

# Chromium(vi) grafted mesoporous polyaniline as a reusable heterogeneous catalyst for oxidation reactions in aqueous medium

Cite this: *RSC Adv.*, 2014, 4, 15431Usha Mandi,<sup>ab</sup> Malay Pramanik,<sup>c</sup> Anupam Singha Roy,<sup>ab</sup> Noor Salam,<sup>ab</sup> Asim Bhaumik<sup>\*c</sup> and Sk. Manirul Islam<sup>†\*ab</sup>

A new Cr(vi)-grafted mesoporous polyaniline material (Cr-MPANI) has been prepared *via* simple and facile *in situ* radical polymerization of aniline followed by reaction with potassium dichromate. This material has been characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), UV-vis diffuse reflectance spectroscopy (DRS) and Thermogravimetric analysis (TGA). Powder XRD and TEM studies suggested the presence of mesophase and disordered wormhole-like mesopores in this sample. Cr-MPANI acts as a very efficient catalyst for the liquid phase oxidation of alkenes, alkanes and aromatic alcohols using 30% H<sub>2</sub>O<sub>2</sub> as oxidant in water. Oxidation reactions were carried out under very mild conditions, and the desired products were obtained with very high selectivity and relatively high yields. Cr-MPANI can be recycled more than five times without an appreciable loss in activity for its respective catalytic reactions.

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## Introduction

Polymer supported metal complexes are gaining importance as efficient heterogeneous catalysts in a variety of organic transformations including oxidation, which constitute an important group of chemical reactions both on laboratory and industrial scale. The polymer supports act in the immobilization of the homogeneous metal complex and this has attracted a lot of attention in recent times. Because of easy separation of the product from the reaction medium, along with the recovery and reuse of these expensive catalysts, the heterogenized catalysts provide an attractive alternative to the corresponding homogeneous catalysts.<sup>1,2</sup>

In recent years, conducting polymer metal composites have been extensively studied because of their synergetic effects and potential applications in chemistry, physics, electronic, optics and biotechnology.<sup>3</sup> Among conducting polymers polyaniline is one of the electrically conducting polymers and has attracted attention due to its ease of synthesis,<sup>4</sup> performance stability<sup>5</sup> and low synthetic cost. It can be synthesized by

electrochemical methods,<sup>6</sup> by oxidation of the monomer using inert electrodes<sup>7</sup> and by oxidative chemical polymerization of the monomer under liquid-phase.<sup>4a,b,8</sup> We have chosen polyaniline (PANI) as a support material because of its distinctive characteristics such as facile preparative protocols from cheap starting material (aniline), high environmental stability and non-solubility in most of the organic solvents. MPANI is of strong interest because of its large conductivity range, good thermal stability and, especially in doped state, high resistance against common solvents. However, its application as an appropriate support material in catalytic processes under gas and liquid phase conditions are very less known. Recently, MPANI-supported metal catalysts, such as molybdenum,<sup>9</sup> vanadium,<sup>10</sup> indium,<sup>11</sup> palladium,<sup>12</sup> cobalt,<sup>13</sup> and rhenium oxides<sup>14</sup> have been synthesized and applied in synthetic organic chemistry. MPANI-supported vanadium complexes catalyze the oxidation of alcohols to aldehydes and ketones using molecular oxygen,<sup>10</sup> whereas MPANI supported with cobalt or cobalt complexes serve as a synthetic metal catalyst in the oxidation of different varieties of alkenes.<sup>15</sup> Moreover, Fe(II), Co(II), and Mn(II) porphyrins supported on MPANI have been used as catalysts in co-oxidation of styrene and isobutyric aldehyde.<sup>16</sup> Furthermore, MPANI/CuCl<sub>2</sub> and MPANI/FeCl<sub>3</sub> form transition metal complexes that are effective catalysts in the dehydrogenation oxidation of cinnamyle alcohols and mandelic acid.<sup>17</sup> These results have motivated us to explore the use MPANI to immobilize Cr(vi)-species in the oxidation reactions. This improvement permits to turn to the advantages of both homogeneous (selectivity, activity) and heterogeneous (separation, recovery, recycling) catalysts.

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From an environmental as well as economic point of view catalytic oxidation processes, especially those in which hydrogen peroxide is used as primary oxidant, are particularly attractive. In recent years, a considerable amount of research was dedicated to the preparation of various solid heterogeneous catalysts and their application for oxidations of various organic compounds.<sup>18</sup> Oxidation of alkenes to give oxygen containing value added products like alcohols, aldehydes, ketones, acids, epoxides, *etc.* is an extremely important and useful reaction in both chemical and pharmaceutical industries.<sup>19</sup> On the other hand the activation of the carbon–hydrogen bonds of an alkane is considerably more difficult due to its stability. The energy required to overcome this stability leads to deep oxidation rather than selective oxidation.<sup>20</sup> Similarly, the oxidation of primary and secondary alcohols to carbonyl compounds (corresponding aldehydes and ketones) is one of the most useful transformations in organic chemistry. In particular, the selective oxidation of primary alcohols to the corresponding aldehyde is an important organic transformation which has applications in the industry of perfumery, pharmaceutical, dyestuff and agrochemicals.<sup>21</sup>

Herein, we report the successful synthesis of the novel heterogeneous Cr(vi) catalysts using mesoporous polyaniline (MPANI) as a support. The nanostructure of the MPANI supported catalysts has been identified with the help of TEM, XRD and FTIR spectrum. The experimental results have shown that MPANI supported Cr(vi) catalyst has shown catalytic activity for the oxidation of alkenes, alkanes and alcohols using 30% H<sub>2</sub>O<sub>2</sub> as oxidant in aqueous medium. The catalytic activities were also tested with the recycled catalyst.

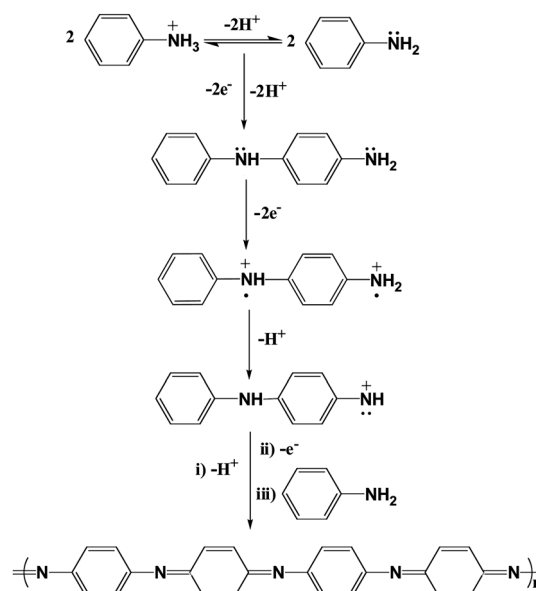
## Experimental

### Materials

Aniline, ammonium persulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) and conc. HCl were obtained from E-Merck. (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was used as initiator for the polymerization of aniline in aqueous medium. Sodium dodecylsulfate (SDS) was purchased from Loba Chemie and used as a structure-directing agent (SDA). Alkenes, alkanes and alcohols were obtained from Merck or Fluka.

### Preparation of mesoporous polyaniline (MPANI)

The templated polymerization of aniline for the synthesis of MPANI (Scheme 1) has been carried out following the previous report.<sup>22</sup> In a typical synthesis, aniline (0.02 mol) was first dissolved into 5 mL aqueous solution of HCl (0.02 mol, ~1.0 mL). This solution was added to 20 mL aqueous solution of SDS (0.01 mol, 2.88 g) under stirring condition. The mixture was then placed in an ice-salt bath, so that the temperature was maintained at 4–5 °C. Finally, 20 mL aqueous solution of the oxidizing agent, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.04 mol, 9.12 g), in ice-cold water was added slowly to the above mixture and the whole mass was allowed to become homogeneous. Then stirring was stopped and the mixture was allowed to age under static condition for 2 days at 4–5 °C. The resultant precipitate was filtered, washed



Scheme 1 Schematic diagram showing the polymerization of aniline.

with deionized water and dried under vacuum at ambient temperature. Finally, the mesoporous polymer MPANI was obtained after extraction in an aqueous solution containing ammonium acetate. The template-free or SDA free MPANI or Cr-MPANI means SDS free material MPANI or Cr-MPANI.

### Preparation of Cr-MPANI

The suspension of 500 mg mesoporous polyaniline in a mixture of 100 mg potassium dichromate taken in 10 mL double distilled water were placed in a round bottom flask (50 mL) and kept it under a vigorous stirring condition for 24 h at room temperature. Finally, the resultant precipitate was filtered and washed with double distilled water and dried under vacuum.

### Physical measurements

Powder samples of MPANI and Cr-MPANI have been characterized simultaneously. Powder X-ray diffraction patterns of the Cr-MPANI was recorded by a Bruker AXS D-8 Advance diffractometer operated at 40 kV voltage and 40 mA current, calibrated with a standard silicon sample using Ni-filtered CuK<sub>α</sub> (λ = 0.15406 nm) radiation. High resolution transmission electron image was recorded in a JEOL JEM 2010 transmission electron microscope. For HR TEM analysis, 10 mg of the template-free material is dispersed into anhydrous ethanol by 5 minute sonication. Then one drop of the dispersed solution is dropped on to the carbon coated copper grid. UV-visible diffuse reflectance spectra were obtained by using a Shimadzu UV 2401PC spectrophotometer with an integrating sphere attachment. FT-IR spectra of these samples were recorded on KBr pellets by using a Perkin-Elmer FT-IR 783 spectrophotometer. Thermogravimetry (TG) analysis of the samples was done by using a Mettler Toledo TGA/DTA 851e.

## General procedure for oxidation reaction catalyzed by Cr-MPANI

The liquid phase oxidation reactions were carried out in a two-necked round bottom flask fitted with a water condenser and placed in an oil bath at different temperatures under vigorous stirring for a certain period of time. Substrates (5 mmol) were taken in water (10 mL) for different sets of reactions together with 20 mg catalyst in which 10 mmol of  $\text{H}_2\text{O}_2$  (30% in aq.) was added. After the reaction, the organic products were separated from the reaction mixture by extraction with dichloromethane ( $5 \text{ mL} \times 2$ ). The combined organic portions were dried and concentrated. Product analysis was performed by Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a Flame Ionization Detector. All reaction products were identified by using Trace DSQ II GC-MS.

## Results and discussion

### Characterization of Cr-MPANI

**XRD studies.** The small angle XRD pattern of the  $\text{Cr}_2\text{O}_7^{2-}$ -loaded material Cr-MPANI is shown in Fig. 1. The material showed one intense peak at  $2\theta = 2.41$ , corresponding to the mesophase. This single broad peak could be attributed to disordered nature of the mesophase, suggesting that after the loading of  $\text{Cr}(\text{vi})$  the nature of the mesophase has been unaltered.

**TEM analysis.** The representative TEM images of the template-free or SDA-free parent MPANI and Cr-MPANI material has been shown in Fig. 2. In the image 2a, the homogeneous distribution of low electron density spots (pores) are seen throughout the specimen, and the pore dimensions *ca.* 3.1 nm are observed. For  $\text{Cr}_2\text{O}_7^{2-}$  loaded MPANI material (Fig. 2b) the same type of low electron density spots are observable but the dimension of the spots decrease to 1.86 nm. Little contraction in the pore width relative to the parent MPANI material (before Cr loading) could be attributed to the loading of  $\text{Cr}_2\text{O}_7^{2-}$  at the pore surface of Cr-MPANI sample.

**$\text{N}_2$  sorption and BET surface area analysis.** The  $\text{N}_2$  adsorption-desorption isotherm for Cr-MPANI material has been shown in Fig. 3. The isotherm is typical type-IV with H3 type hysteresis

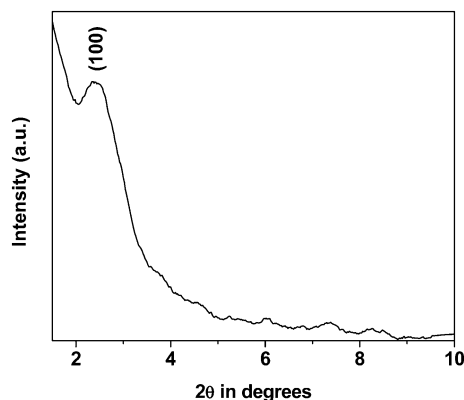


Fig. 1 Small angle XRD of Cr-MPANI.

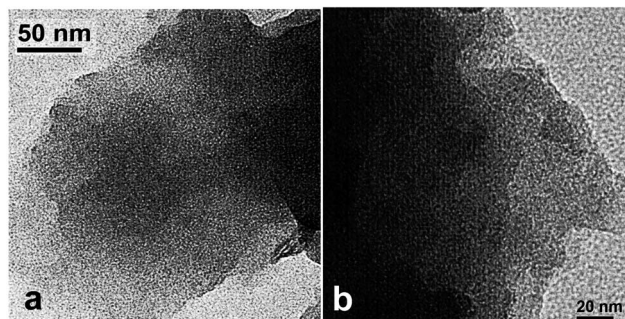


Fig. 2 HR TEM images of template-free MPANI (a) and Cr-MPANI (b) showing the porous structure.

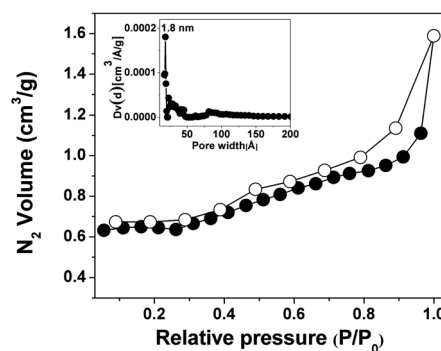


Fig. 3  $\text{N}_2$  adsorption and desorption isotherms for Cr-MPANI. Adsorption points are marked by filled circles and those for desorption by empty circles. NLDFT pore size distribution is shown in the inset.

loop. The BET surface area of the material (Cr-MPANI) is  $2.8 \text{ m}^2 \text{ g}^{-1}$ . This decrease in surface area from parent MPANI material (surface area =  $47 \text{ m}^2 \text{ g}^{-1}$ ) is due to the incorporation of  $\text{Cr}_2\text{O}_7^{2-}$  in the porous framework. The pore size of the material has been determined by NLDFT method (shown in the inset of Fig. 3). The pore diameter of the material is 1.8 nm which completely matches with the TEM data of Cr-MPANI material. The pore diameter (*ca.* 3.1 nm from TEM analysis) of the parent material (MPANI) decreases to 1.8 nm due to the blocking of pores by  $\text{Cr}_2\text{O}_7^{2-}$  in the Cr-MPANI material.

**UV-vis spectra.** The UV-vis spectra of mesoporous MPANI and Cr-MPANI are shown in Fig. 4. Mesoporous polyaniline shows broad bands at wavelengths of 300–450 nm and 650–700 nm. MPANI nanostructured materials usually showed two strong absorptions at 320–340 and 600–660 nm respectively.<sup>23</sup> The first band is assigned to  $\pi \rightarrow \pi^*$  transition and the latter one is associated with the transition of benzenoid rings into quinoid rings. On the other hand, for Cr-MPANI the peak of quinoid ring transition shifts from 700 nm to higher wavelength region (red shift) when  $\text{Cr}(\text{vi})$  was added to MPANI. This could be explained by the fact that the 'compact coil' of Cr-MPANI chain make the energy gap of quinoid ring transition narrower, thus transition of electrons becomes easier. The peak of  $\pi \rightarrow \pi^*$  transition in MPANI seldom shifts, so it can be inferred that the interaction of both  $\text{Cr}(\text{vi})$  and the nitrogen atoms on the quinoid ring is predominant.

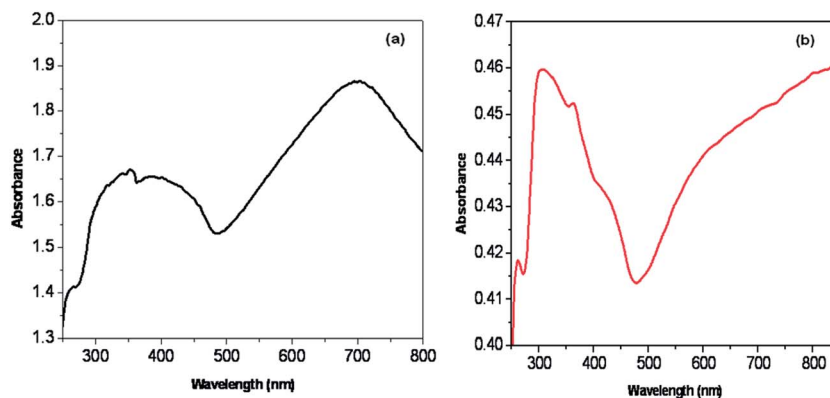


Fig. 4 UV-vis spectra of MPANI (a) and Cr-MPANI (b).

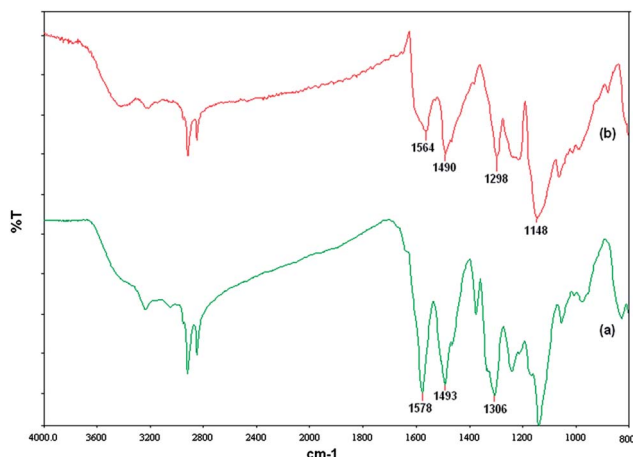


Fig. 5 FT-IR Spectra of mesoporous polyaniline MPANI (a) and Cr-containing mesoporous composite, Cr-MPANI (b).

**FTIR spectra.** Fig. 5 shows the FTIR spectra of MPANI (a) and Cr-MPANI (b) respectively. The characteristic polyaniline vibration bands were observed at 1578, 1493, 1306, 1148  $\text{cm}^{-1}$  which supported the formation of polyaniline through oxidative polymerization.<sup>22</sup> The characteristic peaks at 1578  $\text{cm}^{-1}$  and 1493  $\text{cm}^{-1}$  were assigned to the C=C stretching mode of quinoid and benzenoid rings, respectively.<sup>24</sup> The relatively strong band at 1306  $\text{cm}^{-1}$  was assigned to the C-N stretching of secondary aromatic amine in the alternative unit of quinoid-benzenoid sequences of polyaniline.<sup>25</sup> The peak at 1148  $\text{cm}^{-1}$  was assigned to the in-plane bending of C-H.<sup>26</sup> In addition, the typical C=C stretching modes of the quinonoid ring and benzenoid rings of the MPANI chain in Cr-MPANI nanocomposites have obvious blue shift as compared with those in MPANI,<sup>27</sup> which imply strong interactions between Cr(vi) and MPANI. The band at 1306  $\text{cm}^{-1}$  shifted to lower frequency region when  $\text{K}_2\text{Cr}_2\text{O}_7$  is added in the reactive system of MPANI, which indicates that the Cr(vi) can interact with nitrogen atoms of the MPANI chains. It can be inferred from the results of UV-vis and FTIR spectra that backbone chain of Cr-MPANI hardly changes compared with that of MPANI. So the Cr-MPANI is a complex polymer under the aforementioned condition.

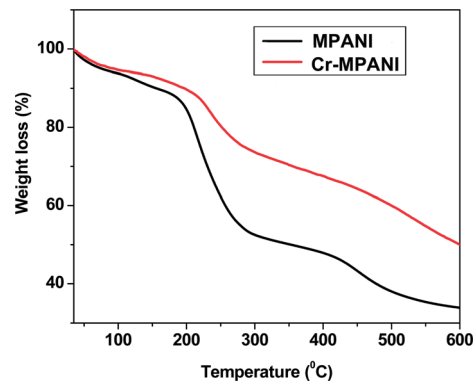


Fig. 6 TGA plots of mesoporous MPANI and Cr-MPANI.

**TG analysis.** Thermogravimetric analysis has been used to understand the stability of mesoporous polyaniline materials. In Fig. 6, the thermogravimetric analysis (TGA) plots of mesoporous MPANI and Cr-MPANI nanocomposite are shown. Thermal analyses were investigated at a heating rate of 10  $^{\circ}\text{C min}^{-1}$  in  $\text{N}_2$  atmosphere over a temperature range of 50–600  $^{\circ}\text{C}$ . Mesoporous MPANI showed a large weight loss at 190–475  $^{\circ}\text{C}$ . Whereas, Cr-MPANI showed similar weight loss in this region but thermal stability improved by 40–50  $^{\circ}\text{C}$ . In case of Cr-MPANI, TG curve showed that mass loss started at 230  $^{\circ}\text{C}$ . The thermograph shows that the Cr-MPANI nanocomposite degraded at higher temperature than that of polyaniline which can be explained by the strong interaction between MPANI and  $\text{K}_2\text{Cr}_2\text{O}_7$  which restricts the thermal motion of MPANI chains.<sup>28</sup>

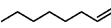
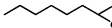
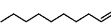
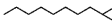



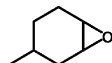


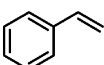
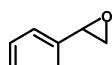
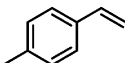
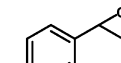
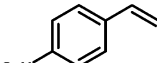
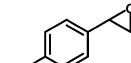


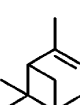
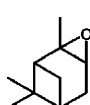

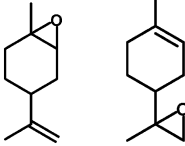

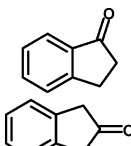
Table 1 Epoxidation of cyclooctene to the corresponding epoxide with 30%  $\text{H}_2\text{O}_2$ <sup>a</sup>

Entry	Catalyst	Conversion <sup>b</sup> (%)	Selectivity <sup>b</sup> (%)
1	Cr-MPANI	96	100
2	MPANI	55	98
3	$\text{K}_2\text{Cr}_2\text{O}_7$	87	99

<sup>a</sup> Reaction conditions: cyclooctene (5 mmol),  $\text{H}_2\text{O}_2$  (10 mmol), catalyst (MPANI and Cr-MPANI = 0.02 g and  $\text{K}_2\text{Cr}_2\text{O}_7$  = 0.0015 g), water (10 mL), reaction temperature (60  $^{\circ}\text{C}$ ), reaction time (4 h). <sup>b</sup> Conversion and selectivity were determined by GC.



**Table 2** Epoxidation of unsaturated organic compounds catalyzed by Cr-MPANI catalyst with 30% H<sub>2</sub>O<sub>2</sub><sup>a</sup>

Entry	Substrate	Time (h)	Conversion <sup>b</sup> (%)	Product	Selectivity <sup>b</sup> (%) [TOF (h <sup>-1</sup> )]
1		12	76		100 [66.95]
2		12	69		100 [60.78]
3		4	92		97 [243.13]
4		4	94		95 [248.41]
5		5	82		93 [173.36]
6		8	89		95 [117.60]
7		8	90		94 [118.92]
8		8	78		90 [103.06]
9		8	82		89 [108.35]
10		4	48		67 [126.85]
11		3	56		72 <sup>c</sup> [197.32]
12		3	86		86 <sup>c</sup> [303.03]

<sup>a</sup> Reaction conditions: catalyst (0.02 g,  $4.73 \times 10^{-3}$  mmol), alkene (5 mmol), water (10 mL), 30% aq. H<sub>2</sub>O<sub>2</sub> (10 mmol), temperature (60 °C).<sup>b</sup> Conversion and selectivity were determined by GC. <sup>c</sup> Selectivity calculated as a sum of both isomers.

**Catalytic activity.** Since mesoporous polymer supported metal systems exhibit high catalytic activity in important organic reactions<sup>29</sup> we have investigated the catalytic activity of mesoporous Cr-MPANI in the oxidation of alkenes, alkanes and aromatic alcohols with 30% H<sub>2</sub>O<sub>2</sub> as oxygen source and water as a green solvent.

**Oxidation of alkenes with H<sub>2</sub>O<sub>2</sub> catalyzed by Cr-MPANI.** The catalytic activity of the resulting Cr-MPANI catalyst has been initially investigated in the epoxidation of alkenes in water using 30% hydrogen peroxide as an oxidizing agent. The comparison of catalytic activity of the same amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as homogenous catalyst and MPANI as support has also been carried out. The activity and selectivity of Cr-MPANI, homogenous K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and MPANI for epoxidation of cyclooctene are

determined by GC (Table 1). Clearly, transition metal complexes are a very effective catalyst for epoxidation of alkenes. It is very interesting to observe from Table 1 that the conversion of cyclooctene by using Cr-MPANI is very high (96%) (Table 1, entry 1), which is even higher than that has been obtained with homogenous catalyst (87%) under similar reaction conditions (Table 1, entry 3). Further, it is interesting to note that MPANI alone when used as catalyst it has shown considerable conversion of 55% (Table 1, entry 2). Hence, it is evident that the catalytic performance of the Cr-MPANI catalyst is superior to that of the MPANI and homogeneous catalyst.

We have used the Cr-MPANI as catalyst in the liquid phase epoxidation of a wide range of alkenes (Table 2). Oxidation of

alkenes with terminal carbon-carbon double bond occurs with high yield and selectivity (Table 2, entries 1 and 2). Corresponding epoxides are formed as an only product. It was also observed that in case of alkenes with single terminal carbon-carbon double bond, increase in the aliphatic chain length cause decreasing in yield of oxidation reaction. Much higher reactivity was observed in the case of cyclic unsaturated hydrocarbons with one or more double bonds in their structure, which were oxidized to corresponding epoxides after 4–6 h, depending on substrate (Table 2, entries 3–5). In the oxidation of cyclohexene over Cr-MPANI, cyclohexane oxide is obtained in 97% selectivity, after 4 hours of reaction (Table 2, entry 3). However, oxidation of the aromatic alkenes requires longer reaction times than that of the carbocyclic alkenes. Styrene was converted to styrene oxide in high yield (Table 2, entry 6). Substituted styrenes selectively produce respective epoxides (Table 2, entries 7 and 8). Corresponding epoxide was detected in the oxidation of  $\alpha$ -methyl styrene as a major product (Table 2, entry 9). Due to high reactivity for the derivatives with double bond in benzyl position, in the oxidation reaction significant amount of by-products are formed. Aldehydes and/or ketones are obtained as major products depending on substrate. Cr-MPANI also catalyzes the oxidation of terpenes in such conditions leading to the corresponding epoxides as main products (Table 2, entries 10 and 11). However, oxidation of indene affords corresponding ketones in high yield (Table 2, entry 12).

#### Oxidation of alkanes with 30% $\text{H}_2\text{O}_2$ catalyzed by Cr-MPANI.

The catalytic oxidation of alkanes with 30%  $\text{H}_2\text{O}_2$  under mild reaction conditions is especially an interesting area of research, because direct functionalization of inactivated C–H bonds in saturated hydrocarbons usually requires drastic reaction conditions such as high pressure and high temperature. Cr-MPANI as a new heterogeneous catalyst was applied to the oxidation of benzylic C–H bonds of toluene and its derivatives with 30%  $\text{H}_2\text{O}_2$ . Reaction conditions of oxidation of benzylic C–H bonds were studied and optimized using toluene as a model substrate (Table 3). Using the MPANI, the yield of benzaldehyde was poor (entry 1). For simple salt  $\text{K}_2\text{Cr}_2\text{O}_7$ , the catalytic activity was bad and only 11% of yield was obtained (entry 2). There was no benzaldehyde was detected when no catalyst was added to the reaction. Based on the catalytic results, Cr-MPANI was the best catalyst for the oxidation of toluene under the reaction

conditions (entry 4). No products were detected when only catalyst was added to the toluene without oxidant. The effect of reaction temperature on the activity of oxidation of toluene was investigated. Reactions were carried out at various temperatures, 50–80 °C (entries 3–6). With increasing temperature, the activity of the reaction was gradually increased. When the reaction was carried out at low temperature, although the selectivity to benzaldehyde was high, the activity of the catalyst was poor (entry 6). Increase in the reaction temperature result in the oxidation of toluene faster, while the selectivity of aldehyde decreased. When the reaction was carried out at 70 °C, the reaction rate markedly increased. A 67% yield of benzaldehyde was achieved after 6 h reaction at 70 °C (entry 4). Although further increase in the temperature was beneficial for the improvement of the conversion, its magnitude was quite limited and the selectivity of benzaldehyde dropped (entry 3). Therefore, 70 °C is the suitable temperature for the oxidation of toluene over Cr-MPANI catalyst.

The catalyst Cr-MPANI has been employed in the liquid phase oxidation of alkyl benzenes with  $\text{H}_2\text{O}_2$  as oxidant at 70 °C. The results shown in Table 4 suggested that Cr-MPANI effectively catalyzes the oxidation of various alkyl benzenes with electron-donating groups; good yield and selectivity for the corresponding aldehydes were observed. For the toluene derivatives with electron donating group, the reaction rate was faster than that of toluene and the reaction was almost completed in 4 h (Table 4, entries 2–4). *p*-Methoxy-toluene containing the electron donating methoxy group also showed the similar high reaction rate and conversion except relative lower selectivity to 4-methoxybenzaldehyde (75%, entry 5). The reason for high reactivity could be ascribed to the electron donating methoxy group. Thus, the substrate was oxidized to some other over oxidized products (carboxylic acid) besides 4-methoxybenzaldehyde. For ethyl benzene, the methyl group could not be oxygenated; only benzylic C–H bonds were oxidized to the carbonyl compound (Table 4, entry 8) with high yield (94%) and selectivity (96%) to acetophenone. For those toluene derivatives containing electron-withdrawing group, the activity was less than that of the ones having electron donating groups (Table 4, entries 6 and 7). The electron withdrawing group made the benzene ring electron deficient and inactivate. So, it was harder for them to be oxidized. *p*-Chlorotoluene gave a 85% selectivity to 4-chlorobenzaldehyde (entry 6). The toluene derivative of *o*-nitro-toluene which has a stronger electron withdrawing group of nitro-group gave a poor reactivity; 91% selectivity to 2-nitrobenzaldehyde and a 34% yield were obtained after 6 h (entry 7).


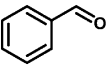
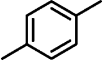
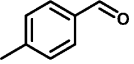

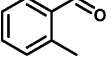


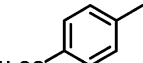
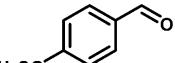
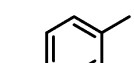
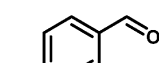
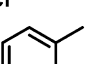
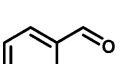
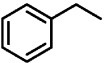
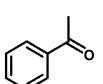
**Oxidation of aromatic alcohols with  $\text{H}_2\text{O}_2$  catalyzed by Cr-MPANI.** Liquid phase catalytic oxidation of alcohols requires organic solvents and addition of base. Thus in line with the requirements of “green chemistry”, we have chosen water as a reaction medium to conduct the oxidation of alcohols in the absence of base (Table 5). Cr-MPANI has been used for the oxidation of benzyl alcohol using 30%  $\text{H}_2\text{O}_2$  in water as oxidant at 60 °C for 6 h. The oxidation took place smoothly and afforded benzaldehyde in 86% yield (Table 5, entry 1). Whereas the oxidation of benzyl alcohol using  $\text{K}_2\text{Cr}_2\text{O}_7$  was less selective and

Table 3 Oxidation of toluene using 30%  $\text{H}_2\text{O}_2$ <sup>a</sup>

Entry	Catalyst	Temperature (°C)	Yield of benzaldehyde <sup>b</sup> (%)	Selectivity of benzaldehyde <sup>b</sup> (%)
1	MPANI	70	6	98
2	$\text{K}_2\text{Cr}_2\text{O}_7$	70	11	95
3	Cr-MPANI	80	69	77
4	Cr-MPANI	70	67	84
5	Cr-MPANI	60	41	89
6	Cr-MPANI	50	19	92

<sup>a</sup> Reaction condition: catalyst (0.02 g) in 10 mL water, toluene (5 mmol),  $\text{H}_2\text{O}_2$  (30%, 10 mmol), reaction time 6 h. <sup>b</sup> Yield and selectivity were determined by GC.

Table 4 Oxidation of various toluene derivatives catalyzed by Cr-MPANI<sup>a</sup>

Entry	Substrate	Time (h)	Conversion <sup>b</sup> (%)	Product	Selectivity <sup>b</sup> (%) [TOF (h <sup>-1</sup> )]
1		6	79		84 [139.18]
2		4	87		90 [229.92]
3		4	92		86 [243.13]
4		4	81		92 [214.06]
5		4	86		75 [227.27]
6		6	46		85 [81.04]
7		6	37		91 [65.19]
8		4	94		96 [248.41]

<sup>a</sup> Reaction condition: substrate (5 mmol), H<sub>2</sub>O<sub>2</sub> (10 mmol), water 10 mL, catalyst (0.02 g, 4.73 × 10<sup>-3</sup> mmol), reaction temperature 70 °C.

<sup>b</sup> Conversion and selectivity were determined by GC.

provided a mixture of benzoic acid and benzaldehyde in a 80% combined yield. To evaluate the scope of this catalytic system, the oxidation of other aromatic and aliphatic alcohols was studied. Substrates having both electron donating and electron withdrawing groups in the aromatic ring, 4-methoxy-, 4-nitro-, and 4-hydroxy- were oxidized to the corresponding aldehydes in high yields (Table 5, entries 3–5). A similar reactivity was observed with the allylic alcohol, cinnamyl alcohol (Table 5, entry 6). The saturated alcohol, heptan-1-ol was less reactive (Table 5, entry 7), while secondary alcohols, benzoin and cyclohexanol provided the corresponding ketones in quantitative yields (Table 5, entries 8 and 9). Likewise, furfural and pyridine-2-methanol could be oxidized to the respective aldehydes in high yields (Table 5, entries 10 and 11). It is pertinent to mention that other reactive groups like phenolic OH, the N-atom of pyridine-2-methanol and the carbon-carbon double bond of the allylic alcohols could not undergo any oxidation over Cr-MPANI under this liquid phase reaction conditions.

### Comparison with other reported systems

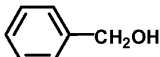
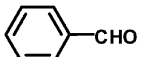
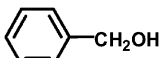
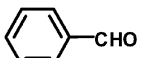
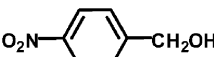

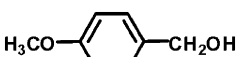
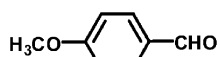
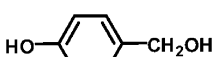
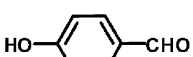
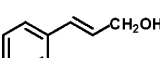
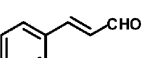
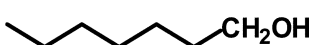
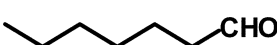
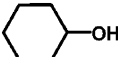
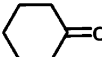
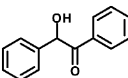
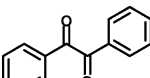
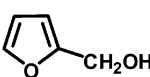
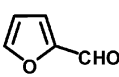
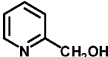
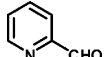
Oxidation of alkenes, alkanes and alcohols under heterogeneous conditions over a variety of catalysts has been studied (Table 6). Table 6 provides a comparison of the results obtained for our present catalytic system with those reported in the literature.<sup>10,30–33</sup> From Table 6, it is seen that present catalyst exhibited higher conversion/yield compared to the other

reported system.<sup>10,30–33</sup> Reactions conducted at moderate temperature, shorter reaction time was required for these reactions and most importantly the reactions occurred in water using our catalyst.

### Heterogeneity test

To check the leaching of metal into the solution during the reaction, styrene oxidation was taken as a representative reaction and it has been carried out under the optimum reaction conditions. The reaction was stopped after the reaction proceeds 3 h. The separated filtrate was allowed to react for another 3 h under the same reaction condition, but no further increase in the conversion was observed. The UV-vis spectroscopy was also used to determine the stability of this heterogeneous catalyst. The UV-vis spectrum of the reaction mixture after the first run did not show any absorption peaks characteristic of chromium metal, indicating that the leaching of metal did not take place during the course of the oxidation reaction. These results suggest that this catalyst was heterogeneous in nature. IR spectrum of the recycled catalyst was quite similar to that of fresh sample. These studies clearly demonstrated that chromium species is strongly bound at the polyaniline surface and no significant amount of leaching occurred during reaction. The results indicate that this catalyst is stable for carrying out the repeated cycles in the oxidation reaction without much loss in activity. To verify the morphological

**Table 5** Oxidation of alcohols to aldehydes and ketones with catalyst Cr-MPANI<sup>a</sup>

Entry	Alcohol	Time (h)	Product	Yield (%) <sup>b</sup> [TOF (h <sup>-1</sup> )]
1		6		86 [151.51]
2 <sup>c</sup>		6		54 [95.14]
3		8		79 [104.39]
4		6		89 [156.80]
5		6		90 [158.56]
6		7		90 [135.91]
7		10		64 [67.65]
8		6		96 [169.13]
9		6		94 [165.61]
10		8		87 [114.96]
11		8		83 [109.67]

<sup>a</sup> Reaction condition: alcohol (5 mmol), H<sub>2</sub>O<sub>2</sub> (10 mmol), water 10 mL, catalyst (0.02 g,  $4.73 \times 10^{-3}$  mmol), reaction temperature 60 °C. <sup>b</sup> Yield was determined by GC. <sup>c</sup> K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was catalyst ( $4.73 \times 10^{-3}$  mmol).

change before and after the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> loading in the MPANI material and after catalysis, we have checked the TEM of the materials. (Fig. 7) From the TEM images of MPANI and Cr-MPANI it is clear that the morphology of the MPANI material does not change after Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> loading. In aqueous medium Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> remain in equilibrium with CrO<sub>4</sub><sup>2-</sup>, but in the two form chromium remain in +6 oxidation state, which is the prime factor for our catalytic reaction. Here in every oxidation reaction Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> is used for the production of active oxidizing agents

(hydroxyl/hydroperoxide) from hydrogen peroxide, so there will be no change of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> after catalytic oxidation, observable from the TEM images of fresh Cr-MPANI (Fig. 7b) and reused Cr-MPANI (Fig. 7c).

### Recycling of the catalyst

The advantage of the heterogeneous catalysis is its easy recovery and further recycling. The catalyst remains insoluble in the

**Table 6** Comparison of catalytic activity of the present catalyst in the oxidation of cyclohexene, ethyl benzene and benzyl alcohol with other reported systems

Entry	Catalyst	Oxidation of cyclohexene	Oxidation of ethyl benzene	Oxidation of benzyl alcohol	Ref.
		Conversion (%)	Conversion (%)	Yield of benzaldehyde (%)	
1	Cr-MPANI	92	94	86	This work
2	Cr(MCM)-48	67.4	76.3	—	30
3	CrSBA-15 (8), CrSBA-15 (16)	—	95.6, 82.3	—	31
4	CHRISS	—	50 (yield)	—	32
5	VO(acac) <sub>3</sub> -MPANI	—	—	68	10
6	MPANI microspheres-Mo(vi)	83	—	—	33



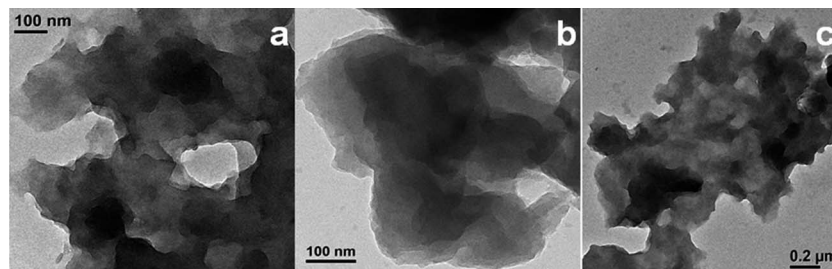


Fig. 7 TEM images of MPANI (a), Cr-MPANI (b), Cr-MPANI after catalysis (c) showing the same morphological structure.

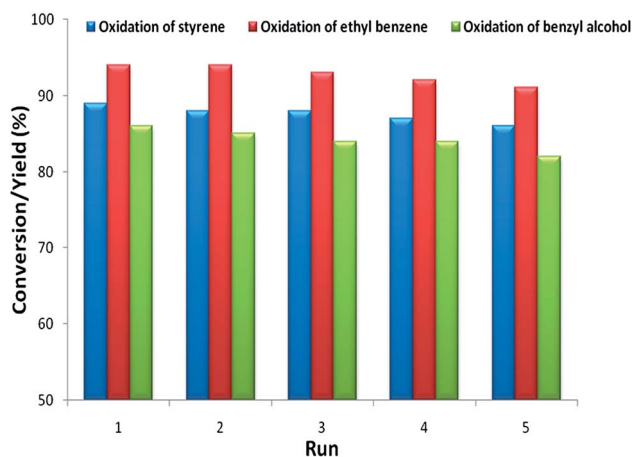


Fig. 8 Recycling efficiency for the oxidation of styrene, ethyl benzene and benzyl alcohol with Cr-MPANI.

present reaction conditions and hence can be easily separated by simple filtration followed by washing. We have studied the reusability of the heterogeneous Cr-MPANI catalyst in the oxidation of styrene, ethyl benzene and benzyl alcohol (Fig. 8). After completion of the reaction, the catalyst was recovered by simple filtration and washed with ethyl acetate followed by acetone then dried under reduced pressure at 60 °C. The recovered catalyst was employed in the next run with further addition of substrates in appropriate amount under optimum reaction conditions. As seen from Fig. 6, the recycled catalyst did not show any appreciable change in the activity indicating that the catalyst is stable and can be regenerated for repeated use in long run.

## Conclusions

We have synthesized mesoporous Cr-MPANI by grafting of chromate anion at the polyaniline surface. The developed heterogeneous catalyst shows high catalytic activity in oxidation of alkenes, alkanes and alcohols. This heterogeneous catalyst produces selectively epoxide products for alkenes, aldehydes and ketones from alkanes and aromatic alcohols. Another important factor is the stability and recyclability of the catalyst under the reaction conditions used. This heterogeneous catalyst shows no significant loss of activity in the recycling experiments. The active sites do not leach out from the support and

thus can be reused without appreciable loss of activity. Leaching test indicates that the catalytic reaction is mainly heterogeneous in nature. The reusability of this catalyst is high and can be reused several times without significant decrease from its initial activity. High catalytic activity for the chromium grafted mesoporous polymer could open new catalytic applications of related mesoporous organic polymers in future.

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