

### Research Article

## Ionothermal Synthesis of Metal Oxide-Based Nanocatalysts and Their Application towards the Oxidative Desulfurization of Dibenzothiophene

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Herein, different types of metal-containing ionic liquid (IL) complexes and various metal oxide-based nanocatalysts have been successfully prepared (from ionic liquids) and applied for the oxidative desulfurization (ODS) of dibenzothiophene (DBT). The ILs complexes are comprised of N,N'-dialkylimidazolium salts of the type [RMIM-Cl]<sub>2</sub>[MCln], where [RMIM+] = 1 alkyl-3-methylimidazolium and M = Mn(II)/Fe(II)/Ni(II)/Co(II). These complexes were prepared using an easy synthetic route by refluxing the methanolic solutions of imidazolium chloride and metal chlorides under facile conditions. The as-prepared complexes were further used as precursors during the ionothermal and chemical synthesis of various metal oxide-based nanocatalysts. The resulting ILs salts and metal oxides NPs have been characterized by FT-IR, TGA, XRD, SEM, and TEM analysis. The results indicate that thermal and chemical treatment of ILs based precursor has produced different phases of metal oxide NPs. The calcination produced  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, and Co<sub>3</sub>O<sub>4</sub>, NPs, whereas the chemical treatment of the ILs salts have led to the production of Fe<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Co(OH)<sub>2</sub>. All the as-prepared salts and metal oxide-based nanocatalysts were used as catalysts towards ODS of dibenzothiophene. The oxidation of dibenzothiophene was performed at atmospheric conditions using hydrogen peroxide as the oxygen donor. Among various catalysts, the thermally obtained metal oxide NPs such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, and Co<sub>3</sub>O<sub>4</sub>, have demonstrated relatively superior catalytic activities compared to the other materials. For example, among these nanocatalysts,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has exhibited a maximum conversion (~99%) of dibenzothiophene (DBT) to dibenzothiophene sulfone (DBTO<sub>2</sub>).

#### 1. Introduction

The increasing demand for petroleum products has led to a significant enhancement in the environmental pollution, due to the emission of poisonous gases during combustion [1]. This has led to the formulations of stringent regulations for fuel specifications, which has tremendously increased the demand of deep desulfurization of transportation fuels. Particularly, the presence of sulfur-containing compounds, such as sulfides, disulfides, and thiophenes in transportation fuels, which typically produce SOx, is a major cause of air contamination [2]. To limit the emission of hazardous sulfur compounds, several countries have legislated stringent

environmental regulations and strongly promoted the desulfurization of fuels ("S-free" fuels (S content <10 ppm)) [3]. Besides, the presence of excessive sulfur compounds also causes irreversible damage to the metal catalysts used in automobiles, including the reduction of lifetime and activity of the catalytic converters. [4]. Typically, the sulfur contents in fuel is removed using the conventional hydrodesulfurization (HDS) technique, which efficiently removes various sulfur compounds including thiols, sulfides, and disulfides [5, 6]. However, several aromatic sulfur compounds, like benzothiophene (BT), dibenzothiophene (DBT), and 4,6-dimethyl dibenzothiophene (4,6-DMDBT), which are usually present in large proportion in diesel are difficult to remove by HDS due to their steric hindrance [7, 8]. These compounds demand deep desulfurization, which is typically performed under the conditions of high temperature and pressure and also require highly active catalysts, leading to significant increase in process cost [9].

To overcome this, several deep desulfurization techniques have been developed, including extraction, oxidation, photooxidation, bioprocess, adsorption, and extraction by ionic liquids [10-12]. Among these techniques, oxidative desulfurization (ODS) effectively removes the aromatic sulfur compounds from fuels under mild condition and thus has gained significant prominence [13]. During the ODS, sulfur compounds are converted into their corresponding sulfones which are generally extracted using polar solvents. So far, several oxidants have been used during this process, such as, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), organic peroxides, molecular oxygen, and ozone [12, 14]. Out of these oxidants, H<sub>2</sub>O<sub>2</sub> has been found to be more effective and produces only water as a side product [15]. The ODS can be performed by several methods which include solvent extraction, photocatalytic oxidation, microwave catalytic oxidation, and so on [16-18]. Apart from this, several other methods are being intensively studied to improve the current HDS technology by developing more effective catalysts and other materials used in this process [19].

In this regard, ionic liquid- (IL-) assisted ODS has also been used extensively due to the high efficiency of IL in the removal of sulfur compounds [20]. So far, ILs have demonstrated great potential in ODS due to their remarkable properties such as, good thermal stability, extremely low volatility, enhanced solubility, excellent ionic conductivity, and wide liquid temperature range [21]. Moreover, they can be used effectively both as catalysts and extractants (solvents) to replace volatile organic compounds which are flammable, hazardous, and are threat to the environment [22, 23]. Currently, the process of catalytic ODS, in which ILs are applied as both homogeneous and/or heterogeneous catalysts have received greater attention when compared to the extraction of sulfur compounds with ILs [24]. Particularly, the trend of applying supported ILs as heterogeneous catalysts has become more popular, as being a solid catalyst it can offer greater advantage. For instance, IL-based solid catalysts demonstrate superior chemical properties such as, increased active sites and enhanced dispersion, and they are also easy to separate from the reaction mixture [25].

Recently, in several studies, metallic or metal oxide nanoparticles (NPs) together with ILs have been applied either as support or active catalyst for the catalytic conversion of sulfur compounds [26]. These IL-based nanocatalysts exhibit both homogeneous and heterogeneous catalytic properties, which not only facilitate rapid and selective chemical transformations but also offer enhanced yield and easy separation and recovery of catalysts [27]. In several studies, ILs have demonstrated excellent potential for the synthesis of various inorganic metal and metal oxide NPs [28]. Particularly, the thermal synthesis of nanomaterials using ILs (ionothermal synthesis) has received considerable attention of researchers. However, the ionothermal synthesis of metallic or metal oxide NPs has been rarely studied. In our previous study, we have demonstrated the ionothermal synthesis of NiO NPs using N,N'-dialkylimidazolium salts of the type  $[RMIM-Cl]_2[MCln]$ , where [RMIM+] = 1-alkyl-3-methylimidazolium and M = Ni(II) ionic liquid [29]. The asprepared IL was used a precursor, which was calcined at 500°C for several hours to produce Ni NPs. The study has revealed the significant effect of IL on the shape and morphology of resultant NPs Scheme 1.

For further continuation of our previous work, in this study, we demonstrate the preparation of transition metalcontaining IL-based complexes. The as-prepared complexes were used as precursors for the synthesis of different metal oxide NPs including Manganese (Mn), Iron (Fe), Cobalt (Co), and Nickel (Ni) NPs using thermal and chemical treatment methods. The IL-based precursors are made up imidazolium and N,N'-dialkylimidazolium salts of the type  $[RMIM-Cl]_2[MCl_n]$ , where [RMIM+] = 1-alkyl-3-methylimidazolium and M = Mn(II), Fe(II), Ni(II), and Co(II). The resultant complexes and metal oxide NPs have been characterized by powder X-ray diffraction, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Both the IL-based precursors and resultant NPs have been tested for their catalytic activity towards the oxidative desulfurization of dibenzothiophene (DBT).

#### 2. Materials and Methods

2.1. Materials. Iron(III) chloride (FeCl<sub>3</sub>. 4H<sub>2</sub>O), Manganese(II) chloride (MnCl<sub>2</sub>·n 4H<sub>2</sub>O), Cobalt(II) chloride (CoCl<sub>2</sub>), and Nickel (II) chloride (NiCl<sub>2</sub>. 6H<sub>2</sub>O) were purchased from Fluka AG Ltd. 1-Ethyl-3 methylimidazolium, (C<sub>6</sub>H<sub>11</sub>ClN<sub>2</sub>), dibenzothiophene, and NaBH<sub>4</sub> were procured from Sigma-Aldrich. All chemicals and solvents were used without any further purification.

2.2. Preparation of  $[EMIM-Cl][MCl_2]$  Complexes. [EMIM-Cl][MCl\_2] complexes were prepared according to our previously reported method [29]. Briefly, equimolar quantities of metal salt (FeCl<sub>3</sub>·4H<sub>2</sub>O, 0.009 mmol) and 1ethyl-3 methylimidazolium (0.009 mmol) were taken in 30 ml of methanol in a 250 mL three-neck flask. The mixture was stirred for several hours (4 hrs). After that, the reaction was stopped and cooled to room temperature. Then the mixture was kept overnight in an acetone ice bath to obtain a dark blue liquid. Finally, the solid product was isolated on a rotary evaporator under reduced pressure and dried in an oven for 3 h at 120°C.

2.3. Chemical Treatment of [EMIM-Cl][MCl<sub>2</sub>] Complexes. The chemical treatment of as-prepared metal-containing IL-based complexes was performed as reported by our group earlier [29].

2.4. Calcination of [EMIM-Cl][MCl<sub>2</sub>] Complexes. The calcination of as-prepared metal-containing IL-based complexes such as [EMIM-Cl][MCl<sub>2</sub>] was performed by a process reported by us earlier [29].



SCHEME 1: Schematic representation of the preparation of metal-containing ionic liquid complexes and the preparation of metallic nanoparticles (NPs). Both ionic liquid complexes and NPs were used as catalysts for the catalytic oxidative desulfurization of dibenzothiophene.

2.5. Catalytic Oxidation of Dibenzothiophene (DBT). The catalytic reactions were performed using a previously reported method by changing the catalyst [30]. A mixture of n-hexadecane and acetonitrile (50 mL each) was taken in 250 ml round bottom flask. To this mixture, small amount of catalyst (1 g·L<sup>-1</sup> with respect to the solvent which is 100 ml) and DBT (2.932 g, with sulfur content of 500 ppm) was added, and the mixture was allowed to stir continuously. Subsequently, 50 mL of the H<sub>2</sub>O<sub>2</sub>/glacial acetic acid (1.5 M ratio, H<sub>2</sub>O<sub>2</sub>/DBT molar ratio 5:1) was slowly added in several steps to avoid the release of molecular oxygen. The reaction was continued for 60 min at atmospheric pressure. Samples were collected from the reaction mixture to analyze the oxidation of DBT and formation of DBTO<sub>2</sub>.

2.6. Characterization. The thermal decomposition of the metal-containing ILs complexes ([EMIM-Cl][MCl<sub>2</sub>]) was evaluated by simultaneous TGA/DTA analysis using the PerkinElmer Thermogravimetric Analyzer 7 (PerkinElmer, Waltham, MA, USA). Fourier transform infrared spectroscopy (FT-IR) spectra were recorded as KBr pellets using a PerkinElmer 1000 FT-IR spectrophotometer (PerkinElmer, Waltham, MA, USA). X-ray diffraction measurements were recorded using an Altima IV (Rigaku, Shibuyaku, Japan) X-ray diffractometer. SEM measurements were carried out using a JEOL SEM model JSM 6360A (JEOL Ltd., Akishima-shi, Japan), whereas, TEM analyses were performed on a JEOLTEM model JEM-1101 (JEOL Ltd., Akishima-shi, Japan). The conversion of the catalytic products was analyzed using GC, 7890A, Agilent Technologies Inc., equipped with a flame ionization detector (FID) and a 19019S-001 HP-PONA column.

#### 3. Results and Discussion

3.1. TGA Analysis. In this study, ILs has been used as precursors for the synthesis of different metallic NPs. For

this purpose, "task-specific" metal-containing IL based on imidazolium and N,N'-dialkylimidazolium salts of the type  $[RMIM-Cl]_2[MCl_n]$ , where [RMIM+] = 1-alkyl-3-methylimidazolium and M = Mn(II), Fe(II), Ni(II), and Co(II) have been prepared. The IL-based salts were synthesized in a simple single step method by the refluxing of imidazolium with respective metal salts, including FeCl<sub>2</sub>, MnCl<sub>2</sub>, NiCl<sub>2</sub>, and CoCl<sub>2</sub> in methanolic solution under aerobic conditions. The formations of the complexes of IL and metal NPs were confirmed by TGA and FTIR.

Initially, the thermal stability of transition metal-based 1-ethyl-3 methylimidazolium chloride (EMIM-Cl) complexes such as [EMIM-Cl][FeCl<sub>2</sub>], [EMIM-Cl][MnCl<sub>2</sub>], [EMIM-Cl][NiCl<sub>2</sub>], and [EMIM-Cl][CoCl<sub>2</sub>] salts were determined in order to confirm the upper temperature limit (cf. Figure 1). For this purpose, the samples were heated over a temperature range of 25-800°C at a heating rate of 10°C·min<sup>-1</sup>. Measurements demonstrated that all the samples melt around between 40 to 60°C and decomposed in several steps to form the corresponding metals. As reported earlier, the [EMIM-Cl][NiCl<sub>2</sub>] began to decompose around 220°C, similarly, in case of [EMIM-Cl][FeCl<sub>2</sub>], [EMIM-Cl] [MnCl<sub>2</sub>], and [EMIM-Cl][CoCl<sub>2</sub>], the onset of decomposition was also observed in the same range of temperature, which clearly indicated towards an ionic liquid window of 40 to 220°C [29]. The [EMIM-Cl][FeCl<sub>2</sub>] and [EMIM-Cl] [NiCl<sub>2</sub>] melt at 40°C, whereas, EMIM-Cl][MnCl<sub>2</sub>] and [EMIM-Cl][CoCl<sub>2</sub>] demonstrated a melting temperature of 50 and 60°C, respectively. Typically, these types of complexes are classified as low-temperature ILs and belong to a class of RMIM-Cl chlorotransition metalates (with a 1:1 stoichiometry). The [EMIM-Cl][FeCl<sub>2</sub>] and [EMIM-Cl][NiCl<sub>2</sub>] demonstrated the IL behavior from 40 to 220°C, whereas, [EMIM-Cl][MnCl<sub>2</sub>] and [EMIM-Cl][CoCl<sub>2</sub>] showed similar behavior between 50 and 60 to 220°C, respectively. The TGA curves of the complexes [EMIM-Cl][FeCl<sub>2</sub>], [EMIM-Cl] [MnCl<sub>2</sub>], and [EMIM-Cl][CoCl<sub>2</sub>] are stable up to 340, 330 and 350°C, respectively, whereas, the sharp peaks at 420, 410,



FIGURE 1: Thermal analysis of (a) [EMIM-Cl][FeCl<sub>2</sub>], (b) [EMIM-Cl][MnCl<sub>2</sub>], (c) [EMIM-Cl][NiCl<sub>2</sub>], and (d) [EMIM-Cl][CoCl<sub>2</sub>].

and 400°C represent the  $\sim$ 50 to 60% weight loss of the total weight by the [EMIM]<sup>+</sup> cations belonging to all the complexes.

3.2. FTIR Analysis. All the metal-containing IL-based complexes were further characterized by FTIR spectroscopy, as shown in Figure 2. The FT-IR spectra of [EMIM-Cl][FeCl<sub>2</sub>], [EMIM-Cl][MnCl<sub>2</sub>], and [EMIM-Cl][CoCl<sub>2</sub>] displayed similar prominent peaks above 3000 cm<sup>-1</sup>, which corresponds to the different vibrational modes of the imidazolium ring. The two sharp and intense bands between 3100 and 3155 cm<sup>-</sup> correspond to antisymmetric and symmetric stretching vibrational modes of the C-H stretching of imidazolium ring, whereas the small band at the shoulder (~2985 cm<sup>-1</sup>) corresponds to the aliphatic asymmetric (C-H) stretching due to the alkyl groups [31]. The broad peak above  $3400 \text{ cm}^{-1}$  in all the spectra indicates the formation of quaternary amine salt formation with chlorine Although all the ionic liquids complexes have similar spectra above 3000 cm<sup>-1</sup>, however, they display slightly different pattern in the region between 500 to  $2000 \text{ cm}^{-1}$  due to the presence of different metallic species. For example, the [EMIM-Cl][FeCl<sub>2</sub>] gave a characteristic peak at 1105 cm<sup>-1</sup>, which corresponds to FeO<sub>2</sub> species, while the absorption at  $622 \text{ cm}^{-1}$  can be attributed to the coupling mode between Mn-O stretching modes in MnO<sub>2</sub> as observed in the FT-IR spectrum of [EMIM-Cl][MnCl<sub>2</sub>] [32].

Once the formation of metal-containing IL complexes was confirmed, they were used as precursors for the preparation of respective metal NPs via two different methods, including a chemical and thermal decomposition method. In

general, the chemical synthesis was performed in a methanolic solution containing IL complex and NaBH<sub>4</sub>. Stirring of mixture under aerobic conditions produced dark precipitates which were isolated by filtration. On the other hand, the thermal decomposition of the complexes was performed by calcination at 600°C for several hours at the rate of 10°C·min<sup>-1</sup>, in static air. Notably, the complexes have produced different phases of NPs (which were identified by XRD) depending upon the method of decomposition. Typically, under chemical treatment methods, in the presence of reducing agents the initial reduction of metal cations occurs through a number of redox reactions. When the reductant is introduced into the aqueous solution of metal precursors, electrons are donated to the metal ions through a series of redox reactions, which is followed by the nucleation and growth of the metal atoms to form nanoparticles. In some cases, stable metal nanoparticles are formed. However, in many cases, when the metal NPs are not stable under certain circumstances, subsequent oxidation occurs to produce metal oxides nanoparticles. For instance, e.g., in our previous study, we have demonstrated that the chemical treatment of [EMIM-Cl][NiCl<sub>2</sub>] produces stable Ni NPs in the *hcp* phase, whereas the thermal decomposition at high temperature has generated *fcc* phase of NiO NPs [29].

3.3. XRD Analysis. Similarly, [EMIM-Cl][FeCl<sub>2</sub>] has also generated two different phases of NPs depending upon the method of reduction. The chemical treatment of [EMIM-Cl] [FeCl<sub>2</sub>]-CR has generated Fe<sub>3</sub>O<sub>4</sub> NPs, whereas the calcination has led to the production of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase. This is in



FIGURE 2: FT-IR spectra of (a) [EMIM-Cl][FeCl<sub>2</sub>], (b) [EMIM-Cl][MnCl<sub>2</sub>], (c) [EMIM-Cl][NiCl<sub>2</sub>], and (d) [EMIM-Cl][CoCl<sub>2</sub>].

agreement with an earlier study, in which the chemical treatment of ferric chloride hexa-hydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O) with NaBH<sub>4</sub> has produced Fe<sub>3</sub>O<sub>4</sub> nanoparticles at ambient temperature [33]. As shown in Figure 3, the diffraction peaks in the XRD pattern of chemically reduced Fe<sub>3</sub>O<sub>4</sub> at (211), (220), (311), (321), (322), (331), (422), (333), and (440) corresponds to the cubic structure of Fe<sub>3</sub>O<sub>4</sub> phase. The lattice parameter is in good agreement with the standard data (JCPDS: 19-0629). Besides the peaks belonging to the Fe<sub>3</sub>O<sub>4</sub> phase, the pattern also contains some additional peaks which points towards the presence of some other phase of iron oxide as impurities, whereas thermally reduced [EMIM-Cl][FeCl<sub>2</sub>]-TR has produced iron oxide NPs belonging to the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase. This was confirmed by XRD as shown in Figure 3(b). The exhibited peaks correspond to the (012), (104), (110), (113), (024), (116), (018), (214), and (300) of a rhombohedral structure of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which is in agreement with the standard data. Notably, the calcination of iron oxide NPs at high temperature (above 500°C) is known to produce a pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase [34].

In case of [EMIM-Cl][MnCl<sub>2</sub>], the calcination at high temperature has produced  $Mn_3O_4$  NPs. The spectrum shown in Figure 4(a) exhibits several diffraction peaks at  $2\theta$  values of 18.1°, 29.5°, 31.9°, 33.1°, 36.8°, 38.6°, 44.9°, 50.9°, 54.4°, 56.1°, 58.7°, 60°, and 64.9°, which corresponds to (1 0 1), (1 1 2), (2 0 0), (1 0 3), (2 1 1), (0 0 4), (2 2 0), (1 0 5), (3 1 2), (3 0 3), (3 2 1), (2 2 4), and (4 0 0), respectively. All the

characteristic diffraction peaks are perfectly indexed and match well with the reported tetragonal structure of Mn<sub>3</sub>O<sub>4</sub> nanoparticles (JCPDS card no. 24-0734) [35]. Additionally, there is no evidence for the presence of any other oxidation state of manganese, which indicates the high phase purity of the prepared  $Mn_3O_4$  sample. The obtained diffraction peaks are relatively broad and of low intensity, suggesting that the prepared Mn<sub>3</sub>O<sub>4</sub> particle is smaller in size. However, the identity of product obtained from chemical treatment is slightly ambiguous. Most of the peaks shown in the XRD pattern match the spinel structure of the Mn<sub>2</sub>O<sub>3</sub> phase (JCPDS no. 41-1442). For instance, the peaks at  $2\theta$  values of 32.0°, 45.2°, 55.2°, and 65.8° are ascribed to the reflections of (222), (332), (440), and (622) planes of the spinel Mn<sub>2</sub>O<sub>3</sub>, respectively [36]. However, many other peaks, such as peaks at 23.1°, 38.3°, 49.3°, and 60.6°, belonging to the spinal structure of Mn<sub>2</sub>O<sub>3</sub> phase are still missing from the pattern. Interestingly, some of the peaks (e.g., the peak at  $\sim 29^{\circ}$ ) in the pattern of [EMIM-Cl][MnCl<sub>2</sub>]-TR also match with that of the Mn<sub>3</sub>O<sub>4</sub> phase. Therefore, further investigation needs to performed to identify the structure of the product obtained from the chemical treatment of [EMIM-Cl][MnCl<sub>2</sub>].

Apart from this, [EMIM-Cl][CoCl<sub>2</sub>] has also produced two different phases of cobalt oxide NPs upon chemical treatment and calcination. The XRD pattern shown in Figure 5(a), belonging to the thermally reduced sample of [EMIM-Cl][CoCl<sub>2</sub>], clearly exhibits the cubic phase of



FIGURE 3: XRD spectra of iron oxide nanoparticles obtained from (a) chemical treatment and (b) calcination.



FIGURE 4: XRD spectra of manganese oxide nanoparticles obtained from (a) calcination and (b) chemical treatment. The identity of the  $Mn_2O_3$  is still ambiguous as some of the characteristic peaks belonging to the spinal structure of  $Mn_2O_3$  are missing from the spectrum.

Co<sub>3</sub>O<sub>4</sub> NPs. The characteristic crystal planes of the Co<sub>3</sub>O<sub>4</sub> include (111), (220), (311), (222), (400), (422), (511), (440), and (531). All these diffraction peaks point to the cubic crystalline phase (space group: Fd-3m 227) of Co<sub>3</sub>O<sub>4</sub> (JCPDS, no. 74-1656) [37]. On the other hand, the chemically reduced sample has produced a mix phase of cobalt oxide NPs including alpha cobalt hydroxide ( $\alpha$ -Co(OH)<sub>2</sub> belonging to JCPDS file no. 02–0925) and cubic phase of Co<sub>3</sub>O<sub>4</sub> [38].

3.4. TEM, SEM, and EDX Analysis. The formation of metal oxide NPs via thermal and chemical decomposition is further confirmed by EDX analysis (data not show here). The EDX of all the samples obtained from both chemical and thermal methods indicated the formation of different types of metal oxide nanoparticles. The presence of oxygen and respective transition metals such as Fe, Mn, and Co in each sample confirms the formation of metal oxide NPs. Furthermore, morphology of as-prepared metal oxide NPs is determined by both SEM and TEM. Figure 6 shows the SEM images of all the metal oxide NPs obtained from both thermal and chemical treatments. The SEM images show cubic, spherical, and prismatic morphologies for  $Fe_3O_4$ ,  $\rm Mn_3O_4,$  and  $\rm Co_3O_4$  metal oxide NPs with moderate agglomeration.

Furthermore, the morphology of metal oxide nanoparticles obtained from the thermal and chemical treatment is determined by high-resolution TEM. The TEM images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, and Co<sub>3</sub>O<sub>4</sub> obtained from calcination mainly exhibit smaller size spherical nanoparticles (5–25 nm) with slight agglomeration, while the samples obtained from chemical treatment such as, Fe<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Co(OH)<sub>2</sub> show agglomerated, irregular-shaped, largesize nanoparticles (cf. Figure 7).

3.5. Catalytic Activity of As-Prepared Metal Oxide Nanoparticles. As-prepared metal oxide nanocatalysts obtained from both thermal and chemical methods were tested for their catalytic efficiency towards the oxidation of dibenzothiophene. Metal oxides belong to an important class of solid catalysts, which have been extensively applied in heterogeneous catalysis due to their unique outer electron configuration and excellent acid-base and redox properties [39]. These materials are typically applied as active phase or as support to the existing catalysts. Most of the single component metal oxides crystallize with an isotropic



FIGURE 5: XRD spectra of cobalt oxide nanoparticles obtain from (a) calcination and (b) chemical treatment.



FIGURE 6: SEM images of Fe<sub>3</sub>O<sub>4</sub>, Mn<sub>3</sub>O<sub>4</sub>, and Co<sub>3</sub>O<sub>4</sub> metal oxide NPs obtained from the calcination of [EMIM-Cl][FeCl<sub>2</sub>], [EMIM-Cl] [MnCl<sub>2</sub>], and [EMIM-Cl][CoCl<sub>2</sub>], respectively, at 600°C, whereas  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Co(OH)<sub>2</sub> were obtained from chemical treatment.

morphology (without preferential orientation) and the surface may terminate with M–OH, M–O–M, M = O or M-() functionalities where M-() represents an oxygen vacancy [40]. Particularly, the transition elements based metal oxides have been widely used due to their low cost of production, easy regeneration, and selective action for various organic transformations including oxidation [41]. Metal oxides have also played an active role in the catalytic oxidation of DBT. So far, oxides of various metals including Cu, Ti, Cr, Mn, Fe, Co, W, and V have been applied. Metal oxide-based catalysts typically promote the formation of peroxyacid from oxidants such as  $H_2O_2$  and carboxylic acid (e.g., formic or acetic acid). Besides, they also enhance the activation of the H-O-O-H bonds by forming active oxygen species [30].

The catalytic activities of metal oxide NPs, such as thermally prepared  $Fe_3O_4$ ,  $Mn_3O_4$ ,  $Co_3O_4$ , and NiO and

chemically prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Co(OH)<sub>2</sub>, Ni NPs were investigated for DBT oxidation. Besides, the asprepared metal-containing IL complexes like [EMIM-Cl] [FeCl<sub>2</sub>], [EMIM-Cl][MnCl<sub>2</sub>], [EMIM-Cl][CoCl<sub>2</sub>], and [EMIM-Cl][NiCl<sub>2</sub>] have also been used as catalysts for the similar reaction. The oxidation was performed by a procedure described in the experimental section using hydrogen peroxide as the oxygen donor.

The results for the DBT oxidation show that most of the aforementioned nanocatalysts successfully catalyzed the oxidation of DBT to dibenzothiophene sulfone (DBTO<sub>2</sub>). However, high conversions for DBT oxidation were observed in the case of thermally prepared metal oxide nanocatalysts, whereas chemically prepared nanocatalysts have demonstrated least catalytic activity towards the conversion of DBT. Notably, metal-containing IL-based complexes have also



FIGURE 7: HRTEM images of Fe<sub>3</sub>O<sub>4</sub>, Mn<sub>3</sub>O<sub>4</sub>, and Co<sub>3</sub>O<sub>4</sub> metal oxide NPs obtained from the calcination of [EMIM-Cl][FeCl<sub>2</sub>], [EMIM-Cl] [MnCl<sub>2</sub>], and [EMIM-Cl][CoCl<sub>2</sub>], respectively, at 600°C, whereas,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>, and  $\alpha$ -Co(OH)<sub>2</sub> were obtained from chemical treatment with NaBH<sub>4</sub>.



FIGURE 8: Schematic representation of the overall scheme of the oxidation of dibenzothiophene (DBT) to dibenzothiophene sulfone (DBTO<sub>2</sub>) and conversion percentage of the products formed by using different nanocatalysts.

showed moderate catalytic activity. All the reactions were performed under similar set of conditions using DBT/ $H_2O_2 = 1:10$  at room temperature. The formation of DBTO was not observed when the reaction was performed in the absence of catalyst, whereas in the presence of catalysts under the same reaction condition, DBT was oxidized to DBTO<sub>2</sub> and

a small ratio of DBTO (dibenzothiophene sulfoxide) was formed due to partial oxidation of DBT with  $H_2O_2$ . Highest conversions of ~99.5% and 93.6% were observed in the presence of thermally obtained nanocatalysts such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>, respectively, (cf. Figure 8). Notably, iron oxides have shown potential application in ODS system, as observed in this case where  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has demonstrated the highest catalytic activity. For example, an amphiphilic catalyst developed by using naturally occurring magnetite particles has demonstrated 97% conversion of DBT to DBTO<sub>2</sub> in 180 min [42]. However, the catalytic application of other metal oxides used in this study such as Co<sub>3</sub>O<sub>4</sub> and Mn<sub>2</sub>O<sub>3</sub> towards ODS has been rarely appeared in the literature, while thermally prepared Mn<sub>3</sub>O<sub>4</sub> and NiO nanocatalysts have demonstrated negligible conversions of 0.25 and 2.3%, respectively. Chemically prepared metal oxide nanocatalysts have exhibited lowest catalytic activity towards the conversion of DBT to DBTO<sub>2</sub>. For example, nanocatalysts Fe<sub>3</sub>O<sub>4</sub> and  $Mn_2O_3$  and mixed phase of  $\alpha$ -Co(OH)<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> have produced the conversion of 1.04, 1.6, and 0.02, respectively. These dismal catalytic activities of chemically prepared nanocatalysts can be possibly attributed to the preparation conditions of the catalyst, as the chemical preparation of catalysts have produced different phases of metal oxide nanoparticles, when compared to the thermally produced methods. Moreover, the products obtained do not consist of single phases but were contaminated with other phases of metal oxides. Among chemically produced nanocatalysts, only the Ni-based catalyst has demonstrated excellent catalytic activity and has produced high conversion of DBT (~95.5%), since, exceptionally, only the chemical treatment of Ni containing IL complex ([EMIM-Cl][NiCl<sub>2</sub>]) has led to the production of Pure Ni NPs, as described in our earlier study [29]. Apart from this, all the as-obtained metal-containing IL complexes such as [EMIM-Cl][FeCl<sub>2</sub>], [EMIM-Cl][MnCl<sub>2</sub>], [EMIM-Cl][CoCl<sub>2</sub>], and [EMIM-Cl][NiCl<sub>2</sub>] have demonstrated moderate catalytic activities. ILs have demonstrated considerable catalytic activity towards ODS due to their high affinity to sulfur-containing compounds. Various studies have been published on the catalytic efficiencies of ILs of ODS. For example, fenton-like reagents, such as Co<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>,  $Cr^{3+}$ ,  $Fe^{3+}$ , and  $H_2O_2$ , were used for desulfurization in ILs. Among these reagents, FeCl<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and [bmim]BF<sub>4</sub> exhibited high catalytic activity (~96%) [43]. In this study, [EMIM-Cl][NiCl<sub>2</sub>] [EMIM-Cl][CoCl<sub>2</sub>], and [EMIM-Cl] [MnCl<sub>2</sub>] have exhibited significant conversions of 52.2%, 26.1%, and 29.4%, respectively, whereas [EMIM-Cl][FeCl<sub>2</sub>] has shown very low conversion of 1.5%. The reason for poor oxidation of DBT by several catalysts might be due to competitive oxidation of DBT and decomposition of H<sub>2</sub>O<sub>2</sub> by these catalysts.

#### 4. Conclusion

In summary, different types of metal-containing IL complexes and metal oxide-based nanocatalysts were successfully prepared and applied for the oxidation of DBT. The ILbased complexes were applied as precursors during the thermal and chemical synthesis of metal oxide based nanocatalysts. The calcination of the IL-based metal salts has produced high-quality, single-phase metal oxide NPs, whereas mixed phases of aggregated metal oxides NPs were obtained by the chemical treatment. Among all the asprepared materials, including IL-based complexes and metal oxide NPs, the thermally obtained metal oxides such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, and Co<sub>3</sub>O<sub>4</sub> have exhibited superior catalytic activities towards the oxidation of DBT, whereas ILs salts Mn-, Co-, and Ni-based ILs complexes, such as [EMIM-Cl][MnCl<sub>2</sub>], [EMIM-Cl][CoCl<sub>2</sub>], and [EMIM-Cl][NiCl<sub>2</sub>], have shown moderate catalytic activity. However, most of the chemically produced metal oxide nanocatalysts have exhibited poor catalytic activities, except the product obtained from [EMIM-Cl][NiCl<sub>2</sub>].

#### **Data Availability**

The data for all results are included in the manuscript.

#### **Conflicts of Interest**

The authors declare no conflicts of interest.

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