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Metal free catalytic conversion of veratryl and benzyl alcohols through nitrogen enriched carbon nanotubes

Neeraj Gupta [1,2], Ilaria Barlocco [3], Oleksiy Khavryuchenko [4], and Alberto Villa [3,*]

1   Catalysis Division, IMR-Shenyang National Laboratory, Chinese Academy of Sciences, Shenyang, China-110016 E-mail: gupta_nrj@hpcu.ac.in (N.G.)

2   Department of Chemistry and Chemical Sciences, Central University of Himachal Pradesh, Shahpur Campus, Dharamshala, Kangra (HP) India – 176206

3   Dipartimento di Chimica, Università degli Studi di Milano Via Golgi 19, 20133 Milano, Italy: Ilaria.Barlocco@unimib.it (I.B.)

4   Shupyk National Healthcare University of Ukraine, Dorohozhytska Str. 9, Kyiv, 04112 Ukraine

*   Correspondence: alberto.villa@unimi.it

Abstract: Nitrogen rich carbon nanotubes NCNT700 and NCNT800 were prepared by chemical vapour deposition method (CVD). The catalysts were characterized via High-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) analysis. Both the catalysts were found to have an inverted cup stack like morphology. The XPS analysis reveals that catalysts are rich in pyridinic sites with variable amount of nitrogen on their surface. The NCTN700 with a higher nitrogen content and pyridinic sites on its surface was found to be a good catalyst for the oxidation of benzyl and veratryl alcohols into respective aldehydes. It was observed that toluene and 4-methyl veratrole were also produced in this reaction. The amount of toluene produced is as high as 21% with 99% conversion of benzaldehyde in presence of NCNTs-700. The mechanistic pathway was revealed through DFT studies, where the unusual product formation of aromatic alkanes such as toluene and 4-methyl veratrole was explained during the reaction. It was astonishing to observe the reduced product in the reaction that proceeds in the forward direction in presence of a peroxide (tert-butyl hydroperoxide, TBHP). During the computational analysis, it was revealed that the reduced product observed in the reaction did not appear to proceed through a direct disproportionation reaction. Rather the benzyl alcohol (the reactant) used in the reaction may undergo oxidation by releasing the hydrogen radicals. hydrogen atoms released during the oxidation reaction appear to have been trapped on pyrrolic sites on the surface of catalyst and later transferred to the reactant molecules to produce toluene as a side product.

Keywords: metal free; nitrogen functionalization; alcohol oxidation; veratryl alcohol.

1. Introduction

Nowadays, there is a consensus that petroleum based chemicals and fuels are unsustainable, promoting the attention to renewable resources. Replacing these products with biomass resources is important to maintain economical, scientific, social and political goals [1]. Waste biomass resources such as fallen leaves, waste wood and non-edible plants are mainly rich in hemicelluloses, cellulose and lignin. The amount of these components varies based upon the plant type and origin. Utilization of these components is made possible due to the emergence of bio-refineries [2]. The pyrolysis of ligno-cellulosic biomass normally affords liquid oils that are rich in phenolic compounds. Normally, the components of bio-oil need efficient separation and up-gradation technology to make them usable as fine chemicals. Most commonly used processes are oxidation [3] and hydrodeoxygenation [4], which generally require metal based homogenous or heterogeneous catalysts. Again, the use of metal based catalyst is not promoted much to attain the

sustainability. Therefore, the use of metal free catalysts for the valorisation processes are highly recommended.

Past decade has seen extensive efforts for the depolymerisation of lignin by the reductive and oxidative processes [4]. Transition metal based catalysts are the first choice for implementing the activity [4]. Ni@C is used for the hydrogenolytic cleavage of lignin derived from native birch wood lignin [5,6]. High chemoselectivity of monomeric phenols was achieved over Ni based carbon catalyst, and the lignin was cleaved into propylsyringol and propylguaiacol with a selectivity of more than 50%. Similarly, Cobalt chloride in ionic liquid 1-ethyl-3-methylimidazolium diethylphosphate is used for the oxidative cleavage of model lignin compounds using molecular oxygen [7]. The catalyst was able to oxidize the benzyl alcoholic group in lignin molecules, and the phenolic –OH along with 5–5′, β-O-4 and phenylcoumaran groups remained intact. The nitrogen rich carbon nanomaterials act as good support for depositing metals on its surface, thereby increasing the efficiency of the catalyst. Wang *et al.* synthesized N-doped CNTs to support Ni nanoparticles on its surface and the resulting catalyst was used for the hydrogenolysis of lignin.[8] The doped nitrogen atoms provided anchoring sites for Ni metal, promoting its dispersion and forming stable Ni-N bonds on support. The electron transfer between Ni and N atoms facilitated hydrogen activation and thus proving useful for hydrogenolysis. The DFT calculations have revealed the role of doped nitrogen atoms in promoting electron rich states for enhanced hydrogen adsorption. Similarly, catalytic depolymerization and hydrodeoxygenation of Kraft lignin with a bimettalic Zn-O-Co deposited on nitrogen doped carbon nanotubes was performed in water.[9] The catalyst exhibited exceptional catalytic activity, achieving excellent lignin conversion with a small amount of residue and high bio-oil yield. This process yielded cyclohexanone derivatives and alkylated phenols as major products. Furthermore, Li et al. (2020) investigated the impact of nitrogen species and content on the catalytic activity for C–O bond cleavage in lignin using N-doped carbon nanosheets supported Ru-based catalysts. The catalyst, obtained by pyrolysis of glucosamine hydrochloride and melamine, featured highly-dispersed and small-sized Ru nanoparticles. This catalyst efficiently converted lignin, yielding 40.70% aromatic monomers—2.3 times higher than a commercial catalyst (Ru/C). The presence of pyridinic nitrogen in the support not only stabilized and dispersed Ru nanoparticles but also enhanced the proportions of Ru(0) through electronic interactions, contributing to improved catalytic activity. The study demonstrated the potential of nitrogen-rich carbon nanotubes in promoting lignin conversion to valuable aromatic monomers. Three metal based catalysts based on copper(II) bromide complexes were synthesized for the eco-friendly aerobic oxidation of veratryl alcohol in water. The reaction was performed at ambient conditions with copper catalyst and TEMPO in the presence of air as an oxidant. The presence of base was necessary for good yield of aldehyde and over oxidation took place in its absence.[10] However, no base is required for the aerobic oxidation of vanillyl alcohol in presence of a copper (II) based complexes and TEMPO, which mainly provided vanillin as an end product.[11]

Though metal based catalysts are capable to perform the oxidative/reductive cleavage of lignin, but metal free catalysts are promoted to achieve sustainability. S. S. Stahl and coworkers have performed the metal free oxidation of lignin using catalytic system consisting of 4-acetamido-2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) with HCl and HNO₃ [12]. The aerobic oxidation proceeds with chemoselective oxidation of secondary alcoholic groups in presence of unprotected –OH groups. The method was first tested on model molecules followed by studying the catalytic activity on real lignin.

In the last few decades metal free carbocatalysts attracted a lot of attention as substitutes to metal based heterogeneous catalysts for several reactions [13–16], including alkenes and alkanes dehydrogenation [17] and liquid phase dehydrogenation [18,19], oxidation [20–22] and hydrogenation [23]. In particular, metal free nitrogen functionalized carbons have been already reported to be effective catalyst for the oxidation of alcohols to carbonyl compounds and pyridinic nitrogen species were believed to be the active sites

for these reactions. For example, the group of Su et al. demonstrated that pyridine group was the main active sites in the aerobic benzyl alcohol oxidation by forming N-O group while graphitic nitrogen was less active.[24] The catalytic activity of graphitic nitrogen was attributed to the formation of sp2 $N-O_2$ transition state in the oxidation of alcohol.[24]

As it has been previously demonstrated, CNTs act as electrons "reservoirs" in oxidative dehydrogenation reactions of alkanes, promoting stabilization of intermediate radicals and guiding to the selective pathways for functionalized molecules instead of nonselective full oxidation.[25] Use of TEMPO, well-known spin trap, as shown above, underlines the importance of controlling radical pathways in contrast with conventional acid/base ones, since they might lead to both unique or undesirable products. Hence, special attention should be given to the role of spin chemistry in catalytic conversion of lignin and its by-products.

The complete analysis of literature reveals that metal based catalysts on carbon support, including the nitrogen rich CNTs, is the first choice of the researchers for doing hydrogenolysis and/or oxidation of lignin or its monomers. There are few reports of metal free catalytic systems for this particular conversion. Keeping in mind the importance of metal free catalytic systems for the oxidation of lignin (or related model molecules), we have used nitrogen containing carbon nanotubes for this purpose. The present work focused on the preparation of two different nitrogen functionalized carbon nanotubes NCNT700 and NCNT800, prepared by chemical vapour deposition method and tested in the benzyl and veratryl alcohols oxidation. The nature of the nitrogen groups was modulated by varying the reaction temperature (700°c and 800°C for NCNT700 and NCNT800, respectively). The functionalized carbo-catalysts were tested in the alcohol oxidation in presence of tert-butyl hydroperoxide (TBHP) as the oxidant. To understand the effect of the nitrogen species on the carbonaceous materials, the catalysts were thoroughly characterized through TEM and XPS in combination with computational techniques (DFT) to unveil the mechanism of the reaction.

2. Materials and Methods

2.1 Chemicals and Reagents

All the chemicals such as veratryl alcohol, xylene, tert-Butyl hydroperoxide (TBHP), benzaldehyde, benzoic acid, toluene and imidazole (99% purity) used for the preparation of NCNTs were purchased from Sigma Aldrich and were of laboratory reagent grade. They were used as such without any further purification.

2.2. Synthesis of catalyst

CNTs with a significant nitrogen content were synthesized using a catalytic chemical vapor deposition process. The method involved the use of Imidazole as the source for carbon and nitrogen over a Fe–Mo–Al catalyst. The catalytic CVD growth was achieved on a 10 mg of the catalyst dispersed evenly on a quartz boat, which was positioned at the center of a horizontal quartz tube. Subsequently, the furnace was heated by adopting this program, where the heating was started from 25 °C and gradually increasing to 700 °C at a heating rate of 10 °C min^{-1}. The heating was performed under ammonia flow at a rate of 0.4 mL min^{-1} and 700 °C temperature was maintained for a duration of 35 minutes, and then cooled to room temperature. The resulting nanotubes, enriched with nitrogen, were denoted as "NCNT700." Another catalyst "NCNT800" was prepared by adopting a similar procedure and keeping the temperature constant at 800 °C for 35 min. Commercial CNT (Pyrolytically Striped Carbon Nanofibers, PS-CNFs Applied Science) were used as reference.

2.3. Catalytic oxidation test

The catalytic oxidation tests were performed in a hydrothermal reactor. The veratryl alcohol (0.3 M) solution in xylene (10 mL) was mixed with tert-Butyl hydroperoxide (TBHP) (6 mMol, 70% in decane) followed by the addition of catalyst ensuring a 25:1 weight-to-weight ratio of alcohol to catalyst. The contents were stirred at 100°C for specified period of time mentioned in Table 1. After the desired reaction time, the reactor was cooled and the reaction mixture was analyzed by GC analysis, using a HP 7820A gas chromatograph equipped with a capillary column HP-5 30m x 0.32mm, 0.25 µm Film, by Agilent Technologies. Quantitative analyses by an external standard method (n-octanol) were carried out. Identification of the products was performed using a Thermo Scientific Trace ISQ QD Single Quadrupole GC-MS equipped with a capillary column HP-5 30 m x 0.32 mm, 0.25 x m Film, by Agilent Technologies. Recycling tests were carried out under the same experimental conditions. The catalyst was filtered and recycled in the subsequent run after filtration without any further treatment.

2.4. Characterization of the catalysts

Transmission electron microscopy (TEM), High-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) were performed on a FEI Tecnai G2 F20 microscope operated at 200 kV. Specimens were prepared by ultrasonically suspending the sample in ethanol and depositing a drop of the suspension onto a TEM holey carbon grid. The X-ray photoelectron spectroscopy (XPS) measurements carried out using an ultra-high vacuum ESCALAB 250 set-up equipped with a monochromatic Al Kα X-ray source (1486.6 eV; anode operating at 15 kV and 20 mA). The XPS spectra were fitted using mixed Gaussian–Lorentzian component profiles after subtraction of a Shirley background using XPSPEAK41 software. The specific surface area was measured by the BET method using nitrogen adsorption isotherms obtained on a Micrometrics ASAP 2020 system. Metal content was verified by atomic absorption spectroscopy (AAS) using a Perkin Elmer 3100.

2.5. Quantum-chemical Calculations

Quantum-chemical calculations were performed within the framework of density-functional theory (DFT), employing the three-parameter hybrid functional by Becke Lee-Yang-Parr (B3LYP) [26] together with Ahlrichs' double-zeta split-valence basis set augmented by Coulomb fitting (def2-SVP) [27]. The unrestricted Kohn-Sham (UKS) formalism was employed for open-shell states. Molecular geometries were optimized for various relevant multiplicities to gradients of 5•10-6 Eh/bohr or less. The ORCA ab initio, DFT and semiempirical SCF-MO package [28] was used for all calculations. Resolution of identity with "chain of spheres exchange" (RIJCOSX) algorithm for the calculation of the exchange terms was applied [29].

3. Results

The first task was to prepare the metal free catalyst rich in nitrogen content. The NCNTs were prepared with variable nitrogen content with chemical vapor deposition method (See experimental details). The two metal free catalysts NCNT700 and NCNT800 were prepared at two different temperatures. The difference in temperature ensured variable amount of nitrogen incorporated into the carbon matrix. Once the catalysts were prepared, the morphology of NCNT 700 and NCNT800 was observed by HRTEM analysis (Figure 1). Both the Nitrogen rich carbon nanotubes exhibited inverted cup shape structure, with ~20 nm average diameter. The ends of the tubes appear to be open, whereas inner portions appear to be blocked by a carbon wall. The structure appears to be beneficial because some impurities, which might have been trapped inside the NCNT, can remain inaccessible during the catalytic test runs. The external metal impurities in both the

NCNTs were removed after their treatment with concentrated HCl followed by subsequent rinsing with demineralised water until the washings becomes pH neutral.
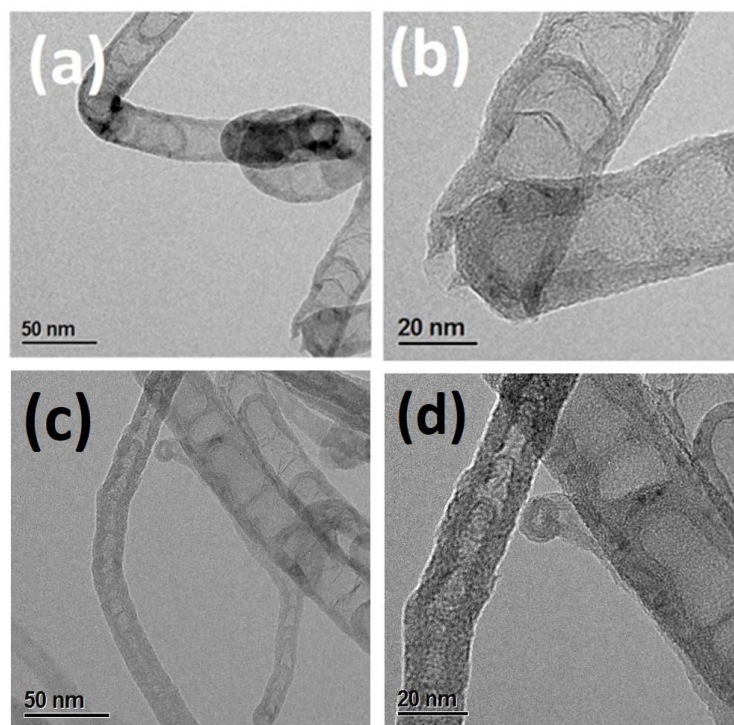

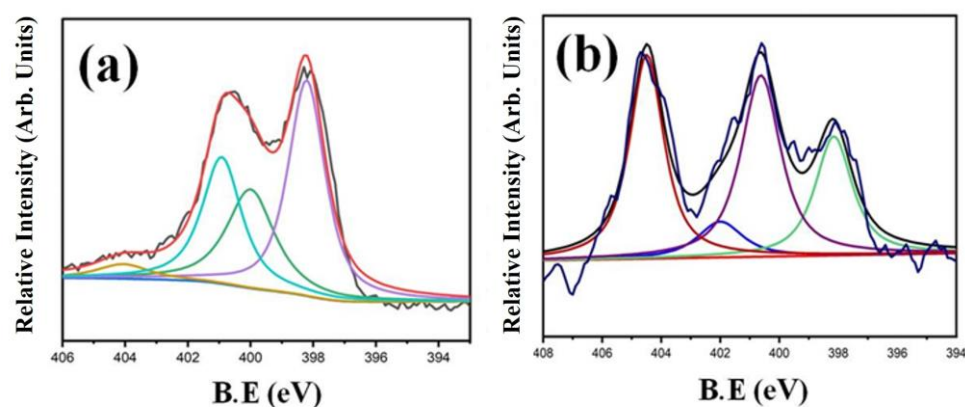**Figure 1.** (a) and (b) HRTEM images of NCNT700 and (c) and (d) HRTEM images of NCNT800

Figure 2. XPS analyses of (a) NCNT700 and (b) NCNT800

X-ray photoelectron spectroscopy (XPS) was used to determine the surface functional groups and the analysis revealed the presence of nitrogen, carbon and oxygen on the catalyst surface. The HRTEM images did not show any metal particles on the surface therefore, atomic absorption spectroscopy (AAS) was used to determine the metal content. It displayed the presence of 0.1% of Fe, but as the structure is inverted cup like, therefore this much impurity might have remained trapped inside the catalyst. The probable nitrogen containing functional groups were determined by the deconvolution of the N 1s spectrum. The elemental percentage and the percentage of individual functional group is tabulated in Table 1. The nitrogen content determined was higher on NCNT700, whereas NCNT800 showed lower N content. It was 13.7 atom% for NCNT700 and 2.3 Atom% for NCNT800.   The nitrogen peak was further deconvoluted into four sub-peaks. The

pyridinic nitrogen peak at 398.1 eV, pyrrolic nitrogen peak at 400.0 eV, quaternary nitro- 213
gen peak at 400.9 eV and pyridinic N-oxide peak at 404.1 eV were deconvoluted. All the 214
nitrogen functional groups were present on the catalyst surface with a maximum concen- 215
tration for pyridinic groups in NCT700 (45.8%) followed by NCNT800 (22.6%). 216

Table 1. Composition of different elements on the surface of catalysts. 217

Catalyst	Composition (%)			N1s			
	C	O	N				
CNT700	82.8	3.5	13.7	398.1	400.0	400.9	404.4
contribution (%)				*45.8*	*21.2*	*28.6*	*4.3*
CNT800	94.3	3.3	2.3	397.2	399.5	400.9	403.3
contribution (%)				*22.6*	*32.0*	*8.8*	*36.5*
CNTcomm	95.7	4.3	-	-	-	-	-
contribution (%)							

Once the catalysts were prepared and characterized, they were used for the oxidation of 218
aromatic alcohol (benzyl alcohol) with tert-butyl hydrogen peroxide (TBHP). The reaction 219
was performed by taking a ratio of 25:1 (alcohol: catalyst wt/wt) at 100 °C and the results 220
are tabulated in Table 2. Blanck experiments performed in absence of the catalyst or the 221
oxidant did not show any significant activity. The reaction provided benzaldehyde as 222
main product by all the NCNTs with a minor content of benzoic acid. Hence, nitrogen rich 223
carbon nanotubes were selectively providing aldehyde instead of carboxylic acid (usual 224
end product in most of the oxidation reactions). The reaction almost did not proceed with 225
CNTs without any nitrogen content in them. Surprisingly, two catalysts displayed the for- 226
mation of toluene in the reaction mixture. It was ascertained that no toluene was used in 227
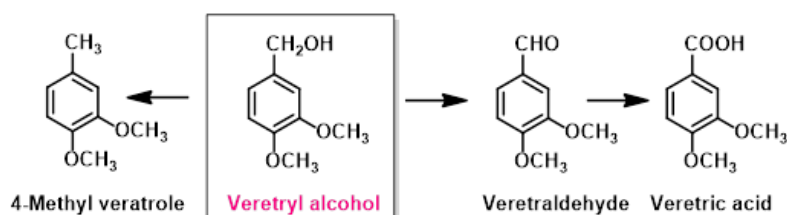the reaction; therefore, it is generated in due course of the reaction. 228

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Table 2. Catalytic activity of nitrogen rich carbon nanotubes and commercial CNTs for the benzyl 230
alcohol oxidation 231

Catalyst[a]	Activity[b]	Conversion (after 6h)	Selectivity		
			Benzalde-hyde	Benzoic acid	Toluene
N-CNTs 700	186	>99	76	1	21
N-CNTs 800	54	59	67	1	28
CNTs comm	5	8	99	-	-

[a] Reaction conditions: alcohol 0.3M, TBHP 6 mMol (TBHP 70% in decane), alcohol/catalyst 25/1 232
wt/wt, 100°C, 1250 rpm. 233
[b] Converted mmolgly gcat^{-1} h^{-1} 234

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After the optimization of benzaldehyde oxidation, the catalysts were tested for the metal 236
free oxidation of a model lignin molecule veratryl alcohol using TBHP as an oxidant. Vera- 237
tryl alcohol is an aromatic compound containing ether and primary alcoholic group. It has 238
two methoxy and one alcoholic group that represents alcohol and ether linkage present in 239
the lignin. Its oxidation can generate three compounds that are shown in Scheme 1. The 240
catalytic tests were performed by the optimized method and the results are shown in Table 241
3. 242

243

Scheme 1. Oxidation of veratryl alcohol to different products (The reaction also involved formation of 4-methyl veratrole)

Table 3. Catalytic activity of nitrogen rich carbon nanotubes and commercial CNTs for the veratryl alcohol oxidation

Catalyst[a]	Activity[b]	Conversion (after 6h)	Selectivity		
			Veretralde-hyde	Veretric acid	4-Methyl veratrol
N-CNTs 700	104	95	75	1	23
NCNTs 800	37	42	63	2	32
CNTs comm	3	3	99		

[a] Reaction conditions: alcohol 0.3M, TBHP 6 mMol (TBHP 70% in decane), alcohol/catalyst 25/1 wt/wt, 100°C, 1250 rpm.
[b] Converted mmolgly gcat^{-1} h^{-1}

The stability of N-CNTs 700 was evaluated in the veratryl alcohol oxidation. The catalyst was found to exhibit almost the same conversion and selectivity after 8 cycles and the results are summarized in figure 3.
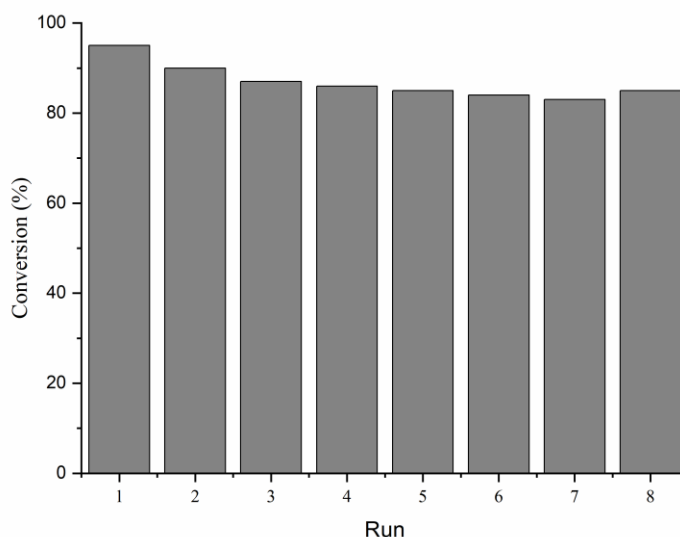

Figure 3. Stability tests of NCNT700 in the veratryl alcohol oxidation

4. Discussion

The formation of toluene under oxidative conditions is quite unique for the base free carbo-catalysts, therefore the mechanism of veratryl alcohol oxidation was investigated by DFT calculations. The analysis was performed by choosing benzyl alcohol (BA) as model compound in comparison to veratryl alcohol due to its easiness for running the calculations and the results are shown in Scheme 2. The conversion of BA into

benzaldehyde is a facile process and shows easiness to proceed in forward direction. The
formation of toluene in this oxidation reaction may be explained by the self-oxidation and
reduction reaction of BA [30]. While investigating the toluene formation by dispropor-
tionation reaction the barriers were found to be very high and this pathway did not appear
to be feasible. Therefore, it appears that there is no direct pathway from BA to toluene.
Hence second option for the toluene formation was considered. It was observed that tol-
uene was formed through formation of intermediate $PhCH_2^*$ that involves water for-
mation. Formation of H_2 is kinetically preferable (although another pathway leads directly
to $PhCH_2^* + 2 H_2O$). The results are shown in Scheme 2.
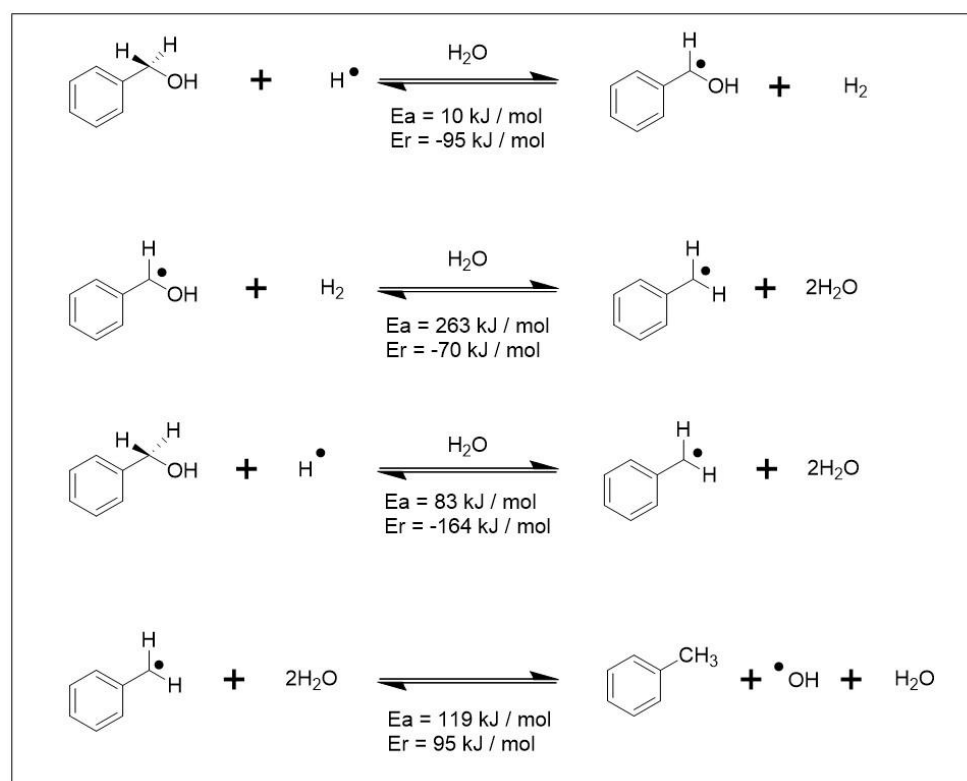
Scheme 2. Plausible pathway leading to formation of toluene in the reaction BA with TBHP over
NCNT. The homolytic cleavage of -OH bond by free radicals or the homolytic cleavage of C-H bond
during oxidation reaction can generate H* in the reaction. These radicals can be stabilized on catalyst
surface during the reaction. During DFT analysis stabilization from water molecules in the reaction
mixture was considered (H_3O^*) for obtaining the reported results. The *OH generated in the end
can be reused for generating the peroxide reagent.

The reaction involves formation of radical intermediates, which are preferred in compari-
son to their ionic or charged analogues. The hydrogen radical that is involved in the reac-
tion may come during the oxidation process of BA. The radical species may also be formed
in presence of a radical initiator TBHP. Once this radical $PhCH_2^*$ is formed, it may be sta-
bilized on the catalyst surface along with other radical species. Recently, the formation of
radicals is also explained during the self-oxidation and reduction reaction of 5-HMF.[31]
The reaction mechanism of 5-HMF reduction with HI involves a substitution-reduction
process.[31] Initially, the -OH group is replaced by iodide, which is further reduced to form
an alkane. During this process, hydrogen iodide is used and iodine is generated simulta-
neously. The reaction also follows the radical pathway. Initially, iodine radicals are formed
from iodine, which then attack the alcoholic group. This attack leads to the formation of a
hydrogen radical and other reaction intermediates. Benzyl alcohol was used as a model
substrate instead of unstable 5-hydroxymethylfurfural in this work, and it supports the
claim for the evolution of H*. Another work by J.A. Puértolas has demonstrated that Multi-

walled carbon nanotubes (MWCNTS) have the tendency to combine with free radicals. MWCNTs were incorporated into ultrahigh molecular weight polyethylene by a ball milling process. MWCNTs were found to exhibit the radical scavenging behavior. The electron spin resonance detection confirmed the radical scavenging characteristics of MWCNTs in response to radiation-induced radicals.[32] As the concentration of nanotubes increased, there was a significant reduction in the quantity of radicals generated during the gamma irradiation process. This observation validates the ability of MWCNTs to effectively scavenge radicals, demonstrating a concentration-dependent impact on the radical generation associated with gamma irradiation. Therefore, it is highly likely that the radicals formed in the reaction may be stabilized on catalyst's surface. Moreover, Xiong et al, demonstrated that N-doped carbon nanotubes containing are efficient in the nitrobenzene hydrogenation [33]. In particular, they showed that pyrrolic groups are the main active center by chemisorption of hydrogen during the reaction. Therefore, we attribute the formation of toluene to the present of pyrrolic groups on NCNT catalysts, chemisorbing the H-specie generated during the dehydrogenation of benzyl alcohol.

5. Future Perspective

The development of metal free catalytic system based on nanocarbon materials especially the NCNTs is very promising for sustainable catalytic systems. The metal free nature of this catalytic system aligns perfectly with green chemistry principles and offers a potential avenue for environmentally friendly lignin valorization. The use of toxic metals in the designing of catalysts can be minimized and the fear of being their leaching into the environment can be overpowered. Future perspective further includes better control on surface functional groups for enhanced yields and its capability to work effectively on lignin molecule. Moreover, the bulk reactions need to be optimized for increasing the industrial applicability of this catalysts or related NCNTs. The development of such catalytic systems can avoid waste production (especially the one with toxic metals). However, more insights are required to unravel the true behavior of this catalyst during the conversion. The radical formation needs to be ascertained in near future for making them viable in near future.

6. Conclusions

To conclude, nitrogen rich carbon nanotubes NCNT700 and NCNT800 were prepared as metal free catalyst for the oxidation of benzyl alcohol and veratryl alcohol. Nitrogen rich sites such as pyridinic or pyrrolic sites in the carbon matrix are targeted to achieve the desirable conversion. The concentration of these active sites leads to the different selectivity of the product. NCNT700 was found to be the best catalyst in term of activity (186 h^{-1} and 104 h^{-1} for benzyl and veratryl alcohols, respectively) compared to NCT800 (54 h^{-1} and 37 h^{-1} for benzyl and veratryl alcohols, respectively, whereas the non-functionalized carbon nanotubes showed a negligible activity for both alcohols. In term of selectivity the aldehyde is the main product in all cases. NCN700 showed a selectivity of 76% to benzaldehyde and 75% to veratraldehyde, whereas NCN800 a selectivity of 67% to benzaldehyde and 63% to veratraldehyde. Surprisingly, in addition to the oxidized products, both catalysts also promoted the formation of reduced product, such as toluene 4-methyl veratrol. In particular NCNT 800, which present a higher amount of pyrrolic groups, showed a selectivity of 28% and 32% to toluene and 4-methyl veratrol, respectively, whereas NCNT700 a selectivity of 21% and 23% to toluene and 4-methyl veratrol, respectively. These products are unlikely to be formed by a disproportionation reaction and is probably formed by the transfer of H* trapped on the pyrrolic groups present on the catalyst surface. The catalyst can be found to be effective for oxidation of lignin derived alcohols into aldehydes and aromatic hydrocarbons, also showing a good stability upon deactivation during recycling tests.

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