^0 . Compare with Co/NC and $\text{Co}@C$,
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8 the diffraction peak (111) of $\text{CoN}_x@NC-650$ shift to lower angle from 44.5° to 43.9° , which
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10 was very close to the diffraction peak (111) of Co_4N . Considering that the Co-N ratio and
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12 structure may change with the reaction and preparation condition, and the peak also shifts
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14 accordingly, the Co-N component in the catalysts was defined as CoN_x . Stronger and sharper
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16 diffraction peaks were observed in $\text{CoN}_x@NC-700$ (Figure 2), implying a higher ordering
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18 and crystallinity of the cobalt species. The peak at 26° of $\text{CoN}_x@NC-800$ indexed to the (200)
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20 plane of graphite-type carbon, indicating the graphitization of nitrogen-doped carbon formed.
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22 When the XRD pattern of $\text{CoN}_x@NC-800$ was enlarged (Figure S1), it could find that the
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24 peaks were the overlap of Co^0 and CoN_x . Comparing with $\text{CoN}_x@NC-600$ and 650, the
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26 diffraction peaks of Co species of $\text{CoN}_x@NC-700$ and 800 shifted to higher angle. Previous
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28 research found that the Co_4N could decompose to Co^0 stepwise at elevated temperatures:
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30 $\text{Co}_4\text{N} \rightarrow \text{Co}_3\text{N} + \text{Co}$, $\text{Co}_3\text{N} \rightarrow \text{Co}_2\text{N} + \text{Co}$, $\text{Co}_2\text{N} \rightarrow \text{CoN} + \text{Co}$.⁶¹ Maybe more Co^0 was formed
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32 from CoN_x with the pyrolysis temperature increasing. Additionally, no peak of cobalt oxide
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34 species was found.
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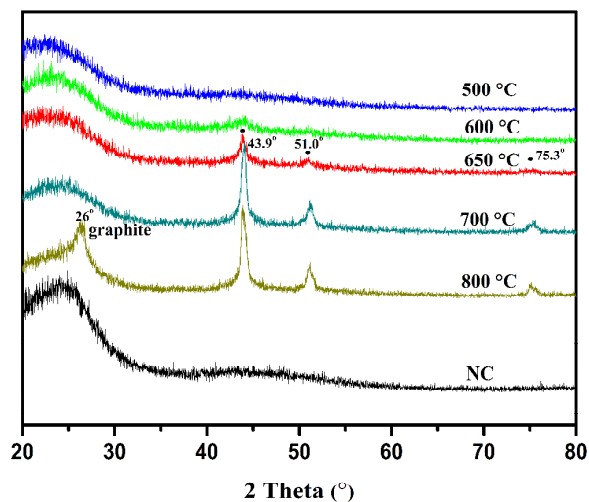


Figure 2. XRD patterns of the CoNx@NC catalysts with different pyrolysis temperatures.

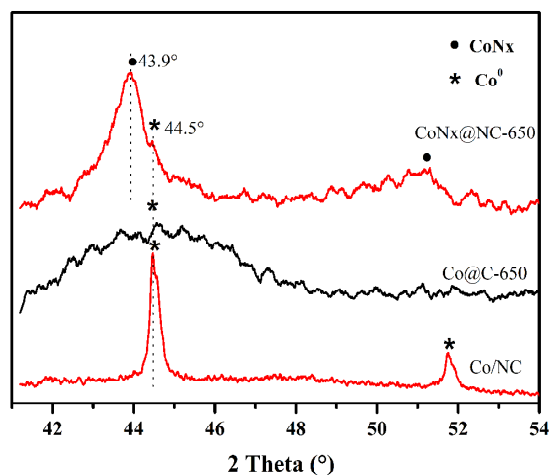


Figure 3. Partial XRD patterns of the CoNx@NC-650, Co@C-650 and Co/NC. The peak intensity of Co/NC has been reduced by 5 times.

In order to confirm the valence states of Co and N, XPS was used to analyze the catalysts. Deconvolution of the N1s and Co2p regions by peak fitting for CoNx@NC catalysts is shown in Figure 4. All of the binding energies were corrected by C1s and the binding energy of C-C was 284.6 eV (Figure S3). Three distinct peaks were observed in the N1s spectra of

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CoNx@NC. The peaks at binding energies of 398.6 eV, 400.5 eV and 402.3 eV can be attributed to pyridine-type, pyrrole-type and quaternary-type nitrogen, respectively.^{62, 63} The percentage of pyridine-type nitrogen decreased with the increase of pyrolysis temperature (Table 2). The contents of pyrrol-type nitrogen increased first and then decreased, while the quaternary-type nitrogen increased along with temperature. The trend of nitrogen content was consistent with previous reports.⁴² The NC materials with different type nitrogen could function as ‘heterogeneous N-type ligands’ to stabilize metal and improve the catalytic activity.⁶² Some studies indicated that pyridine-type nitrogen play an important role for ORR activity and the quaternary-type nitrogen was the most active specie for catalyzing hydrocarbon activation.^{51, 64}

For Co2p_{3/2} spectra of the catalysts, the binding energies in 778.7 eV, 780.6 eV, 782.6 eV, and 786.2 eV can be attributed to Co⁰, Co-O, Co-N and the satellite peak of Co-O, respectively^{54, 65}. The existence of Co-O was because the cobalt ions could combine with O in cellulose and O could partially retain during the pyrolysis process, which could be proven by the XPS of C1s (Figure S3) that much C-O and C=O were presented in the CoNx@NC catalysts. In addition, the surface of Co could be partially oxidized when the catalysts exposed to air. These cobalt oxides were amorphous and revealed no diffraction peaks in XRD patterns, as discussed above. Under low pyrolysis temperature, much O was retained to form CoOx (Co²⁺, Co³⁺). For CoNx@NC-500 catalyst, the content of Co-O was 62.5%. Further increasing temperature, the content of Co-O decreased and reached 28.5% at 800 °C. This trend could also be verified by the intensity decrease of the typical satellite peak of Co-O. The percentage of Co-N increased first and then decreased with temperature

increasing. The CoNx@NC-650 had a maximum value of Co-N as 32.9%. The percentage of Co⁰ increased from 9.3% to 47.1% when the pyrolysis temperature increased from 500 °C to 800 °C (Table 2). It indicated that with pyrolysis temperature increasing, CoOx formed firstly followed by CoNx with the substitution of N for O under ammonia atmosphere, and then the CoNx would decompose to Co⁰ at higher pyrolysis temperature, which agreed well with the XRD characterization.

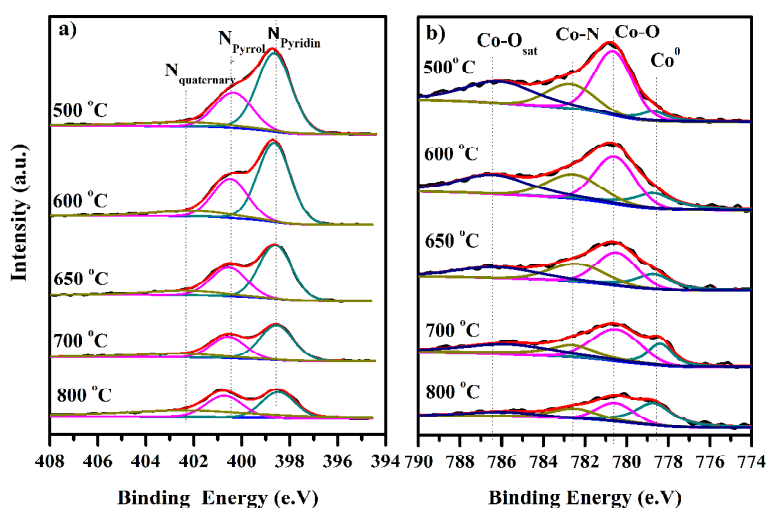


Figure 4. XPS spectra of the (a) N1s and (b) Co2p_{3/2} of CoNx@NC catalysts

Table 2. Ratio analysis of the peaks in XPS spectra in CoNx@NC

Sample	Content %					
	N _{pyridin}	N _{pyrrol}	N _{quaternary}	Co-N	Co ⁰	Co-O
CoNx@NC-500	59.7	27.6	12.6	28.2	9.3	62.5
CoNx@NC-600	59.1	30.5	10.4	31.6	20.6	47.8
CoNx@NC-650	56.1	33.1	10.8	32.9	23.3	43.8
CoNx@NC-700	51.4	31.4	17.3	27.0	29.0	43.0
CoNx@NC-800	31.0	28.5	40.5	24.4	47.1	28.5

Catalytic Activity

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4 The catalytic activities of the catalysts were tested by HDO of eugenol at 200 °C and 2
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6 MPa. As shown in Table 3, catalysts with different pyrolysis temperature demonstrated
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8 significant difference in activity. As the pyrolysis temperature increased, the catalytic activity
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10 increased first and then decreased. For CoNx@NC-500, in 1.5 h, the eugenol conversion was
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12 5.2% and the products were dihydroeugenol and trace propylcyclohexanol (entry1). The
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14 catalytic activity of CoNx@NC-600 increased remarkably. The conversion of eugenol was
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16 100% and the yield of propylcyclohexanol was 45.5%. Besides propylcyclohexanol and
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18 dihydroeugenol, 15.6% yield of propylphenol that could be the intermediate was detected.
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20 The CoNx@NC-650 showed the highest catalytic activity with 100% conversion and 86.6%
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22 yield of propylcyclohexanol (entry 3). The propylcyclohexanol yield reached 99.9% after 2 h
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24 (entry 6). As the pyrolysis temperature further increasing, the catalytic activity decreased.
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26 The propylcyclohexanol yield was 38.9% for CoNx@NC-700 and only 3.7% for
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28 CoNx@NC-800 in 1.5 h. Among CoNx@NC catalysts, CoNx@NC-500 had the most Co-O
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30 content, CoNx@NC-800 had the most Co⁰ content and CoNx@NC-650 had the most Co-N
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32 content. Because CoNx@NC-650 showed the best performance, the cobalt nitrides in the
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34 catalyst should play an important role in the catalytic process.
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43
44 In order to further explore the hypothesis, NC-650, Co@C-650 and Co/NC were
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46 synthesized and tested for catalyzing HDO of eugenol (Table 3, entry 6-9). The NC-650
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48 almost had no activity for eugenol conversion (2.9%). For Co@C-650, the conversion of
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50 eugenol was 24.7% and no propylcyclohexanol was produced. From XRD pattern and XPS
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52 of Co@C-650 (Figure S5 and Figure S6), Co⁰ was the main component of the catalyst, which
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54 could come from the cobalt precursor reduced by the non-condensable reductive species (e.g.,
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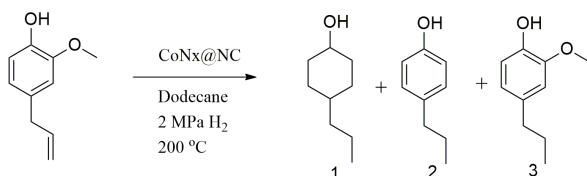
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4 H₂, CO, C_xH_y) produced during the fast pyrolysis of cellulose in the absence of oxygen.^{66,67,68}

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6 It indicated that the Co⁰ in our catalytic system was not the key factor for catalyzing eugenol
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8 to propylcyclohexanol. To further investigate if the NC support can promote Co⁰ to catalyze
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10 eugenol to produce propylcyclohexanol, the Co/NC was also synthesized for the test.
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12 Although the conversion of eugenol increased to 100%, the yield of propylcyclohexanol was
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14 only 0.6%. Therefore, the catalytic activity of CoNx@NC-650 from eugenol to
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16 propylcyclohexanol can mainly be ascribed to the CoNx.
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21 So far, equivalent of propylcyclohexanol has been achieved from eugenol under the
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23 catalysis of CoNx@NC-650. Propylcyclohexanol can be further converted to
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25 propylcyclohexane, a C₉ naphthene, via dehydration and hydrogenation. Because the
26
27 CoNx@NC-650 catalyst is alkaline, acid can be added to the reaction system to help achieve
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29 propylcyclohexane from eugenol. As shown in Table 4, when SiO₂ and γ-Al₂O₃ were added,
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31 the products had no significant change (entries 2, 3). However, when HZSM-5 was added to
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33 the system, the main product was propylcyclohexane (96%) with small amount of
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35 propylcyclohexene (3.2%) (entry 4). The propylcyclohexane yield reached 99.1% after the
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37 reaction time prolonged to 2 h (entry 6). When homogeneous acid H₃PO₄ was added, no
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39 propylcyclohexane was detected and the propylcyclohexanol yield was only 7.7%. The
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41 catalyst was possibly destroyed by H₃PO₄ in the reaction system. Compared with entry 1 and
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43 entry 4 (Table 4), the yield of propylcyclohexane (96%) was greater than propylcyclohexanol
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45 (86.6%), indicating that the addition of HZSM-5 could not only catalyze dehydration of
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47 alcohol, but also promote the reaction rate. The catalysts with different pyrolysis temperature
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were also tested to produce propylcyclohexane and the trend of catalytic activity was same as that to produce propylcyclohexanol.

Table 3. HDO of eugenol over CoNx@NC catalysts



Entry	Catalyst	Time (h)	Conversion(%)	Yield %		
				1	2	3
1	CoNx@NC-500	1.5	5.2	0.5	0	4.6
2	CoNx@NC-600	1.5	100	45.5	15.6	38.8
3	CoNx@NC-650	1.5	100	86.6	8.6	4.7
4	CoNx@NC-700	1.5	100	38.9	48.7	9.3
5	CoNx@NC-800	1.5	100	3.7	4.7	90.2
6	CoNx@NC-650	2	100	99.9	0	0
7	NC-650	2	2.9	0	0	2.9
8	Co@C-650	2	24.7	0	0	21.7
9	Co/NC	2	100	0.6	0.2	99.1

164 mg (1mmol) of eugenol, 10 ml of n-dodecane, the dosage of catalysts contained 5 mg of cobalt. For CoNx@NC-650, the content of cobalt was 6.53 wt% and the dosage of the catalyst was 76 mg.

Table 4. HDO of eugenol over CoNx@NC with acid

Entry	Catalyst	Additives	Conversion (%)	Yield(%)				
				1	2	3	4	5
1	CoNx@NC-650	--	100	0	0	86.6	8.6	4.7
2	CoNx@NC-650	SiO ₂	100	0	0	85.8	7.1	5.6
3	CoNx@NC-650	Al ₂ O ₃	100	0	0	85.7	6.4	6.8
4	CoNx@NC-650	HZSM-5	100	96	3.2	0	0	0
5	CoNx@NC-650	H ₃ PO ₄	100	0	0	7.7	8.7	83.6
6 ^a	CoNx@NC-650	HZSM-5	100	99.1	0.6	0	0	0
7	CoNx@NC-500	HZSM-5	58.6	0	0	0.5	1.3	56.2
8	CoNx@NC-600	HZSM-5	100	87.1	11.3	0.5	0	0
9	CoNx@NC-700	HZSM-5	100	24.6	24.9	3.7	11.5	30.1
10	CoNx@NC-800	HZSM-5	100	3.4	3.5	2.5	10.6	80

164 mg (1mmol) of eugenol, 50 mg of additives (SiO₂, Al₂O₃ or HZSM-5) or with 0.2 wt% H₃PO₄, 10 ml of n-dodecane, the dosage of catalysts contained 5 mg of cobalt. [a] reaction time 2 h.

Temperature is an important parameter for a reaction. Figure 5 shows the results of HDO of eugenol at different reaction temperature over CoNx@NC-650 catalyst. When the reaction temperature was 170 °C, the product was dihydroeugenol. When the temperature reached 180 °C, propylcyclohexane started to generate and accompanied by a series of intermediate products. The yield of propylcyclohexane increased and reached 31.8% at 190 °C. A sharp increase happened when the temperature was 200 °C and the propylcyclohexane yield increased to 99.1%. The reaction rates at different reaction

temperatures were calculated. At 170 °C, only allyl group was hydrogenated. With the temperature increasing from 190 °C to 200 °C, the reaction rate accelerated greatly from 1.87 h⁻¹ to 5.84 h⁻¹, indicating that the conversion of eugenol to propylcyclohexane is temperature-sensitive reaction (Table S2).

The effect of hydrogen pressure on eugenol HDO was also studied (Figure 6). When the hydrogen pressure was 0.5 MPa, the main product of the reaction was dihydroeugenol and trace intermediates. The yield of propylcyclohexane increased from 34.6% to 93.6% when the pressure increased from 1 MPa to 1.5 MPa. The yield was greater than 99% when the pressure increased to 2 MPa. Interestingly, when the pressure was 1 MPa, nearly 30% of cyclo-olefin generated, indicating that in this reaction system, the hydrogenation of cyclo-olefin was slow under low hydrogen pressure.

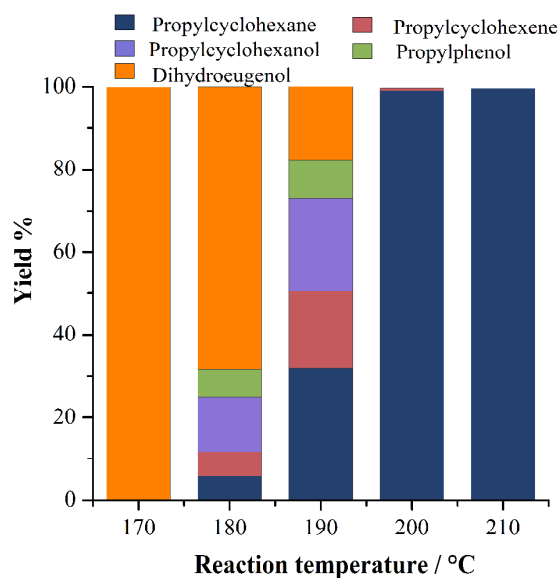


Figure 5. Effect of reaction temperature. Reaction conditions: 164 mg (1mmol) of eugenol, 50 mg of HZSM-5, 10 mL of n-dodecane, 76 mg of CoN_x@NC-650, 2 MPa H₂, 2 h.

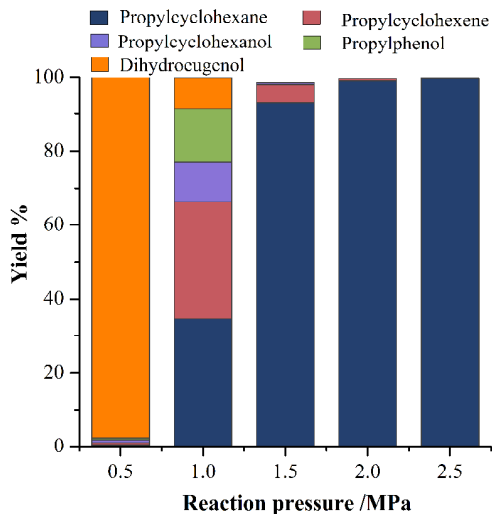


Figure 6. Effect of reaction pressure. Reaction conditions: 164 mg (1mmol) of eugenol, 50 mg of HZSM-5, 10 mL of n-dodecane, 76 mg of CoNx@NC-650, 200 °C, 2 h.

Mechanism

In order to explore the mechanism of CoNx@NC-650 catalyzed HDO of eugenol, we tracked and analyzed the distribution of products at different reaction time (Figure 7). At 200 °C and 2 MPa H₂, eugenol was completely converted into dihydroeugenol by hydrogenation of allyl group in the initial 10 min. Trace intermediates were detected as 4-propylphenol, 4-propylcyclohexanol and 4-propylcyclohexene. With the extension of reaction time, the content of dihydroeugenol decreased rapidly and disappeared in 60 min. Meanwhile, the 4-propylphenol was also disappeared. Other intermediates increased first and then decreased gradually. The 4-propylcyclohexanol disappeared in 90 min. However, the 4-propylcyclohexene decreased very slowly and disappeared until 150 min. The hydrogenation of 4-propylcyclohexene was slow and became the rate control step. Based on the above results, we proposed a possible reaction pathway (Figure 8). Eugenol was hydrogenated to dihydroeugenol with a very fast reaction rate. Then the C_{aryl}-OCH₃ of

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4 dihydroeugenol was cleaved by the cobalt catalyst. The aromatic ring of 4-propylphenol was
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6 then hydrogenated to 4-propylcyclohexanol and dehydrated to propylcyclohexene under the
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8 catalysis of cobalt catalyst and solid acid HZSM-5. Finally, the propylcyclohexene was
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10 hydrogenated to the propylcyclohexane. This pathway suggests that the mechanism of
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12 catalyzing methoxyphenols to the corresponding cycloalcohols by CoN_x@NC is different
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14 from other catalysts like Pd, Ru and Ni. Previous reports show that hydrogenation of the
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16 aromatic ring is prior to the hydrolysis of C_{aryl}-OCH₃ for Pd¹⁹, Ru²⁵ or occurs in parallel for
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18 Ni⁶⁹. Pd/C, Ru/C and Ni/C were tested under the same reaction system and the results were
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20 consistent with the previous researches (Table S3). Generally, compared with phenolic
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22 monomers, the corresponding fully hydrogenated products are more stable due to the steric
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24 hindrance and electronic effect that restrain the cleavage of C_{alkyl}-OR.^{27,69} In this reaction,
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26 2-methoxy-4-propylcyclohexanol was not detected, indicating that the CoN_x@NC-650
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28 catalyst could selectively cleave C_{aryl}-OCH₃ bond to 4-propylphenol without producing
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30 2-methoxy-4-propylcyclohexanol. This may be the reason why the catalyst could catalyze
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32 HDO of eugenol with high yield of propylcyclohexanol under milder conditions.
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41 In order to further verify the reaction mechanism, the 2-methoxy-4-propylcyclohexanol
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43 was synthesized and used as the reactant under the same reaction conditions (Table S4). Only
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45 12.1% conversion of 2-methoxy-4-propylcyclohexanol was obtained.
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47 2-Methoxy-4-propylcyclohexanol should have been detected if it was produced in eugenol
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49 conversion. It further proved that the catalyst could selectively cleave C_{aryl}-OCH₃ bond
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51 before hydrogenating the aromatic ring. 47% yield of methanol was detected when the
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53 eugenol was totally converted with 88.8% total yields of propylcyclohexanol and
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4-propylphenol (83.2% and 5.6%, respectively). The gas products were analyzed, only hydrogen and methane were detected after the reaction (98.5% and 1.5% of volume fraction, respectively). The yield of methane was 40.3%. Based on previous research,²⁷ methane could be produced from methanol under the reaction condition. All of these verified that the CoNx@NC-650 catalyst had good property to cleave C_{aryl}-OCH₃ bond.

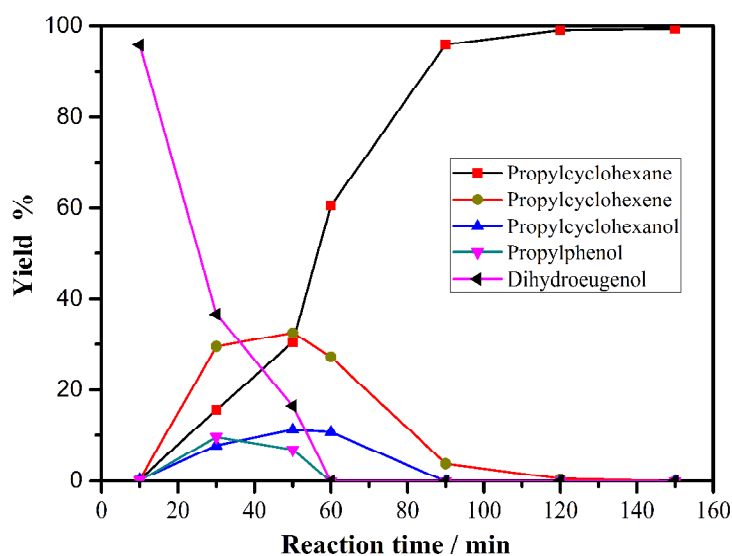


Figure 7. Product distributions as functions of time for CoNx@NC-650 catalyst. Reaction conditions: 164 mg (1mmol) of eugenol, 50 mg of HZSM-5, 76 mg of CoNx@NC-650, 10 ml of n-dodecane, 2 MPa H₂, 200 °C.

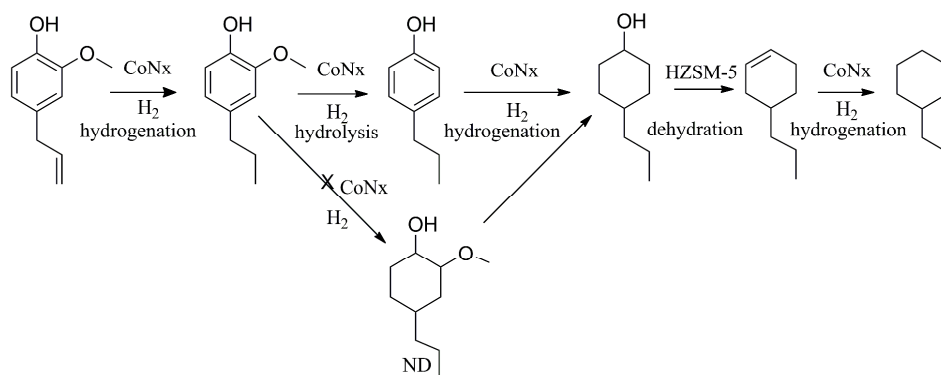






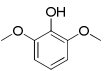


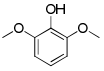















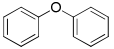

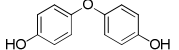

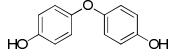



Figure 8. Proposed reaction pathway.

HDO of other phenolic compounds

In order to investigate the applicability of the catalyst, other lignin-derived phenolic compounds were evaluated under 2 MPa H₂, 200 °C for 2 h (Table 5). For the phenolic compounds like phenol, guaiacol, 3-methoxyphenol, 3-isopropylphenol and 4-isopropylphenol, the catalyst showed a high catalytic activity and the yield of naphthene were greater than 95%. Compared with guaiacol and 3-methoxyphenol, the HDO of catechol and resorcinol was more difficult and the yield of cyclohexane was 5.2% and 45%, respectively (entry 8 and 10), probably because the substrates were difficult to dissolve in dodecane. After prolonging the reaction time to 8 h, the cyclohexane yield was greater than 98% (entry 9 and 11). For 2,6-dimethoxyphenol, the conversion was 43.4% and the cyclohexane yield was 9.1%. In addition to cyclohexane, 9.7% yield of guaiacol was detected. It further verified the mechanism that proposed above. 99.9% yield of cyclohexane was achieved when the reaction time was 12 h. Diphenyl ether has also been used to evaluate the catalyst activity and achieved a good result. When hydroxyl was existed in para-position, the yield of cyclohexane decreased to 65% (entry 13). However, equivalent of cyclohexane was produced when the reaction time was 8 h (entry 14). All of the above results suggest that the CoNx@NC-650 catalyst has a high HDO activity for various phenolic compounds under mild conditions.

Table 5. HDO of other phenolic compounds

Entry	Substrates	Conversion (%)	Products	Yield(%)
1		100		91
2		100		99.6
3		100		95
4		43.4	 	9.1 9.7
5 ^a		100		99.9
6		100		98.2
7		100		99.9
8		100	 	5.2 62.4
9 ^{bd}		100		99.9
10		100	 	45 43.2
11 ^{bd}		100		98.6
12 ^c		100		92
13 ^c		100		65
14 ^{bc}		100		99.9

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4 Reaction conditions: 1mmol of Substance, 50 mg of HZSM-5, 10 mL of n-dodecane, 76 mg
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6 of CoN_x@NC-650, 2 MPa H₂, 200 °C for 2 h. [a] Reaction time was 12 h. [b] Reaction time
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8 was 8 h. [c] The dosage of the substance was 0.5 mmol and the yield was calculated by 1mol
9
10 substance generate 2 mol cyclohexane. [d] The dosage of HZSM-5 was 100mg.
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13 14 **Recyclability of the Catalyst**

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16 The stability of CoN_x@NC-650 catalyst was investigated by catalyzing eugenol to
17
18 propylcyclohexanol. The results of the recycle experiments are shown in Figure 9. After four
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20 runs, the yield of propylcyclohexanol had a certain decrease. In order to analyze the reasons
21
22 for deactivation of the catalyst, some characterizations were carried out. From the TEM
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24 image (Figure 1f), no apparent aggregation of cobalt (13.5 nm) was found after recycles.
25
26 However, from the XRD patterns (Figure S8), the peaks of the catalyst shifted and the peak
27
28 intensities decreased after the recycles, indicating that the cobalt nitrides had a certain loss.
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30 The elemental analysis showed that the N content decreased from 11.32% to 10.5% and AAS
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32 analysis indicated that the Co content decreased from 6.53% to 5.88% after four runs.
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34 Moreover, the catalyst would have a loss during the separation processes. All of these would
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36 lead to a decrease in the product yield. We will continue to study this kind of catalysts to
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38 improve the stability in the future work.
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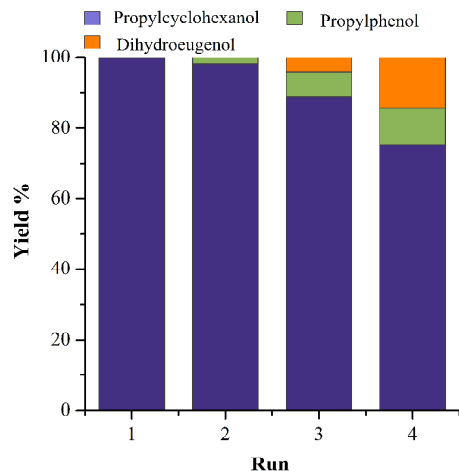


Figure 9. Recycle of the catalyst. Reaction conditions: 164 mg (1mmol) of eugenol, 10 mL of n-dodecane, 76 mg of CoNx@NC-650, 2 MPa H₂, 200 °C, 2 h.

CONCLUSIONS

A simple method with cellulose as the carbon source, cobalt nitrate as the metal source and ammonia as nitrogen source has been proposed for preparation of CoNx@NC catalysts. Under the high temperature and ammonia atmosphere, the cobalt ions formed cobalt nitrides that play an important role in the catalytic HDO reactions. The N-doped carbon support can help to promote the reaction. Using eugenol as a model compound, the CoNx@NC-650 exhibited an excellent HDO activity. The conversion of eugenol was 100% and the yield of propylcyclohexanol was greater than 99.9% under 2 MPa H₂, 200 °C for 2 h. Moreover, high yield of propylcyclohexane (99.1%) could be achieved when solid acid HZSM-5 was added to the reaction system. The reaction pathway is different from other catalysts like Pd, Ru and Ni. It can selectively cleave C_{aryl}-OCH₃ bond to 4-propylphenol before the hydrogenation of the aromatic ring, which could be the main reason that the catalyst can catalyze HDO of

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3 eugenol under mild conditions. Moreover, this catalyst showed a high HDO activity for
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5 various phenolic compounds.
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8 9 ASSOCIATED CONTENT

10 11 **Supporting Information**

12
13 The enlarged XRD pattern of the CoN_x@NC-800 catalyst, standard PDF card and TCPDS
14
15 dates of Co⁰ and Co₄N, XRD, XPS of Co@C-650 and Co/NC, TPR, catalyst recycle and
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17 XRD analysis, XPS and XRD of CoN_x@NC-650 before and after reaction, GC-MS of
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19 substrates are provided in supporting information. This material is available free of charge via
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21 the Internet at <http://pubs.acs.org>.
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