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Metal Free Oxidation of Glycerol over Nitrogen Containing Carbon Nanotubes

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Abstract: Nitrogen rich carbon nanotubes have been used as a metal free catalyst for the conversion of glycerol into dihydroxyacetone using tert-Butyl hydroperoxide (TBHP) as an oxidant. Pyridine nitrogen embedded in carbon matrix is identified as an active site for the reaction. Computational studies have demonstrated that oxidation of pyridine site to pyridine oxime followed by hydrogen abstraction from secondary alcohol is most probably responsible for the oxidation process.

Sustainable development requires use of biorenewable feedstocks to produce clean fuels and commodity chemicals. In this respect glycerol is of significant interest, which is available widely as a primary by-product during biodiesel production. Numerous industrially valuable products such as hydroxyacetone, glyceric acid, tartronic acid, oxalic or formic acid and glyceraldehyde can be synthesized by the selective oxidation of glycerol by heterogeneous catalysts^[1] (Figure S1). The oxidation of a primary alcohol group in glycerol leads to glyceric acid formation and, subsequently to tartronic acid. Similarly, the oxidation of a secondary hydroxyl group affords dihydroxyacetone, while the oxidation of both primary and secondary alcohol groups gave ketomalonic acid. One of the most important among these is dihydroxyacetone (DHA), a specialty chemical used mainly as a sunless tanning agent in the cosmetics industry. Also, DHA is an effective nutritional supplement combined with pyruvate that helps in fat burn.

Recently, Y Nakagawa and K Tomishige^[2] have performed the oxidation of glycerol to dihydroxyacetone over Pd–Ag catalysts, and the mechanism was discussed in detail. It was suggested that terminal OH group of glycerol is adsorbed on the silver site and the neighboring secondary OH group is attacked by the oxygen species dissociatively adsorbed on the Palladium site. Similarly, gold nanoparticles supported on activated carbon^[3] were used for the glycerol oxidation using H₂O₂ as oxidant. In this reaction glycerate and tartronate were produced in higher amount with low Au content on catalyst surface,

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whereas larger Au nanoparticles contributed to higher glycolate production. PtSb alloy nanoparticles supported on multiwall carbon nanotubes^[4] afforded selective oxidation of glycerol to dihydroxyacetone (DHA). It was found that DHA is relatively stable over the PtSb alloy nanoparticles, which also suppressed the carbon-carbon bond cleavage. Recently, Pd–Ag/C^[5] was also used for glycerol oxidation with molecular oxygen as an oxidant under neutral conditions. The catalyst exhibited higher activity and selectivity to dihydroxyacetone in comparison to Pd/C. We recently showed^[6] that by doping AuPd/AC catalyst with a small amount of Bi, it is possible to promote the formation of DHA with final selectivity of 65%.

Currently, developing a novel, highly selective catalysts for glycerol transformation to a specific product remains a key challenge due to the presence of three reactive hydroxyl groups. Though, metal based catalysts are reported in literature for attaining good selectivity, but the same are not promoted in order to attain sustainability and hence non-metal analogues should be explored^[7]. Recently, Metal free nitrogen doped carbon materials^[8] have been used for the conversion of alcohols to carbonyl compounds and decomposition of phenols ^[9]. Also, nitrogen doped annealed nanodiamonds were used for the oxidation of benzylic alcohols to aldehydes, and pyridinic nitrogen species were believed to be involved during the conversion^[10]. Metal free nitrogen modified carbon materials are also useful for the oxidation of non-alcoholic substrates such as cyclohexane^[11]. But there seems to be no report for the use of metal free catalyst for the oxidation of polyalcohols such as glycerol and, particularly, mechanistic studies explaining the selectivity issues are scarce (one should note that non-selective degradation only is studied in ^[12]). Therefore, we describe here NCNTs, prepared by chemical vapor deposition (CVD) method, as metal free catalyst for the selective oxidation of glycerol to DHA. To the best of our knowledge no metal free catalyst is reported for the oxidation of glycerol.

CNTs with high N content were synthesized by catalytic chemical vapour deposition (CVD) method over Fe-Mo-Al catalyst synthesized through hydrothermal process and imidazole as carbon/nitrogen feedstocks. In the catalytic CVD growth, 10mg catalysts were uniformly distributed on a quartz boat, which was placed at the center of a horizontal quartz tube with 50 mm inner diameter. The furnace was then thermally treated from 25 °C to 700 °C at a heating rate of 10 K min⁻¹ and kept constant at 700 °C for 35 min under 10% NH₃ atmosphere at a flow rate of 100 mL/min. The obtained N-doped CNTs were flagged as NCNT700. Similarly, NCNTs800 were prepared but at a temperature of 800°C. The morphology of the catalysts was observed by HRTEM analysis (Figure 1 and Figure S3). From the TEM images it was clear that nanotubes show an inverted cup pile structure, with an average diameter of ~20 nm and surface area of 105 m² g⁻¹. In this structure the ends appear to be open but inside portion seems very close blocked by the

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carbon wall formed during the growth of carbon nanotube. This structure seems interesting as few impurities, that might have been trapped inside the NCNT will remain inaccessible during the reaction. In order to exclude the involvement of any external metal impurity, which might be trapped during their preparation, the NCNTs were thoroughly stirred with hydrochloric acid and then washed with demineralized water till all washings were neutral.



Figure 1. HRTEM images of NCNT700 showing inverted cup like structure that are stacked above one another.

The surface functional groups and the metal contents were explored via X-ray Photoelectron spectroscopy (XPS). The survey revealed that surface is mainly rich in carbon, nitrogen and oxygen and no other prominent peak was observed (Figure S2). This indicates absence of metals on the surface. However, in both cases, atomic absorption spectroscopy (AAS) showed the presence of 0.1% of Fe that may be trapped inside the close cup like structure. The N 1s spectrum was scanned and deconvoluted for the possible nitrogen functionalities (Figure 2) and percentage elemental contents are summarized in Table-1. NCNTs700 showed a higher amount of nitrogen on the surface compared to NCNTs800 (atomic % of 13.7 and 2.3, respectively). By comparing the overview of different nitrogen functional groups present on carbon surface,^[13] they can be categorized into following types, pyridinic-N (397.9 ± 0.3 eV), pyrrolic-N/pyridone-N (400.3 ± 0.3 eV), quaternary-N/pyridinic-N-H (401.3 \pm 0.3 eV) and pyridinic-N⁺-O⁻ (402-405 eV). All these four were found to be present on the NCNT surface with maximum concentration of pyridinic groups with a percentage of 45.8% and 22.6% for NCNT700 and NCNT800, respectively .

The catalysts were evaluated in the selective glycerol oxidation using TBHP as oxidant (Table 2-S1). For comparison the activity and selectivity of commercial CNTs (CNTs_{comm}) and the nitrogen functionalized commercial CNTs (NCNTs_{comm}), were also reported (Table 2). NCNTs_{comm} were prepared modifying the procedure reported in Arrigo *et al.* ^[14] and the surface

properties are summarized in Table 1. AAS revealed the presence of 0.3% and 0.1% of Fe for $CNTs_{comm}$ and $NCNTs_{comm}$, respectively, whereas XPS analysis excluded the presence of metals on the surface.

Non functionalized CNTs were almost inactive whereas nitrogen functionalized CNTs reached a conversion of 8.3%, 15.3% and 36.5% after 6h, for NCNTs800, NCNTs_{comm} and NCNTs700 respectively (Table 1). The absence of activity of CNTs_{comm} confirmed that Fe impurities, encapsulated inside CNTs, are not accessible to the reactant.

| | | A | | | | | | | | |
|--|---------------|-----------------------------------|-------|-------|-------|--|--|--|--|--|
| Table 1: Surface elemental composition of different nitrogen functional groups derived by the deconvolution of N-1s spectrum of NCNT-700. | | | | | | | | | | |
| Catalyst | Atomic % | N1s Peak position and percentange | | | | | | | | |
| | | (%) | | | | | | | | |
| | C-O-N | Peak1 | Peak2 | Peak3 | Peak4 | | | | | |
| NCNT700 | 82.8-3.5-13.7 | 398.1 | 400.0 | 400.9 | 404.4 | | | | | |
| Percentage (%) | | 45.8 | 21.2 | 28.6 | 4.3 | | | | | |
| NCNT800 | 94.3-3.3-2.3 | 397.2 | 399.5 | 400.9 | 403.3 | | | | | |
| Percentage (%) | | 22.6 | 32.0 | 8.8 | 36.5 | | | | | |
| CNTs _{comm} | 95.7-4.2-0.1 | - | - | - | - | | | | | |
| Percentage (%) | | | | | | | | | | |
| N-CNTs _{comm} | 92.0-3.8-3.8 | 398.3 | 400.2 | 401.2 | 404.6 | | | | | |
| Percentage (%) | | 49.3 | 44.1 | 3.5 | 3.1 | | | | | |





Figure 2: XP-Spectra of (A) NCNT700 and (B) NCNT800

Correlating the activity with the surface properties showed that the most active catalyst is NCNTs700, which contains the highest amount of pyridinic groups (13.4%) compared to NCNTs_{comm} (3.8%), NCNTs 800 (1.9%) and CNTs (0%) (Table 1). On the contrary the amount of oxygen species is almost the same for both NCNT700 and NCNT800 (3.3-3.5%) (Table 1). It was already reported that the presence of graphitic nitrogen

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enhances the catalytic activity in alcohol oxidation modifying the electronic structure of the adjacent carbon atoms^[15]. We also recently showed that the activity of nitrogen functionalized carbon in the alcohol oxidation is closely correlated to pyridinic nitrogen^[9]. To confirm the same trend in glycerol oxidation, the activity (converted $mmol_{gly} g_{cat}^{-1} h^{-1}$) was correlated to the amount of the pyridinic species present on the surface (Figure 3). The linear correlation between activity and pyridinic groups content confirms the role of these latter ones in the activation of the hydroxyl group in presence of TBHP. On the contrary there was no direct correlation between the activity and the other nitrogen species (Figure S4). All the catalysts showed dihydroxyacetone, obtained from the oxidation of the secondary alcoholic group, as main product with a selectivity of 85.4%, 84.3% and 73.8% for NCNTs_{comm}, NCNTs700 and NCNTs800, respectively (Table 2). Glyceric acid, derived from the oxidation of the primary alcohol was present only as main by-product using NCTs800, whereas using NCNTs700 and NCNTs_{comm} only traces were observed (Table 2). To assess the general use of nitrogen functionalized CNTs to oxidize the secondary alcoholic group in presence of TBHP, different polyols were tested (Table S2). Preliminary study using 1,2 propanediol, 1,4 pentanediol confirmed the peculiar ability of Pyridine rich NCNTs to oxidize secondary alcohol.

| Table 2. Glycerol oxidation using tert-Butyl hydroperoxide (TBHP) ^a | | | | | | | | | | |
|--|-----------------------|---------------------------|-------------------|-----------------------------------|----------------------------|------------|--|--|--|--|
| Catalyst | Activity ^b | Conver sion after 6 | Glyceri c acid | Selectiv Dihydroxy- acetone | ity Hydroxy -piruvic | For mic | | | | |
| | | h | | | acid | acid | | | | |
| CNTs _{comm} | 0.01 | 0.5 | - | - | - | - | | | | |
| NCNTs _{comm} | 3.61 | 15.3 | 0.5 | 85.4 | 0.3 | 5.8 | | | | |
| NCNTs800 | 2.06 | 8.3 | 14.2 | 73.8 | - | 6.9 | | | | |
| NCNTs700 | 13.39 | 36.5 | 0.2 | 84.3 | 1.7 | 6.5 | | | | |
| ^a Reaction | conditions: | Glycerol | 3 mmol. | TBHP 6 mm | ol (TBHP 7 | 0% in | | | | |

Reaction conditions: Glycerol 3 mmol, TBHP 6 mmol (TBHP 70% in water), glycerol/catalyst 5/1 wt/wt, 60°C, 1250 rpm
 ^b converted mmol_{gly} g_{cat}⁻¹ h⁻¹



Figure 3. Correlation between activity and pyridinic N1/C atomic ratio.

In order to investigate the preferential formation of DHA by NCNT-700, quantum-chemical calculations were finally performed to verify the proposed pathway and calculate the reaction barriers. Computational process with glycerol having three OH bonds would be tedious and time consuming, therefore, in order to make the process simple, propane-1,2,-diol was chosen as a model molecule to study the reactivity of primary and secondary OH-groups. Moreover, the impact of sigmaneighbours on electronic properties is minor, therefore

calculated energies will have little impact on shifting from propane-1,2-diol to glycerol. Phenanthridine (pyrene) - a polyaromatic hydrocarbon molecule doped with N atom in pyridinic position (NdP) was chosen as a model of N-doped active carbon. Nitroxyl radical and its oxidised forms are known to perform the oxidation of alcohols^[16]. The similar phenomenon may be observed on the surface of N-rich CNTs. In presence of oxidising groups active centres analogous to oxidised nitroxyl radicals may be generated on the catalyst surface. Hence, it was postulated that N-O group formed in course of oxidation by TBHP is present at the edge of the cluster. Activity of NdP with N-O group was compared to that of NdP with additional C=O quinone groups in different positions near N-O at the edge (pONdP and mONdP). It was demonstrated that the reaction passes in two stages: (i) abstraction of secondary C-H, (ii) abstraction of alcoholic proton. Product of the first stage is a Ccentered radical, which spontaneously attaches to the surface of carbon cluster. The second stage is limiting. These two stages are probably followed by abstraction of H₂O formed from N-O and should be catalyzed by Brønsted acids. It should be noted that non-oxidized NdP demonstrates much higher barrier for the first stage of reaction (~204 kJ/mol) than oxidized ones, and, thus, can be considered as non-reactive.



Figure 4. Schematic representation of the conversion of glycerol into DHA involving N-rich pyridine sites. Quantum-chemically calculated reaction barriers in kJ/mol for propane-1,2,-diol are given in paranthesis. Reaction barrier for the oxidation of primary alcoholic group is given at the bottom for comparison.

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Edge-oxidized NdP clusters contain two C=O groups in 3,5- and 5,6-positions, respectively. It was demonstrated that the latter one (pONdP) is by 27.6 kJ/mol less stable than the former (mONdP) due to different stabilization of quinones, caused by different alteration of CC bonds. Moreover, reaction with mONdP is much more exothermic and exhibits lower barrier of the second stage (68 vs. 122 kJ/mol). The product of the first stage is a surface ether which is formed upon spontaneous addition of C-centered radical to a C=O quinone, analogously to previous results of oxidative dehydrogenation of hydrocarbons on edge-oxidized carbon nanotubes (CNTs)^[17]. Quinone groups themselves are less reactive in H abstraction from ternary carbon atom (more than twice higher barrier, less exothermic), so N-O groups can be undoubtedly considered as the only active center for oxidation of glycerol. Abstraction of H from secondary carbon atom of propane-1,2,-diol by N-O group of mONdP led to spontaneous conversion of the substrate into hydroxyaldehyde. The barrier of the reaction is ~20% higher than that of the ternary H abstraction, and the reaction is less exothermic. Therefore, guantum-chemical calculations suggest that N-O groups formed by edge oxidation of N-doped active carbon by TBHP are active sites of glycerol-to-DHA conversion, with quinone groups playing important role in the mechanism. The reaction has a radical nature, and oxidation of secondary OH-group is preferred over the primary ones.

The resistance against deactivation was investigated performing stability tests on NCNTs700, the catalyst presenting the highest activity. Recycling experiments were carried out by filtering and using the catalyst in the next run without any further purification. The catalyst exhibits good stability for eight consecutive runs in term of activity and selectivity (Table 5). TEM of the used catalyst did not evidence modifications of the morphology (Figure S5).



Figure 5. Stability tests on NCNTs700. Reaction conditions: Glycerol 3 mmol, TBHP 6 mmol (TBHP 70% in water), glycerol/catalyst 5/1 wt/wt, 60°C, Reaction time 6h.

In summary, nitrogen rich two CNTs were prepared by chemical vapor phase deposition method and used as a metal free catalyst for the glycerol oxidation using TBHP as an oxidant. TEM characterization reveals that prepared catalyst has closed stacked cup like structure with no trace of metal on its surface. The catalytic activity of the NCNT was assigned to the pyridinic

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groups present on its surface that are most probably converted into N-O groups formed by edge oxidation of N-doped active carbon by TBHP. The catalyst exhibited good recycling ability, and provides an environmentally-friendly way for the conversion of glycerol to dihydroxyacetone. Moreover, it demonstrates a proof of concept for the development of metal free carbon based catalyst for biomass derived glycerol.

Experimental Section

Glycerol oxidation: Reactions were carried out in using a stainless steel reactor (50 mL capacity), equipped with a glass inlet, heater, mechanical stirrer, gas supply system and thermometer.

Glycerol 0.3 M, and the catalyst (substrate/ catalyst = 5 wt/wt) were mixed in distilled water (total volume 20 ml) with 6 mmol of TBHP. Once the desired temperature was reached (60°C), reaction was initiated by stirring. Samples were removed periodically and analyzed by high-performance liquid chromatography (HPLC) using a column (Alltech OA- 10308, 300 mm_7.8 mm) with UV and refractive index (RI) detection to analyze the mixture of the samples. Aqueous H_3PO_4 solution (0.1 wt%) was used as the eluent. Products were identified by comparison with the original samples.

Recycling test: Each run was carried out under the following reaction conditions: glycerol 0.3 M, and the catalyst (substrate/ catalyst = 5 wt/wt) were mixed in distilled water (total volume 20 ml) with 6 mmol of TBHP. The catalyst was recycled in the subsequent run after filtration without any further treatment Details of other experimental procedures can be found in the Supporting Information.

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Keywords: Metal free oxidation• Glycerol • NCNT • Biomass Conversion • Carbon Catalysis

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OH Glycerol Dihydroxyac (DHA) **ICN** Green (Metal and Organic Solvent Free) Oxidation of **Glycerol to DHA on NCNTs**

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Metal Free Oxidation of Glycerol over Nitrogen Containing Carbon Nanotubes

A green process for the oxidation of glycerol to value added dihydroxyacetone is developed on nitrogen rich carbon nanotubes as a metal free catalyst using tert-butyl hydroperoxide (TBHP) as an oxidant. Computational studies combined with experimental results have revealed the role of pyridinic sites for the conversion process. The results will open up a gateway for designing a metal free catalyst for the "Biomass Derived Glycerol".