A green approach for phenol synthesis over Fe^{3+}/MgO catalysts using hydrogen peroxide

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ABSTRACT

An efficient green route for the synthesis of phenol from benzene has been reported over Fe^{3+}/MgO catalysts under mild conditions. Fe^{3+}/MgO catalysts are prepared and well characterized using EDX, XRD, FTIR, surface area analysis pore volume determination and UV–vis diffuse reflectance studies. Activity of these systems towards single step oxidation of benzene to phenol at low temperature using H_2O_2 has been analyzed. The catalysts exhibited interesting oxidizing ability which has been attributed to Fe(III) dispersed in amorphous form as isolated units on MgO. Possibility of homogeneous nature of catalysis through leached Fe^{3+} ions has been ruled out by confirming the absence of Fe^{3+} in liquid phase, and the heterogeneous nature of catalysis has been confirmed. The decomposition of H_2O_2 by the catalysts has been studied. Reusability of the system is assured carrying out multiple runs using the recycled catalyst. The activity has been analysed towards reactants with various substituents in benzene ring. A metalloperoxide formation on the surface of MgO through heterolytic cleavage of H_2O_2 has also been suggested for the reaction.

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1. Introduction

Attempts are going on in full swing to develop new efficient oxygenation catalysts for functionalizing feedstock alkanes to raw oxygen-containing chemicals. Recently, new environment friendly catalytic processes using clean oxidants like molecular oxygen or hydrogen peroxide are being explored exhaustively, which has attracted much attention. In this direction, H_2O_2 in presence of active metal oxide catalysts is extensively explored towards low temperature oxidation reactions. However, in presence of transition metal ions, the catalytic applications of hydrogen peroxide have been limited due to the self-decomposition of the oxidant. But fine dispersion of transition metal ions on suitable supports overcomes this demerit by site isolation of redox metal ions, and has been proven as an excellent catalyst for a variety of oxidation reaction [1,2]. In the present investigation, the oxidation activity of Fe(III) dispersed MgO catalysts for direct hydroxylation of benzene activated by H_2O_2 has been reported. Phenol, one of the valuable intermediates for the synthesis of agrochemicals, petrochemicals and plastics has been mainly manufactured by cumene process. But the aforesaid reaction pathway is quite tiresome as it is marked by a multistep process and production of byproduct. Hence synthesis of phenol by direct hydroxylation of benzene in liquid phase is attrac-

tive both economically and energetically. Heterogeneous catalytic systems studied to this effect at elevated temperatures include ZSM-5 system using N_2O [3,4]. Various solid systems under mild conditions have been studied for the same which include Ti/MSM-41 system [5], TS-1 [6] and supported metal oxides in various solvents [7,8]. Heteropoly acids have been analysed for their oxidation activity in the presence of peroxide [9,10]. Other related works on the concerned reaction include supported transition metal oxide systems [11], vanadia based systems [12], poly acids [13,14], Fe(III) complexes [15] etc. Recently, Monfared et al have studied hydrogen peroxide oxidation of benzene over Fe^{3+}/Al_2O_3 systems and have obtained considerable activity [16]. This prompted us to explore Fe/MgO for the same reaction as these systems showed remarkable activity towards various oxidation reactions [17,18]. Magnesium oxide has been shown to stabilize the supported iron particles and retards catalysts sintering. In this report, the nature of iron species in the catalyst has been traced by different characterizations and attempt has been made to relate the activity data and the nature of iron species.

2. Experimental methods

The MgO carrier was prepared by heating alkaline magnesium carbonate (Merck) at 500 °C. The catalyst was prepared by stirring alcoholic solution of $FeCl_3$ (Merck) and MgO for 24 h at room temperature. The solvent was removed by filtration through a fritted funnel. The solid obtained was subsequently washed with

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Table 1
Chemical composition and physical parameters of the catalysts.

Catalyst	Elemental composition (wt%)		Surface area (m²/g)	Pore volume (cm³/g)
	Mg	Fe		
MgO	100	0	91	0.12
1 Fe/MgO	99.02	0.98	136	0.19
2 Fe/MgO	98.10	1.90	161	0.22
4 Fe/MgO	96.20	3.80	165	0.20
8 Fe/MgO	92.31	7.69	124	0.18
12 Fe/MgO	88.26	11.74	111	0.16

methanol and dried overnight in air oven at 110 °C. The prepared catalysts were named according to the wt% of iron in the system. Thus, 1 Fe/MgO, 2 Fe/MgO, 4 Fe/MgO, 8 Fe/MgO and 12 Fe/MgO stands respectively for systems containing 0, 1, 2, 4, 8, and 12 wt% of Fe in MgO. The catalysts were used without any pretreatment.

The chemical composition of catalysts was obtained from Stereoscan 440 Cambridge, UK energy dispersive X-ray analyzer used in conjunction with SEM. Powder X-ray diffraction pattern was collected using Rigaku D-Max Ni fitted with Cu Kα radiation. Micromeritics Gemini Surface Area analyzer was used to determine the BET surface area and pore volume by N_2 adsorption at 77 K. Fourier Transform Infrared spectra of the heat treated samples were obtained by KBr disk method over the wavenumber range 400–4000 cm^{-1} using Jasco FTIR-4100. DR UV–vis spectra were taken in the range 200–800 nm with $BaSO_4$ as reference using Jasco V-550 spectrometer.

Commercially available benzene and acetonitrile of the highest grade (Merck) were used without further purification. Hydrogen peroxide (35% in water) was purchased from Fluka and its concentration was determined according to the standard procedure. Activity studies were performed in a in a R.B. flask, fitted with a reflex condenser. In a typical experiment, a solution of benzene (1.46 mmol) containing catalyst (0.2 g) in acetonitrile (6.0 ml) was allowed to attain the reaction temperature (60 °C). Required amount of (8.76 mmol) 35% H_2O_2 was added, and the mixture was stirred for 6 h. Catalyst was filtered and the filtrate was dried over magnesium sulfate, and was analysed by Chemito 1000 GC equipped with flame ionization detector containing BP-1 capillary column. Analysis condition was programmed from 60 °C to 3 min, 20°/min to 280 °C with injection and detection temperature of 200 °C. Conversion and selectivity were calculated by comparing with relative area of each of authentic samples, which is proportional to the concentration of the substance. The selectivity for a particular product = (yield of the particular compound/total product yield) × 100. Each reaction was carried out in duplicate in order to check reproducibility.

3. Results

The catalyst after loading with Fe was slight yellowish and the colour was intensified as the weight percentage of iron increases in the supported systems. Chemical composition and the physical characterization data is presented in Table 1. It can be seen that the surface area showed an initial increase followed by a drop at higher amounts of Fe(III). The pore volume values also followed the same trend. The similar trend of both the parameters may be due to the concomitant effect of the structural variation of MgO as hinted by the XRD pattern, and the fine dispersion of iron species on the support.

The XRD pattern of pure MgO and ferric ion impregnated MgO are provided in Fig. 1. The diffraction profile of magnesium oxide was rather amorphous, and the addition of Fe(III) increased the crystallinity of the sample as evident from the XRD pattern. Only peaks characteristic of MgO were observed, which gave prominent

reflections at 42.9° and 62.1° (JCPDS 4-829). It is quite evident that no signs were observed for the presence of Fe_2O_3 crystals in all the catalysts. Contradictory to earlier reports, peaks due to $MgFe_2O_4$ of spinel variety was also absent in the samples [19].

The following observation can be gathered from the FTIR spectra of the thermally treated samples provided in Fig. 2. The broad band at 1500–1600 cm^{-1} justifies the presence of physisorbed water in the samples. In the case of pure Magnesium oxide, hydrogen bonded OH appeared ~3440 cm^{-1} region and a sharp band was noticed at 3697 cm^{-1} region, indicating the existence of isolated OH groups without mutual hydrogen bonding interaction. The intensity of the latter diminished with increase in percentage of Fe in the catalysts. The participation of surface hydroxyl groups in bond formation with the dispersed, active surface species has already been established. Both hydrogen bonded and isolated hydroxyl groups may be participating in the creation of Fe–O bond formation. The aforesaid bond gives rise to the broad band seen around 1070 cm^{-1} [20,21]. Another band characteristic of iron species appeared at 470 cm^{-1} in the case of impregnated samples corresponding to the stretching vibration of Fe–O which arises from tetrahedrally coordinated iron atom [22]. Hence, XRD data and FTIR spectral analysis results when considered together hints to the possibility of Fe(III) existing as isolated amorphous tetrahedral species in the catalysts.

Further confirmation about the nature of dispersed iron was attained from Diffuse Reflectance UV spectral studies (Fig. 3). Pure
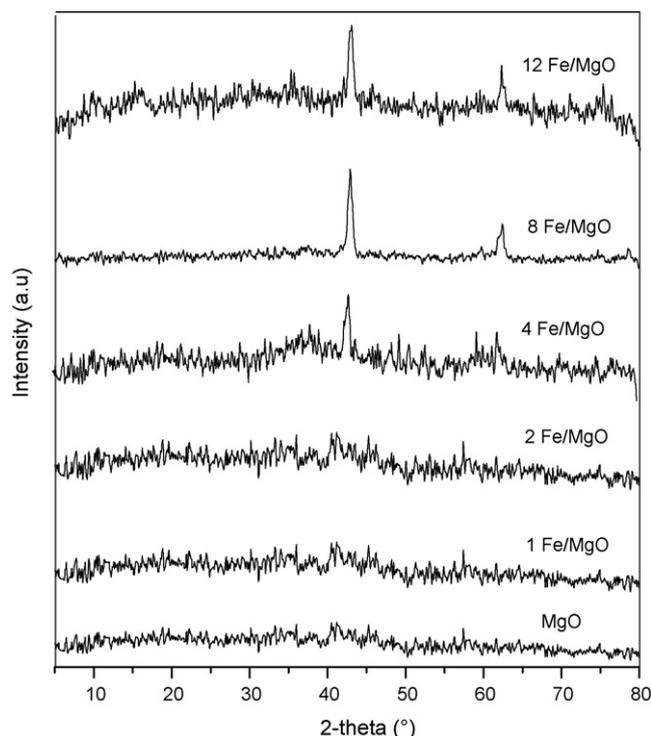
Fig. 1. X-ray diffraction patterns of support and Fe dispersed systems.
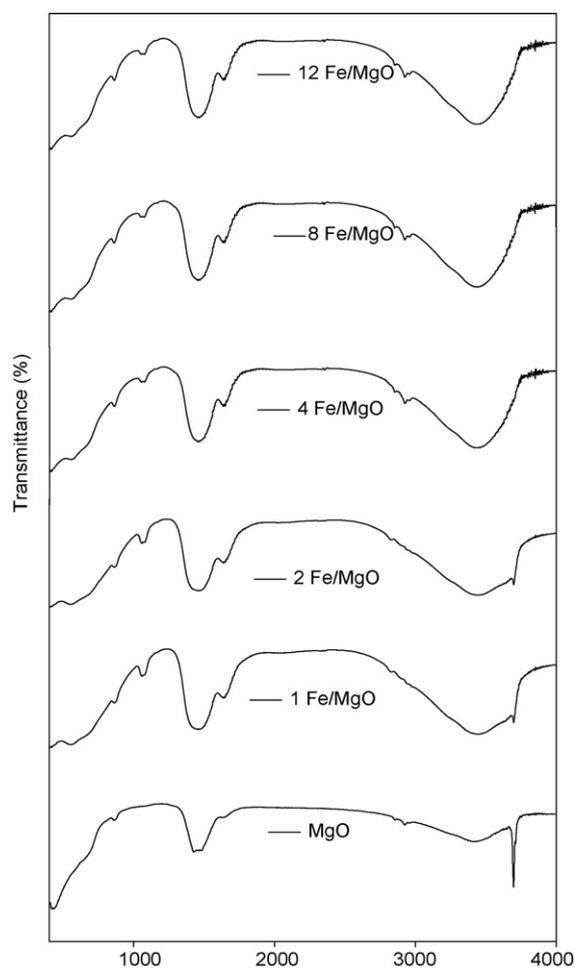
Fig. 2. FTIR spectral pattern of the catalysts.

Fig. 3. Diffuse reflectance UV spectra of the various systems.

MgO support gave no reflectance peaks in the selected spectral region of 200–800 nm. Occurrence of isolated tetrahedral Fe^{3+} in the iron loaded magnesium oxide is quite evident from the band observed at 260 nm, since Fe_2O_3 crystals if present will show absorbance at higher wavelength region [23]. Figure reveals that bulk Fe_2O_3 gives rise to a broad band in the range 320–700 nm, having strong maxima at 560 nm and at 660 nm. Hence it is confirmed that Fe^{3+} is well dispersed over magnesium oxide up to 12 Fe/MgO sample. The position of this band exhibited slight red shifts as the iron content in the catalysts increased. All the above mentioned analytical techniques pave way to the remark that isolated Fe(III) in tetrahedral geometry is present in the impregnated analogues up to 12 wt% Fe incorporation in MgO.

Mild condition of the reaction assures the absence of over oxidation products to a large extent. Temperature above 80 °C causes decomposition of H_2O_2 and hence it is always desirable to select low reaction temperature. Screening experiments were performed at various conditions to optimize the reaction parameters. Temperature range 40–80 °C were tried out for the reaction. Best results were obtained at 60 °C. Obviously, the data presented in Table 2 show that Fe^{3+}/MgO systems are efficient for the oxidation of benzene in presence of H_2O_2 and 100% phenol selectivity was noticed over these systems. Even though the reaction temperature is higher than the normal decomposition temperature of hydrogen peroxide, no over oxidation product has been noticed over the catalysts. Similar reports exist in literature in the concerned reaction reported over metal oxide systems [7,16]. This may be ascribed to the decomposition of H_2O_2 by catalysts, which rules out the possibility of

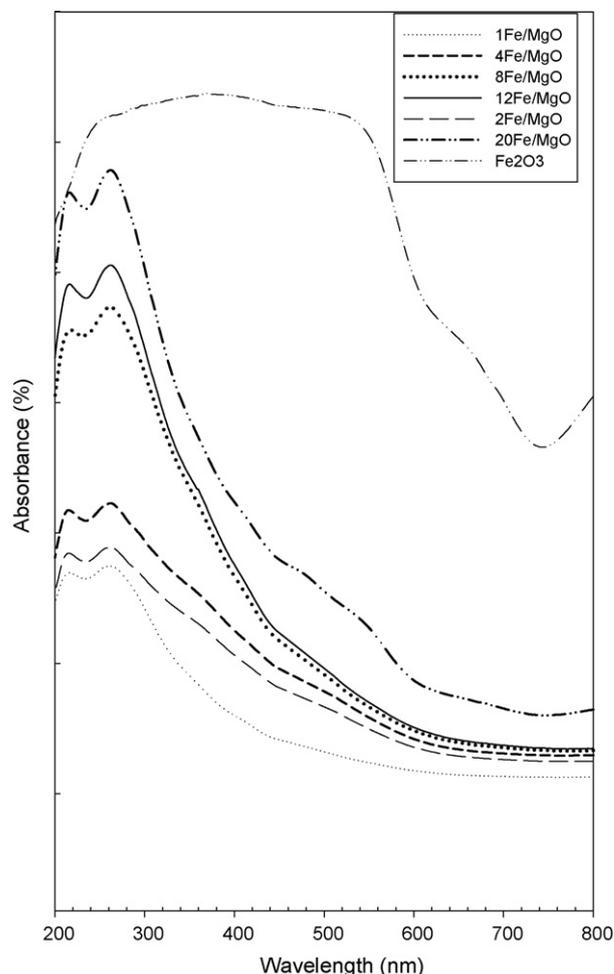excess oxidant. The results of preliminary experiments showed that the oxidising moiety has not been generated from hydrogen peroxide in the presence of MgO or Fe_2O_3 alone. No phenol yield has been obtained when the reaction was carried over iron dispersed catalyst, and hydrogen peroxide in the absence of catalyst also was inactive for the reaction. The reaction was carried out in different solvents with an aim to study the influence of polarity of solvents on the reaction; acetonitrile; $\varepsilon = 36$, dichloromethane; $\varepsilon = 8.93$, and carbon tetra chloride; $\varepsilon = 2.2$ were the solvents used (ε: dielectric constant). Out of the there solvents selected, the activity was maximum in the most polar solvent, acetonitrile. Probably the reaction may be taking place through an ionic intermediate, which is most stabilized in a solvent of highest polarity. Thus acetonitrile has been fixed as the solvent medium for the present study.

Table 2
Benzene hydroxylation data over Fe(III) doped catalysts.

Catalyst	Benzene conversion (%)	Phenol (%)
Fe1	18	100
Fe2	24	100
Fe4	27	100
Fe8	31	100
Fe12	36	100
Fe20	28	100

Catalyst: 0.2 g; acetonitrile: 6 ml; benzene: 1.46 mmol; temperature: 60 °C; time: 6 h.

Table 3
Activity of the catalyst for various reactants.

Reactant	Conversion (%)	Products (%)		
Toluene	41	o-Cresol (50%)		p-Cresol (50%)
Benzene	36		Phenol (100%)	
Chlorobenzene	28	o-Chlorophenol (56%)		p-Chlorophenol (44%)

Reaction conditions: 12 Fe/MgO: 0.2 g; acetonitrile: 6 ml; benzene: 1.46 mmol; H_2O_2: 8.76 mmol; temperature: 60 °C; time: 6 h.

4. Discussion

The ability to initiate oxidation of benzene in the presence of oxidizing agent increases with increase of Fe in the catalysts as obvious from Table 2. The species dispersed on MgO are confirmed to be isolated Fe(III) by various techniques and the increase of isolated species upon increase in iron loading also has been established. Hence the active centers for catalytic oxygen transfer attributable are isolated Fe^{3+} species, which is in agreement with the reports of Monfared and Amouei [16]. Analogous cases of activity for isolated metal species for oxidation of aromatic hydrocarbons in presence of hydrogen peroxide have been established in literature [24]. For further verification, the percentage of iron species in MgO was enhanced to 20 (designated as 20 Fe/MgO) where crystals of Fe_2O_3 appeared in the catalyst and the activity study was carried out. Reduced oxidation activity was observed as anticipated (Table 2), since bulk metal oxide was inactive for the purpose. Diffuse reflectance UV spectra of 20 Fe/MgO provided in Fig. 3 clearly offer confirmation for the presence of crystalline iron oxide via the reflectance band at 560 nm region, which was characteristic for aggregated Fe_2O_3. This conclusion was also confirmed by the XRD pattern of the sample which showed peaks characteristic of Fe_2O_3 crystals (not included in the text). The catalytic activity in terms of turn over number increased as the wt% of Fe(III) increased in the catalysts. The turn over numbers were 7.4, 12.2, 18.0, 21.6, 27.5 and 17.8 for 1 Fe/MgO, 2 Fe/MgO, 4 Fe/MgO, 8 Fe/MgO, 12 Fe/MgO and 20 Fe/MgO respectively, which again establishes the upper hand of isolated Fe(III) species in catalyzing the reaction. A comparison attempted with results reported in literature revealed that the catalytic activity of the present system was almost the same as obtained over Fe/Al_2O_3 system [16] under similar experimental conditions (about 27% conversion with catalyst containing ~0.04 mmol Fe^{3+}).

As it was observed that the activity was enhanced with an increase in the amount of peroxide in the reaction mixture, the percentage conversion of hydrogen peroxide over the catalysts was studied by analyzing non-productive decomposition as reported earlier [24]. Hydrogen peroxide conversion gradually increased with the amount of iron in the catalysts and the conversion percentages were 50, 66, 75, 80, 83 and 92 respectively for 1, 2, 4, 8, 12 and 20 wt% Fe(III) loaded samples. Non-productive decomposition of major portion of the peroxide is evident as the conversion of hydrogen peroxide exceeded significantly that of benzene. Higher hydrogen peroxide decomposition over 20 Fe/MgO can also be factor for the observed reduced activity of the system, which also indirectly hints to the presence of clustered Fe(III) in the sample. Hence gathering evidences from all these, the conclusion can be made that the fraction of iron which is present as isolated species has a decisive role in the catalytic activity.

The most important and attractive feature of heterogeneous catalytic system is the reusability of the catalysts. Fe/MgO system has been checked to this effect, after filtering and washing the catalysts by methanol. The conversion percentages were 18, 23, 26, 30, 36 and 27 for 1 Fe/MgO, 2 Fe/MgO, 4 Fe/MgO, 8 Fe/MgO, 12 Fe/MgO and 20 Fe/MgO systems respectively. It is evident that no much deactivation was noticed as the catalyst maintained the almost the same activity. The possibility of leaching of Fe^{3+} ions to liquid phase is ruled out by this observation, which was again confirmed through the control experiment as described below. The catalytic system in acetonitrile was filtered so that supported iron was removed from the liquid phase. Benzene and H_2O_2 were added and the reaction was carried out to yield nil conversion of benzene. Hence the possibility of homogeneous catalysis is completely ruled out here.

Finally, the oxidation activity of iron dispersed MgO system towards reactants carrying different side chains in the benzene ring has been examined under similar experimental conditions over 12 Fe/MgO system, which was observed as the most active among the series. Toluene and chlorobenzene constitute the two reactants that are selected. From the data provided in Table 3 it can be inferred that, the system has enhanced activity towards the reactant when weak electron-donating groups exist in the ring. It was difficult to oxidize the side chain in the case of toluene. The methyl substituent is a weakly electron-donating group which, when attached to a benzene ring, renders it more susceptible to an electrophilic attack at the ortho and para-positions. Such a result suggests that hydroxylation of the aromatic ring occurs according to an electrophilic-like mechanism [24]. Weakly electron withdrawing chloro substituent lead to reduced activity for ring hydroxylation justifying the above statement.

As the aromatic C–H bonds are stronger than aliphatic C–H, the reaction pathway cannot be via H-abstraction by the active oxidizing moiety. In oxidation reactions using hydrogen peroxide, the cleavage of the oxygen–oxygen bond in peroxides takes either of two distinct pathways, heterolytic or homolytic. In the first case a molecule of H_2O_2 undergoes a heterolytic scission leading to ionic mechanism. In the other, a homolytic cleavage of the oxidant molecule occurs leading to radical pathway [25]. For the oxidation of aromatics with hydrogen peroxide over transition metal substituted oxides, it has been proposed that the hydroxylation of the aromatic ring occurs via the heterolytic mechanism, involving the formation of a metalloperoxide species [24,26,27]. Although no detailed mechanistic studies have been carried out in the present work, hydroxylation of the ring indicates the possibility of heterolytic cleavage in the present case. In accordance with earlier reports, a MgO–Fe(III) η^1-hydroperoxide species stabilized by hydrogen bonding between the hydroperoxide ion and the oxygen atom of support has been proposed [28]. The route can be shown as S-Fe–OOH + $C_6H_6 \rightarrow C_6H_5$-OH + S-Fe–OH (S representing the support oxide).

5. Conclusions

Fe(III) dispersed MgO catalyst systems were prepared and were characterized with various instrumental techniques. Impregnation of MgO with Fe^{3+} titrated the hydroxyl groups of the support and hence the anchoring on the surface is supposed to take place through Mg–O–Fe bond. Isolated Fe(III) dispersed on the MgO was found to be efficient for the conversion of benzene to phenol by direct hydroxylation using hydrogen peroxide. The active species are concluded to be heterogeneous supported Fe^{3+} ions. Clustered iron species were inactive for oxidation in presence of hydrogen peroxide. The catalyst system was more active towards reactants with electron-donating groups on the ring and less activity was observed for arene with electron withdrawing substituent.

A metal hydroperoxide formation on the surface through a heterolytic cleavage of H_2O_2 has been suggested for the reaction.

Acknowledgement

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