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Oxidative coupling of aniline and desulfurization over nitrogen rich mesoporous carbon[†]

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Tungsten loaded mesoporous nitrogen rich carbon (WO_xMCN_x) materials were synthesized using SBA-15 as a hard template. With these new multifunctional materials, we performed a one-pot oxidative coupling of aniline to azo-benzene followed by desulfurization of dibenzothiophene (DBT) to dibenzothiophene sulfone (DBTSO). It was observed that the nature of the support for the catalyst has a strong influence on the activity of the WO_x nanoparticle. Whilst WO_x on MCN_x proved to be a very active and selective catalyst for the formation of azo-benzene *via* oxidation of aniline as well as dibenzothiophene sulfone from dibenzothiophene, WO_x on activated carbon or SBA-15 did not show comparable activity. These multifunctional hybrid catalysts retain their structural framework even after the reaction, and they were recovered easily from the reaction mixture through filtration and reused several times without a significant degradation in activity. Moreover, there was no contribution from leached active species in the activity and conversion was possible only in the presence of the multifunctional catalyst.

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Introduction

Synthesis of important oxygen containing chemicals and intermediates via ecological and economical route is one of the key scientific challenges in the current industrial scenario. Most of the bulk chemicals and fine speciality chemicals are synthesised by using homogenous catalysts and traditional processes.¹ These established processes suffer from the use of hazardous reagents in stoichiometric amounts and generate a large amount of waste for the environment. Heterogeneous catalysis offers a distinct advantage over homogeneous catalysis for facile catalyst separation and recycling, which further meets the requirement of green and sustainable chemistry.² Many efforts have been made in the last few decades to use green oxidants, such as O_2 and H_2O_2 , along with heterogeneous catalysts to convert conventional processes to environmentally friendly technologies. Nevertheless, very limited success has been achieved to date due to the poor efficiency and stability of heterogeneous catalyst systems in the reaction medium in the presence of various oxidants.³ Therefore, there is ample scope to develop an efficient and stable heterogeneous catalyst system for industrial applications. Mesoporous carbon materials are important potential oxygen reduction reaction catalysts as they are environmentally sustainable, cost-effective, and highly durable, and owing to their unique structural properties, such as high surface area, tunable pore sizes, chemical and mechanical stability.⁴ A variety of carbon materials, *e.g.* carbon nanotubes, activated carbon, have been prepared and have been successfully used in heterogeneous catalysis.⁵ Recently, nitrogen functionalized carbon materials have been shown to have high catalytic bifunctional activity in photocatalysis, oxygen reduction reaction, and organic transformations, and as semiconductors.⁶ It has also been reported that carbon nitride materials are promising metal free catalysts and catalyst supports in different hydrogenation and oxidation reactions.⁷

The basicity of the material was achieved by pyridine type N, which resides within the CN_x framework.⁸ For low temperature catalytic applications, the acid–base property of the material needs to be tuned further by the addition of transition metals like tungstate to the CN_x framework. In this work, our idea was to develop a heterogeneous carbon based tungstate catalyst that can display high activity for a variety of oxidant process, like epoxidation of alkenes, alcohol oxidation, oxidative coupling of amines and oxidative desulfurization. An example can be found in our previous report,⁹ where we have shown acid–base cooperative catalysis using WO_x embalmed CN_x material.

Selective formation of aromatic azo compounds through oxidative coupling of aniline is an industrially important



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process because aromatic azo compounds are high value chemicals that are widely used in industry as dyes, pigments, food additive and drugs.¹⁰ Previously, a variety of oxidizing agents, like MnO,¹¹ Hg (OAc)₂¹² BaMnO4 (ref. 13) and peracetic acid,¹⁴ have been used for aryl amine oxidation. Nevertheless, this process generates a large amount of inorganic waste. Nowadays, different metal based (Pd,15 $CuCr_2O_{31}^{16}$ Ag/WO₃ (ref. 17)) heterogeneous catalysts have been applied for azo compound formation. Even Au/TiO₂ has also been reported to carry out aromatic azo compound formation from aryl amines.¹⁸ Oxidative desulfurization is an industrially important and alternative process to hydrodesulfurization.¹⁹ Selective oxidation of organic sulfides to the corresponding sulfide and sulfone is used to decrease the sulfur content of fuels and industrial effluents.²⁰ Recently, Zhang et al. reported carbon nanotubes as an efficient catalyst for the oxidative desulfurization of dibenzothiophene.²¹ The corresponding sulfides or sulfoxides are used as fine chemicals, pharmaceuticals and as valuable intermediates for the construction of chemically and biologically active molecules. Oxidative desulfurization reactions are mainly carried out over a variety of tungsten based complexes.²² Zhang et al. have also reported the oxidation of organic sulfides over mesoporous graphitic carbon nitride material under visible light.23

In this report, we have prepared a highly active, selective reusable heterogeneous WO_x nano cluster supported on mesoporous nitrogen enriched carbon material. The catalyst has been explored for oxidation of aromatic amines and dibenzothiophene oxidation using H_2O_2 as the mild oxidizing agent.

Experimental

Materials

Tetraethylorthosilicate (TEOS), poly(ethylene oxide)-*block*poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer (Aldrich, MW avg. 5800, $EO_{20}PO_{70}EO_{20}$, P123), ethylene diamine (NH₂C₂H₄NH₂), and sodium tungstate (NaWO₄ ·2H₂O) were purchased from Sigma-Aldrich Co. Ethanol, carbon tetrachloride (CCl₄), NaOH, HCl, and NH₃ solution were purchased from Merck KGaA, Darmstadt, Germany. All the chemicals were used without further purification. Double distilled water was prepared with a BOROSIL® water distillation unit.

Catalyst preparation

SBA-15 was synthesized using tetraethylorthosilicate (TEOS) as the silica source and poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer (Aldrich, MW avg. 5800, $EO_{20}PO_{70}EO_{20}$, P123) as a structure-directing agent. In a typical synthesis, 4.0 g of P123 block copolymer was dissolved under stirring in 30.0 g of water. Then, 120.0 g of HCl (2 M) and 9.1 g of TEOS were added under stirring at 40 °C. After 24 h of constant stirring, the gel composition

was kept at 100 °C for 48 h without any further stirring. After cooling to room temperature, the solid product was recovered by filtering, washing, drying, and calcining at 550 °C in order to decompose the triblock copolymer.

Hexagonally ordered mesoporous WO_x/SBA-15 was synthesized by using TEOS as a silica source and poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer (Aldrich, MW avg. 5800, EO₂₀PO₇₀EO₂₀, P123) as a structure-directing agent. In a typical synthesis, 4.0 g of P123 block copolymer was dissolved with stirring in 30.0 g of water and the required amounts (20 mL, 10 mL, 5 mL, 2.5 mL) of aqueous sodium tungstate solution (NaWO₄ ·2H₂O, 0.5 M) were simultaneously and quickly added into the mixture under vigorous stirring. After one hour, 120.0 g of HCl (2 M) and then 9.1 g of TEOS were added with stirring at 40 °C. After being stirred for 24 h at 40 °C, the gel composition was kept at 100 °C for 48 h without stirring. After being cooled to room temperature, the solid product was recovered by filtering, washing, drying and calcining at 550 °C.

Mesoporous nitrogen rich carbon (WO_x/CN_x) materials were synthesized using $WO_x/SBA-15$ as the hard template using the following procedures. 1.0 g of dehydrated $WO_x/SBA-15$ was treated with a mixture of 4.5 g of ethylene diamine $(NH_2C_2H_4NH_2)$ and 11 g of carbon tetrachloride (CCl_4) . The mixture was refluxed at 90 °C for 6 h. Then, the obtained solid mixture (polymer silica composite) was dried and pyrolyzed at two different temperatures (600 and 800 °C) for 6 h under an inert gas atmosphere. The pyrolyzed silica/ nitrogen/carbon composite was washed with 2.5% wt of NaOH solution in ethanol water (1:1) mixture with vigorous stirring at 90 °C for 3 h to remove the silica framework. The process was repeated two times. Then, the product was filtered and washed with a water/ethanol mixture until the filtrate had a pH of 7.0, and then dried.

Catalyst characterization

The prepared mesoporous nitrogen rich carbon materials were characterized by N₂ physisorption measurements at 77 K using an Autosorb 1C setup (Quanta chrome) adsorption analyzer. Prior to the measurements, the samples were degassed under vacuum $(1 \times 10^{-5} \text{ Torr})$ for 2 h at 200 °C. The BET specific surface areas were determined from the adsorption data in the relative pressure (*P*/*P*₀) range from 0.06 to 0.2. The pore size distributions (PSDs) were calculated from the nitrogen adsorption branch using the Barrett–Joyner–Halenda (BJH) method and the maximum of the PSD was considered as the average pore size. The pore volume was considered as the volume of liquid nitrogen adsorbed at $P/P_0 = ca. 1$.

The morphologies of the WO_x/MNC_x materials synthesised at different temperatures and different loadings of tungsten were investigated using SEM (FEI Quanta 3D) and HRTEM. Scanning electron microscopy (SEM) images were taken on a FEI Quanta 200 F instrument, using a tungsten filament doped with lanthanum hexaboride (LaB₆) as an X-ray source, fitted with an ETD detector with high vacuum mode using secondary electrons and an acceleration tension of 10 or 30 kV. Images were recorded at various magnifications. All the samples were analyzed by spreading them on a carbon tape and coating with gold to increase the electrical conductivity. Energy dispersive X-ray spectroscopy (EDX) was used in connection with SEM for the elemental analysis. The elemental mapping was also collected with the same spectrophotometer. A JEOL JEM 2100 high-resolution transmission electron microscope (HRTEM) was employed to observe the porous nature of material. Samples were mounted by dispersing on ethanol on a lacey carbon Formvar coated Cu grid.

Low and wide angle powder X-ray diffractograms (XRD) were obtained with a D8-Advance-Bruker-AXS diffractometer (Cu-*K* α radiation; $\lambda = 1.5418$ Å) in θ -2 θ geometry and a position sensitive detector (capillary technique, thickness: 1 mm).

X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultra-high vacuum (UHV) set-up equipped with a monochromatic AlK_{α} X-ray source (h ν = 1486.6 eV), operated at 14.5 kV and 35 mA, and a high resolution Gammadata-Scienta SES 2002 analyzer. The base pressure in the measurement chamber was maintained at about 7×10^{-10} mbar. The measurements were carried out in the fixed transmission mode with a pass energy of 200 eV, resulting in an overall energy resolution of 0.25 eV. A flood gun was applied to compensate for the charging effects. Resolution spectra for C 1s, O 1s, and N 1s were recorded. The binding energy scales were re-calibrated based on the sp² hybridized C 1s line from graphitic carbon at 284.5 eV. The Casa XPS software²⁴ with a 70:30 Gaussian-Lorentzian product function and Shirley background subtraction was used for peak deconvolution. The obtained spectra from different elements were plotted using the same intensity scale for all the analyzed samples to facilitate comparison. Temperature programmed desorption (TPD) experiments were carried out in a Micromeritics Auto Chem II 2920 instrument connected with a thermal conductivity detector (TCD). The amount and strength of the acid sites were measured by ammonia adsorption-desorption technique using the same Micromeritics Auto Chem II 2920 instrument. About 0.1 g of sample was saturated with NH3 at 100 °C and flashed with He to remove the physically adsorbed NH₃, finally the decomposition of NH₃ was carried out at a heating rate of 10 °C min⁻¹ under He flow.

Multifunctional activity

The oxidation reaction was carried out in a 100 ml two necked round bottom glass reactor fitted with two condensers on a hot plate with magnetic stirring (SI Analytical). The reaction product was identified by GC-MS (HP 5890 GC coupled with 5972 MSD) equipped with a CP-SIL-5 capillary column. The identified product was analysed in an Agilent 7890, fitted with a HP-5 (30 m × 0.28 nm i.d., 0.25 μ m film thickness) capillary column and a FID detector. The conversion and selectivity was measured using chlorobenzene as the internal standard followed by their individual calibration curve. The activity of the catalyst was calculated as:

Conversion (C%) =
$$\frac{\text{Moles of reactant reacted } (C\%)}{\text{Moles of reactant initially used} (C\%)} \times 100$$

Selectivity
$$(C\%) = \frac{\text{Moles of product } (C\%)}{\text{Moles of reactant reacted } (C\%)} \times 100$$

Results and discussion

The low angle XRD patterns of the nitrogen rich carbon materials are shown in Fig. 1a. The XRD pattern of MCN_x reflects one prominent peak at 0.75° corresponding to the (100) plane of the hexagonal p6mm space group. Notably, the XRD pattern coincides well with the XRD pattern of the ordered hexagonal mesoporous SBA-15 material.²⁵ Whereas the wide angle XRD of WO_x/MCN_x catalyst shows a peak at around 25° assigned for graphitic carbon, no peak assigned for any WO_x species is observed, which implies the presence of WO_x species in nanocluster form (Fig. S1 ESI[†]). The 2D hexagonal structure of the prepared samples was confirmed by HRTEM (see Fig. 2a-d). In the case of the sample prepared using ethylene diamine as a source of carbon and nitrogen, and SBA-15 as the template with 5% W loading, the TEM micrograph indicated that the pores were channel-like and their arrangement was similar to that for a 2D hexagonal(honeycomb) structure, however with some imperfections. The homogeneity of the distribution pattern of tungsten has been



Fig. 1 (a) Small-angle X-ray diffraction patterns; (b) N₂ adsorptiondesorption isotherm; (c) pore size distribution of (A) MCN_x and (B) WO_x/MCN_x (5) material. (d) Normalized Raman spectra of WO_x/MCN_x material with a 488 nm laser.



Fig. 2 HRTEM images (a–d) of WO_x/MCN_x (5) material synthesized using ethylene diamine as a source of carbon and nitrogen, and 5% $WO_x/SBA-15$ as the solid template.



Fig. 3 X-ray photoelectron spectra of (a) C 1s and (b) N 1s of WO_x/MCN_x material. (c-d) HRTEM images of WO_x/MCN_x (2.5).

confirmed by the elemental analysis facility associated with the SEM instrument and is shown in Fig. S2, ESI.† Finally, TEM images for the sample prepared with 2.5% WO_x loaded SBA-15, *i.e.* WO_x/MCN_x (2.5), showed (Fig. 3c, d) regular channels and homogenously distributed pores with a wide distribution of sizes. Both MCN_x and WO_x/MCN_x (5) show type IV N₂ adsorption/desorption isotherms with a hysteresis loop H1 at relative pressure in the range of 0.40–0.92, as shown in Fig. 1b. The pore size distribution for the MCN_x shows the mesopores at a diameter of 3.86 nm (Fig. 1c) along with a pore volume of 0.61 cc g⁻¹. The specific surface area (Table S1†) estimated for MCN_x was 457 m² g⁻¹ while for the WO_x/CN_x (5) a decrease in the surface area (427 m² g⁻¹) as well as in pore volume were noticed. The pore volume decreased from 0.61 cc g⁻¹ to 0.36 cc g⁻¹, indicating the incorporation of WO_x inside the mesoporous MCN_x network.

Fig. 1d shows the Raman spectra characteristics of our prepared WO_x/CN_x material. The existence of an amorphous type MCN_x network can be confirmed by the low peak area ratio of the G-band to the D-band. The vibration frequencies of the MCN_x network are expected to come close to the modes of analogous unsaturated CN molecules, which are 1500-1600 cm⁻¹ for chain like molecules and 1300-1600 cm⁻¹ for ring like molecules.²⁶ The signal at about 1598 cm⁻¹ is attributed to the G-band of the tangential mode of graphitelike materials while the peak at around 1365 cm^{-1} is the D-band representing defects in the graphite structures.²⁷ It has been observed that the position of the G-band can vary between 1500 cm⁻¹ and 1600 cm⁻¹; and in the case of sp² bonded amorphous C, the G-mode is around 1520 cm⁻¹ (lower than graphite, mainly due to bond angle distortions). However, the G-band moves up with increasing sp³ bonding in tetrahedral amorphous -C (≥ 1595 cm⁻¹).²⁸ This indicates small distortions in G-D region between the bands because of the special arrangement of the C or N atoms.

The X-ray photoelectron (XP) spectra for C 1s have been obtained in order to determine the local environment of C in the MCN_x network. The deconvoluted C 1s spectra (Fig. 3a) show five individual peaks, of which the major two peaks at 283.9 eV and 284.8 eV are assigned to sp² hybridized graphite-like carbon (C-C sp²) and sp³ hybridized C-C sp³ carbon shouldered with sp² hybridized C-N atom.⁹ The rest of the peaks can be assigned to the surface oxygen groups as -CO (286.4 eV), -C=O (288.2 eV) and -C-OO (289.5 eV). The local environment of the nitrogen atoms also been determined by N 1s XP-spectra (Fig. 3b), which on deconvolution shows three individual peaks. The first N 1s peak at 398.5 eV is assigned pyridine nitrogen (N-py), while the peak at around 401.2 eV can be assigned to the N of the C-N-C network of the graphitic ring. However, the shouldered peak at 399.9 eV has been assigned to nitrogen bonded sp² hybridized (Nb) and nitrogen bonded to a carbon atom in a terminal -C=N group (Nt).²⁹ The total acidity of the samples was measured using NH₃-TPD (Fig. S3 ESI⁺). The TPD pattern shows a strong band in the temperature region between 150-500 °C with the total number of acidic sites of 0.405 mmol g^{-1} (5% WO_x/MCN_x) and 0.260 mmol g⁻¹ (2.5% WO_x/MCN_x).

C-C coupling of aniline

The bi-functional reactivity of the catalyst has been tested in oxidative desulfurization as well as aniline coupling reactions. Selective oxidation of aniline to aromatic azo-compounds has been carried out with the WO_x/MCN_x catalyst, as shown in Table 1. Experimental results showed that with MCN_x , oxidation of aniline is negligible (entry 2) and the WO_x supported catalyst (entries 4–6) shows a significant amount of conversion. It is assumed that during the reaction, single e^- oxidation of aniline took place to form a radical cation, which is exclusively mediated by the WO_x/MCN_x catalyst



0.93 g (10 mmol) aniline, 10 ml CH₃CN, 0.05 g catalyst, temperature 90 °C, and time 12 h, E_0 : H₂O₂ efficiency calculated by (100 × moles of 2b formed)/total moles of H₂O₂ added. C_{aniline} = conversion of aniline, S_{2b} = selectivity of 2b.^{*a*} After 3 reuse, S_{2c} = selectivity of 2c and S_{2d} = selectivity of 2d.

through providing unsaturated W sites. This abstraction is then followed by the coupling of the aniline radical cation with neutral aniline to form azo-benzene.¹⁸ The results clearly demonstrate that tungstate plays an important role in the catalytic process. As observed with the WO_x supported catalyst, the nature of support has a strong influence on the activity of the WO_x nanoparticle. Whilst WO_x on MCN_x proved to be active and selective catalyst for the formation of azo-benzene (2b), WO_x on pure carbon (entry 2) or SBA-15 (not shown) was not found to be active under the present reaction conditions. It is also observed that upon loading of WO_x in the MCN_x network, the activity and selectivity took a positive shift, however, selectivity goes down as loading goes beyond 5%, which may be because of the higher particle size due to higher loading.

The effect of reaction temperature has been studied and we found that the catalyst can effectively convert 70.1% aniline within 12 h with 74.2% azo-benzene selectivity (Fig. 4a) at a reaction temperature of 70 °C. Increasing the temperature from 80 °C to 90 °C leads to a decrease in azo-benzene selectivity from 86.5% to 83.7%, with the formation of nitroso-benzene and azooxy benzene as by-products (Fig. 4a). A longer reaction time of 18 h at 90 °C (Fig. 4b) leads to a decrease in azo-benzene selectivity to 20%, as 75.1% of the excessive oxidation product (azoxy-benzene) was formed with 89% aniline conversion. This trend is decreased for 6 and 9 h reaction times, but selectivity toward azo-benzene goes down, whereas nitroso-benzene was the major product with 66.3% and 21.1%. Hence, it can be assumed that nitrobenzene is the key intermediate for the formation of azo-benzene, which is converted to azoxy-benzene (over oxidation product) with prolonged reaction time.

Aniline conversion increased almost two fold (in Fig. S4, ESI^{\dagger}) form 43.7% to 81.5% with the addition of double the



Fig. 4 Effect of temperature (a) and time-on-stream (b) as a function of aniline conversion and product selectivity. (**■**) Conversion of aniline; (**●**) selectivity of azo-benzene; (**▲**) selectivity of nitroso-benzene and (**▼**) selectivity of azoxy-benzene. Effect of temperature (c) and time-on-stream (d) as a function of DBT conversion and product selectivity. (**■**) Conversion of DBT; (**●**) selectivity of DBTS and (**▲**) selectivity of DBTSO.

amount of H_2O_2 (2 ml, 30 wt.% in H_2O). Moreover, the selectivity of azo-benzene was also found to be doubled (from 31.1% to 67.4%) whereas the selectivity of nitroso-benzene has been decreased. The observation is well concomitant with our previous results that the nitroso-benzene is formed during the reaction (intermediate) and is consumed to form azo-benzene. The WO_x/MCN_x catalyst shows the maximum conversion with the highest azo-benzene selectivity of 83.7% with 3 ml of H_2O_2 . Under the optimized reaction conditions with 3 ml of oxidant, the highest H_2O_2 efficiency (24.0) can be achieved for the formation of azo-benzene (Table 1, entry 6).

Oxidative desulfurization of DBT

Oxidative desulfurization of dibenzothiophene has been carried out with the WO_x/MCN_x catalyst and the results are shown in Table 2. With WO_x/MCN_x (5) catalyst the conversion of DBT was 100% within 2 h and the selectivity of DBTSO (confirmed by GC-MS data shown in Fig. S5, ESI[†]) was 99.8% at a reaction temperature of 100 °C, with small amounts of DBTS (0.2%) remaining as unconverted intermediate product (entry 7), indicating the effectiveness of the WO_x/MCN_x catalyst at the oxidative desulfurization of DBT. Comparing WO_x/MCN_x with other catalysts (entry 2-5) shows nominal activity with poor DBTSO selectivity. With the increase of tungsten loading from 1 to 5 wt%, the conversion of DBT reaches 100% from 26.0% for WO_x/MCN_x (1) with a steady increase in DBTSO selectivity (entry 6-8), indicating that the acidic side provided by tungstic oxide is essential for better conversion and DBTSO selectivity. The catalyst has been reused; no loss in activity and selectivity was noticed, even after 3 successive reuses (entry 10).

Table 2 Oxidative desulfurization of DBT over carbon based catalysts



0.5 g (2.7 mmol) Dibenzothiophene (DBT), 10 ml CH₃CN, 0.05 g catalyst, temperature 100 °C, time 2 h.^{*a*} After 3 reuse, $E_{\rm O}$: H₂O₂ efficiency calculated by (100 × moles of DBTSO formed)/total moles of H₂O₂ added. $S_{\rm 1b}$ = selectivity of DBTS and $S_{\rm 1c}$ = selectivity of DBTSO.

The effect of reaction temperature on oxidative desulfurization is shown in Fig. 4c; the conversion gradually increases up-to 100% with increasing reaction temperature from 60 °C to 100 °C. However, selectivity towards DBTSO was found to be 95.5% at 60 °C, which increase to a maximum of 99.8% at 100 °C after 2 h time-on-stream, although no change was observed in the conversion level with the increase of H_2O_2 at 100 °C (in Fig. S6, ESI†). The selectivity of DBTS gradually goes down to <8% with 3 ml of (1:3 reactant to H_2O_2 ratio) H_2O_2 from 68.1% with 2 ml H_2O_2 . Therefore, sufficient oxidant was necessary for the second step, oxidation of DBTS to DBTSO. With a higher amount (1:5) of H_2O_2 , not much change in product distribution was observed. When the reaction time is 2 h (Fig. 4d), the selectivity of DBTSO was found to be almost 100%.

To check the durability of the catalyst, we carried out time-on-stream studies and the results are shown in Fig. 4d. We found 95.2% DBT conversion within 30 min time-onstream, and 100% with 1 h. Furthermore, a gradual increase in DBTSO selectivity has been experienced with the time-onstream and 100% conversion was noted within 2 h of reaction. We utilized Sheldon's³⁰ hot filtration test, which involves filtration of the catalyst part way through the reaction, followed by continuation of the reaction in the absence of the catalyst. The result shows no further reaction in the absence of catalyst after filtration. Additionally, the hot filtrate was subject for ICP analysis. The test shows a negligible presence of W in the ppb level, which also proves the heterogeneity of the working catalyst. WO_x species play an important role in this reaction; in the presence of peroxide, this WO_x species preferentially forms a metal-peroxo complex.^{31,32} The formation of the metal-peroxo complex is facilitated by polar solvents, especially by acetonitrile, as suggested by Nizova et al.³³ This solvent- peroxometal complex is highly active and has a very short life span. Finally, it transfers oxygen to the activated reactant which then goes to the product through an anionic intermediate, as shown in Scheme S1 ESI.† This anionic intermediate gets stabilized by the donation of a proton from the polar solvent. Along with this, the rate of oxygen transfer from metal-peroxo complex to the activated species may be increased with the surface acidity.

Conclusions

2D hexagonal mesoporous nitrogen-rich carbon materials embedded with highly dispersed WO_x nanoclusters were prepared through a novel approach taking WO_x supported SBA-15 as a hard template. The newly synthesized materials were found to be excellent bifunctional carbon nitride-based catalyst systems for selective oxidation of aniline to aromatic azocompounds as well as for the oxidative desulfurization of dibenzothiophene.

From the results of the present study, it should be possible to develop a wide array of metal embedded MCN_x materials for selective oxidation, provided that enough metal dispersion and defect sites are generated on the surface. However, WO_x/MCN_x not only gives the highest selectivity of the materials tested here but should also allow the efficient one-pot conversion of aniline into azo-compounds as well as dibenzothiophene into dibenzothiophene sulfone.

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