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Nanocrystalline Supported Ceria as a Highly Efficient Catalyst for The Oxidative Coupling of Thiophenol.

Vinod B Mane[1], Shobha A Waghmode[2], and Sharda P Dagade[1]*.

[1]Yashwantrao Mohite College, Bharati Vidyapeeth Deemed University, Pune (India)
[2]Aabasaheb Garware College, SP Pune University, Pune (India)

ABSTRACT

Hydrothermally synthesized nanocrystalline mixed oxide catalysts Fe/CeO_2 by using ferric and cerium nitrate as precursors. The prepared catalysts were characterized by using XRD, TG/DTG, FT-IR, FE-SEM, Raman spectroscopy, surface area and acidity by titrimetric method. The XRD confirmed the crystallite size from 9-14nm of the prepared catalysts. Nanosized of the catalysts were confirmed from FESEM data and showed good agreement with XRD data. Raman spectra revealed the incorporation of Fe on ceria support and high acidic strength were confirmed by acidity measurement technique. Ceria supported iron oxide nanoparticles are found to be efficient and recoverable catalyst in the coupling of thiophenol to their corresponding disulfides using green oxidant, hydrogen peroxide.

Keywords: hydrothermal, mixed oxides, oxidative coupling, thiophenol, green oxidant

*Corresponding author

INTRODUCTION

Mixed oxide catalysts in nano-crystalline form acts as powerful catalysts for many acid catalyzed reactions due to ready availability, cheaper and more efficient catalysts. It is alternative to the traditionally employed metal catalysts as well as homogeneous catalysts [1-3]. Recent years, various nanoparticles are used for organic transformations with greener approach. Among these nanoparticles iron oxide acts as one of the green catalysts in many reactions such as oxidations [4-5], C-C and C-hetero atom couplings [6], alkylations [7], and Fischer-Tropsch reaction [8].

Different kinds of the homogeneous catalysts such as solvent free potassium permanganate [9], hydrogen peroxide [10], cerium (IV) salts [11], chlorochromate [12], and nitric oxide [13] and $KMnO_4/CuSO_4$ [14] were utilized for the conversion of thiols to disulfides reaction. But recycling and separation is more tedious job. To overcome this problem application of solid materials in liquid-phase catalytic reactions has recently been extensively investigated. Few studies reported use of heterogeneous catalysts for the oxidative coupling of thiols to disulfides. Few of them are nano Fe_3O_4 [15, 16], schiff base complex coated with Fe_3O_4 nanocatalyst [17], $LaFe0.9Co0.1O_3$ nanoparticles [18], PVP-capped silver nanoparticles [19], Fe@SBA-15/H_2O_2 [20], Ni-nanoparticles [21] and magnetic nanomaterials [22]. Among the nanoparticles, iron oxide nanoparticles catalyst emerged as the green catalyst, due to their low toxicity, easy work up procedure and interesting activities with the mild reaction conditions [23].

While exploring the catalytic activity of nano catalysts, we have synthesized and characterized nanosized mixed oxide Fe/CeO_2 catalysts for different organic transformations. Herein we report simple and green method for oxidative coupling of thiophenol to diphenyl disulphide. Fe/CeO_2 is found to be an efficient, recyclable, and high yielding catalyst for this reaction.

EXPERIMENTAL

Materials:

All the chemicals and reagents used were pure and A.R. grade. The XRD was carried out on a Rigaku Miniflex X-ray diffractometer with Cu Kα-line radiation source (λ= 1.54A°) scanning rate of 0.020 /s was applied to record the pattern in the 2Ɵ range of 20- 80°, Raman spectra were recorded on LabRAM infinity spectrometer (Horiba-Jobin-Yvon) equipped with a liquid nitrogen detector and a frequency doubled Nd-YAG laser supplying the excitation line at 532 nm with 1-10 mW power. The BET surface area of the prepared catalyst was determined by N2 sorption at -196°C using NOVA 1200 (Quanta Chrome) equipment. Prior to N_2 adsorption and evacuated at 300°C under vacuum condition. Acidity of the prepared catalysts was tested by using titrimetric method. The morphological and elemental analysis was carried out on FESEM instrument FEI, Model NOVANANOSEM-450 microscope, operating with an accelerating voltage of 20 KeV. GC-2014 Shimadzu used for the monitor the reaction samples having Flame Ionization Detector and Capillary column.

CATALYST PREPARATION

Synthesis of pure CeO_2:

Hydrothermal synthesis method used for the synthesis of pure ceria. In a 250 ml beaker 10 ml of 1 M cerium nitrate solution taken and mixed with 100 ml of 30 % H_2O_2 solution slowly under vigorous stirring in an ice bath. After 10 minute the ammonia solution was added to this mixture drop wise till the color of solution changes to dark brown. Further solution was stirred at 3000 rpm for 4 h. The precipitate obtained from the solution was aged for a day. After aging the color of the solution turned yellow. Then this solution was decanted and the wet precipitates were washed by using ethanol several times until the pH was near neutral region. The wet precipitates were filled to 80 volume % in a teflon vessel held in an outer pressure vessel made of stainless steel. After the vessel was sealed, it was placed in a thermostatic oven and heated at 200°C for 6 h. The final products were re-washed several times with ethanol and dried at 80°C for 12 h and sample was calcined at 500°C for 5 h. Finally the calcined powder was used for the further characterization [24-25].

Synthesis of various wt. % loading of Fe on CeO_2 catalysts:

For the synthesis of Fe supported on ceria catalyst, the 10 ml aqueous ferric nitrate solution was added to the 10 ml solution of cerium nitrate and then rest of the procedure was repeated same as above.

Oxidative coupling of thiophenol:

Liquid phase oxidative coupling of thiophenol to diphenyl disulfide reaction was carried out as follows and shown in fig.1. The 50 ml round bottom flask contains solution of thiophenol:H_2O_2 (2:6 mmol) molar ratio, freshly prepared catalyst 0.300g (activated at 200°C for 2 h) using acetonitrile as solvent. The temperature of the reaction was maintained by using oil bath. The mixture was continuously stirred by using magnetic stirrer. The samples were periodically withdrawn by syringe, extracted with diethyl ether. Finally product was analyzed and quantified by Gas Chromatography (GC-2014 Restek, Rtx®-5, Cross bond ® 5% diphenyl / 95% dimethyl polysiloxane capillary column and FID detector). The catalyst was separated by filtration, washed with acetone, heated in an oven at 100°C for 5 h and reused for recycle experiments.

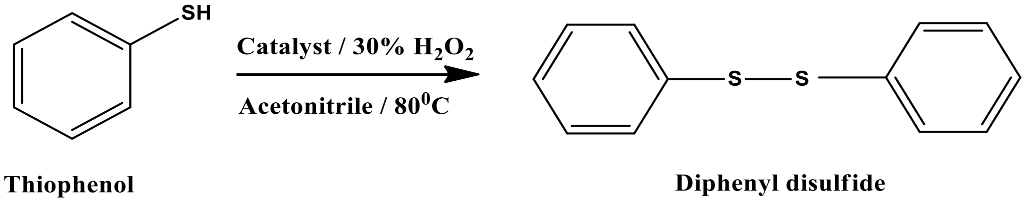


Fig 1: oxidative coupling of thiophenol

RESULTS AND DISCUSSION

XRD:

The XRD pattern of pure CeO_2 and various loading of Fe/CeO_2 catalysts calcined at 500° C for 5h are depicted in fig. 2. All the prepared catalysts synthesized by hydrothermal method were showed highly crystalline nature. The pure CeO_2 mixed oxide showed intense peak at 2ϑ=28.83º, 33.2º, 47.9º, 56.7º, 59.4º, and 70.09º corresponding to (111), (200), (220), (311), (222) and (400) planes respectively. The XRD patterns of pure CeO_2 was compared with the standard data (JCPDS File No. 34-0394) exhibit face centre cubic fluorite structure and no other obvious peak was observed in the powder pattern [26-27]. Furthermore, according to full width at half maxima (FWHM) of (111) reflection plane, the average crystallite size for pure CeO_2 particle was calculated to be 17 nm based on Debye-Scherer equation [28- 29].

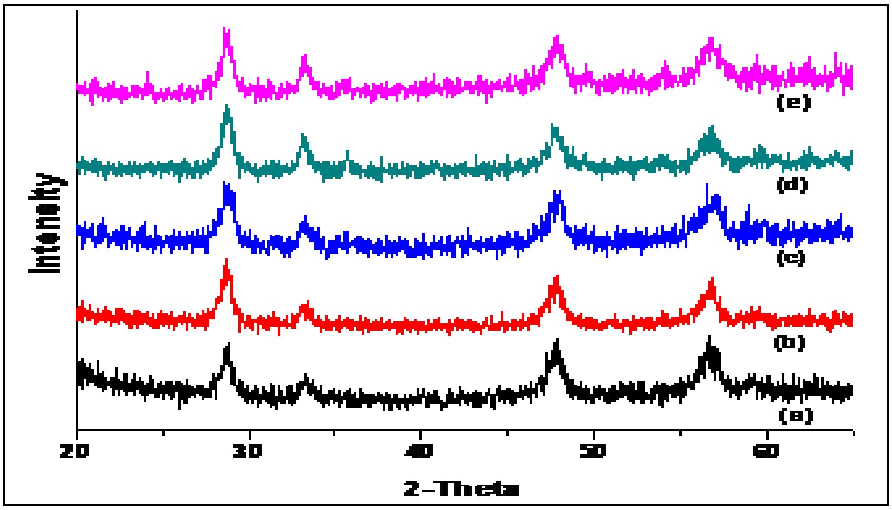


Fig 2: XRD pattern of (a) 0.1, (b) 0.3, (c) 0.5, (d) 0.8, (e) 1.0 wt. % Fe/CeO_2 mixed oxide catalyst

The measured diffraction angles were consistent with the standard XRD patterns of CeO_2, with extra peak of Fe_2O_3 indicating the incorporation of Fe on CeO_2. The prepared Fe/CeO_2 mixed oxide catalysts were showed characteristic peaks for iron oxide material corresponds to (012), (200), (110), (113), (024), (116), (214), (300) planes on CeO_2 support. The obtained XRD peaks confirms the formation of α-Fe_2O_3 over the surface of CeO_2 catalysts in accordance with JCPDS File No. 86-0550. Therefore, with increasing the concentration of Fe content over ceria lattice, decreases the crystallite size was observed. This was due to the insertion of anharmonicities in the ceria lattice structure by the foreign ion. After addition of Fe content over support ceria, the average crystallite size was reduced from 17 nm to 9-14 nm range. Therefore, it can be concluded that loading on CeO_2 catalyst with Fe^{3+} can hinder the crystallite growth and such supports the observance of reduces the crystallite sizes [30-31].

Raman Spectra

Raman spectroscopic analysis after calcination allowed us to have a better insight of the exact nature of deposited iron oxide species over CeO_2 support. The Raman spectra of all the prepared mixed oxide catalysts are shown in the fig. 3. Raman spectra useful for the determination of the CeO_2 stretching and observed the α-Fe_2O_3 phases in the prepared pure CeO_2 and various wt. % loading of Fe/CeO_2 catalysts respectively.

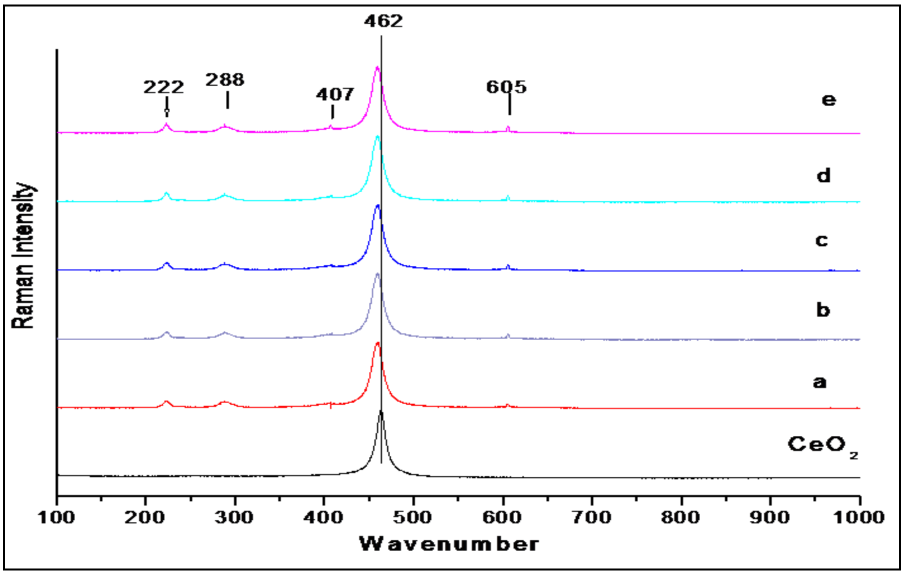


Fig 3: Raman spectra of pure CeO_2, a) 0.1, b) 0.3, c) 0.5, d) 0.8, and e) 1.0 wt. % of Fe/CeO_2 mixed oxide catalysts

Raman spectrum in prepared various wt. % loading of Fe (0.1, 0.3, 0.5, 0.8, 1.0) on CeO_2 mixed oxide catalysts corresponds to that of α- Fe_2O_3, exhibiting four bands at 222, 288, 407 and 605 cm^{-1}. These observed peaks matched with the reported data [32-33] showed Fe-O vibration stretching. With increasing the Fe content in the catalyst, decreases the intensity of pure CeO_2 catalyst peak. As compared to pure CeO_2 spectrum, the intense band of pure CeO_2 at 462 cm^{-1} slightly shifted towards 459 cm^{-1} which was observed in the prepared Fe/CeO_2 catalysts shown in fig. 2. Therefore in Fe/CeO_2 catalysts, the F_{2g} band shifts towards lower frequencies and becomes broader on increasing the Fe content probably due to the Ce-Fe interaction.

BET Surface Area Measurement:

The BET surface areas of pure CeO_2 and various wt. % loading of Fe on CeO_2 mixed oxide catalysts calcined at 500°C are presented in table-1. All the prepared mixed oxide catalysts in present study exhibited reasonably good surface area due to their nanosized nature. In case of pure CeO_2 support catalyst, observed surface area of about 43 m^2/g. After loading of various wt. % loading of Fe on CeO_2 catalyst, decreasing trend surface area was observed. The specific surface area value of 0.1 to 1.0 wt. % Fe/CeO_2 catalysts were decrease from 77.21 to 32.68 m^2/g respectively. The observed specific surface area may be due to the formation of Fe-

O-Ce linkages, resulting in the formation of porous material. The sample with higher Fe content exhibited a lower surface area, may be, due to an increasing size of supported Fe particles or plugging of the pores of the supports with iron oxide species [34].

Table 1: Acidic Strength and BET surface area of prepared mixed oxide catalysts

Catalysts	Acidic Strength (mmol/g)	S_{BET} (m^2/g)	Pore Volume (cc/g)
Pure CeO_2	1.217	43	0.289
0.1 wt.% Fe/CeO_2	2.909	77.21	0.228
0.3 wt.% Fe/CeO_2	3.000	65.73	0.245
0.5 wt.% Fe/CeO_2	3.143	55.56	0.260
0.8 wt.% Fe/CeO_2	3.550	34.47	0.258
1.0 wt.% Fe/CeO_2	3.238	32.68	0.273

Acidic Strength Measurement:

Titrimetric experiments were carried out to determine the acid strength of the prepared ceria catalysts were depicted in the table-1. The pure CeO_2 catalyst showed the lowest acidic strength at 1.217 mmol/g which indicated the presence of weaker acid strength. Among all the Fe/CeO_2 catalysts, 0.8 wt. % Fe/CeO_2 loading was showed the highest acidic strength (3.550 mmol/g) as compared to other prepared catalysts. Therefore with increase the Fe content on CeO_2 support decreases the crystallite size which helped to increases the acidic strength which enhances the catalytic activity. Therefore nano crystallite size of the catalysts enhances the acidity. Thus more the acidic strength showed excellent catalytic performance.

FESEM Analysis:

All FESEM micrographs indicated that, the prepared mixed oxide catalysts have spherical shape of particles [35-36] as shown in fig. 4. With increasing content of Fe over the surface of CeO_2, the particles appeared to be slightly smaller and homogeneity of agglomeration of the particles was observed having average particle size distribution between 9-14 nm.

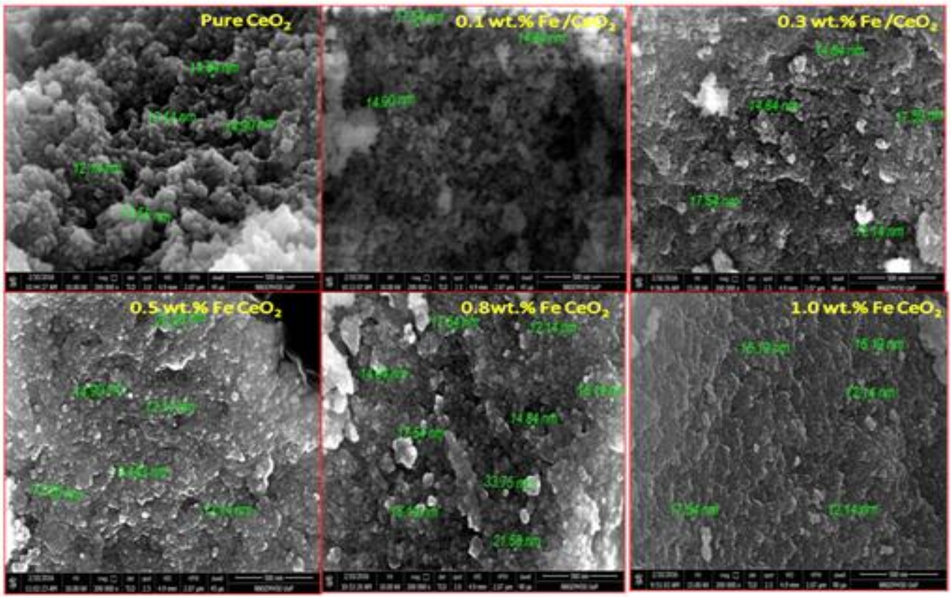


Fig 4: FESEM images of prepared mixed oxide catalysts

Therefore hydrothermal method was more efficient to form the uniform structure of the prepared mixed oxide catalysts. The results are consistent with the results of crystallite size from XRD analysis which revealed the nano particle sizes for all catalysts.

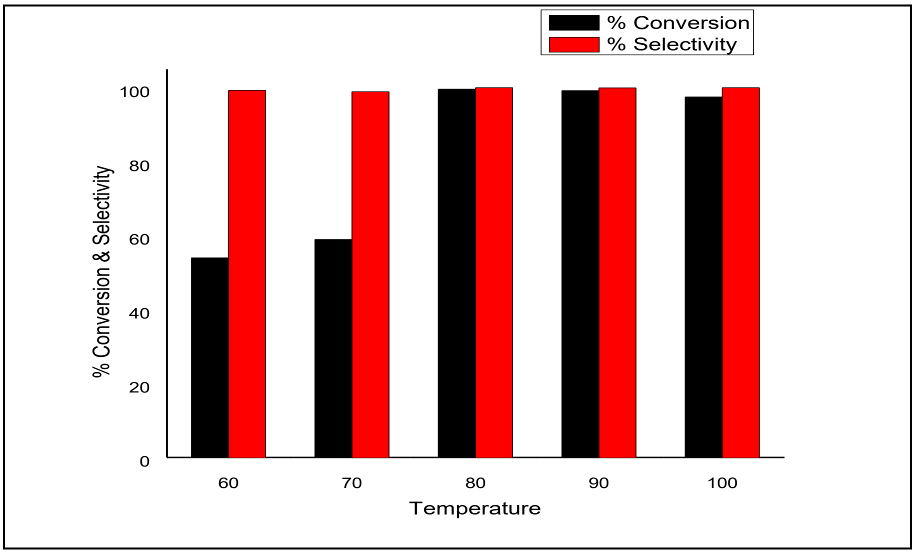
Catalytic reaction:

The results were obtained by liquid phase oxidative coupling of thiophenol to diphenyl disulfide using H_2O_2 as oxidant in presence of various parameters studied such as influence of temperature, oxidant ratio, catalyst amount, various catalysts and solvents as follows.

Influences of various reaction parameters:

Effect of temperature:

The investigation of influence of temperature on the rate of oxidative coupling of thiophenol over prepared catalyst in the range of 60-100°C was shown in fig. 5 under identical reaction conditions. As the temperature increased, the conversion was found to increase. Low conversion of thiophenol was observed at 60° and 70°C of about 54% and 58.90% respectively. With significant change in conversion (99.58%) was observed at 80°C indicating effect of temperature. With increasing the temperature above 80°C to 100°C the slightly decrease of conversion occurred but gave 100% selectivity for product. This may be due to decomposition of hydrogen peroxide at higher temperature. Therefore, overall reaction was optimized at 80°C.



Reaction condition: thiophenol/oxidant- 2/6mmol, ACN-10ml, Catalyst-0.3g

Fig 5: Effect of temperature on oxidative coupling of thiophenol

Effect of various catalysts:

The results of oxidative coupling of thiophenol using H_2O_2 as oxidant over various solid acid catalysts under similar experimental conditions were given in the table-2. Among all the catalysts studied, the 0.8 wt% Fe/CeO_2 catalyst showed higher conversion (99.58%) and selectivity (100%) for diphenyl disulfide. When the reaction was carried out for pure CeO_2 catalyst, the conversion was negligibly low (8.43%) suggesting the acidic strength of CeO_2 was lower than Fe/CeO_2 solid acid catalysts. Reaction was carried out without catalyst which showed no conversion.

Table 2: Effect of various catalysts on oxidative coupling of thiophenol

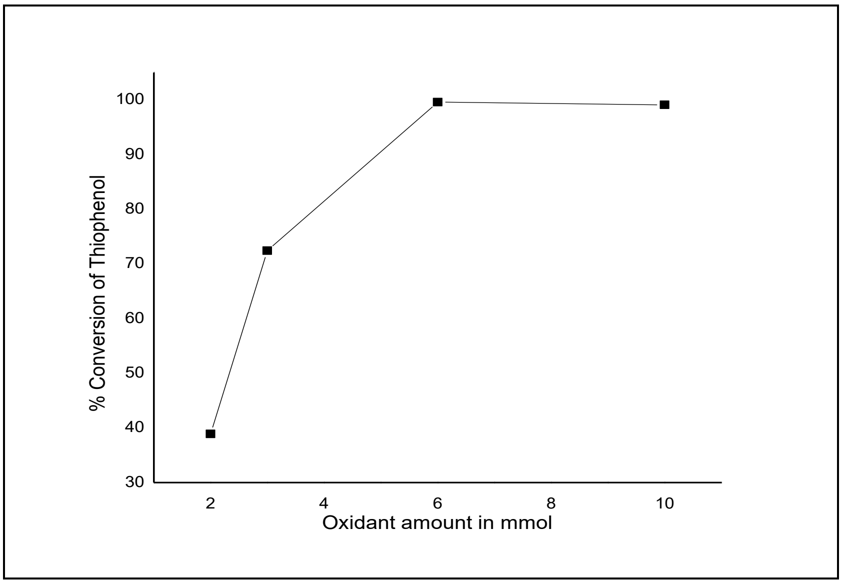
Catalyst	Conversion of thiophenol	% Selectivity of diphenyl disulfide
Without catalyst	No reaction	-
Pure CeO_2	8.43	90.56
0.1 wt.% Fe/CeO_2	61.43	100
0.3 wt.% Fe/CeO_2	79.35	99.94
0.5 wt.% Fe/CeO_2	85.71	100
0.8 wt.% Fe/CeO_2	99.58	100
1.0 wt.% Fe/CeO_2	97.22	99.99

Reaction condition: thiophenol/oxidant- 2/6mmol, ACN-10ml, Catalyst-0.3g. Temp.- 80°C.

The conversion of thiophenol from 0.1 wt.% Fe/CeO_2 to 0.8 wt.% Fe/CeO_2 was observed in increasing trend from 61.43 to 99.58% respectively, while with 1.0 wt.% Fe/CeO_2 catalyst was showed slight decrease in conversion i.e. 97.22%. Similarly acidic strength also increases from 0.1 to 0.8 wt. % Fe/CeO_2 catalysts while acidic strength for 1.0 wt. % Fe/CeO_2 catalyst was decreased slightly. Same trend was observed in the conversion of thiophenol. Therefore acidic strength was responsible for the increasing the catalytic performance. So for the further study 0.8 wt. % Fe/CeO_2 solid catalyst was optimized.

Effect of oxidant:

The influence of oxidant amount on the oxidative coupling of thiophenol reaction was studied over prepared solid acid catalyst was shown in fig. 6. The reaction were carried out under previously optimized conditions and changing the volume of H_2O_2 from 2, 3, 6 and 10 mmol, while keeping the substrate thiophenol constant.



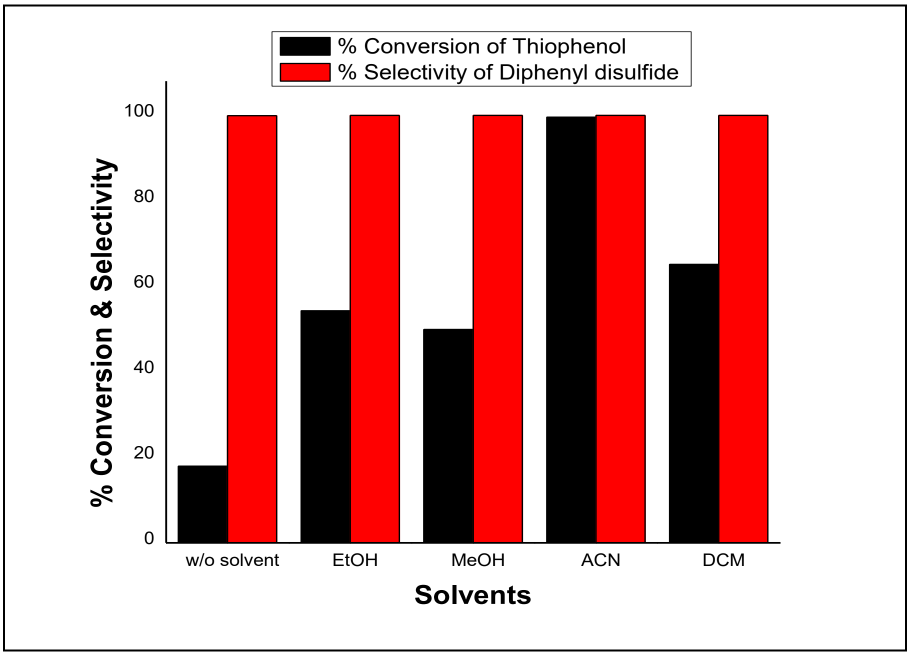
Reaction condition: thiophenol- 2mmol, ACN-10ml, Catalyst-0.3g, Temp.-80°C.

Fig 6: Effect of oxidant on oxidative coupling of thiophenol

Without oxidant, reaction does not show any conversion but in the presence of oxidant higher conversion was observed. The conversion increases from 38.90% to 99.58% upon changing the H_2O_2 amount from 2 to 6 mmol respectively. An increase in H_2O_2 leads to a continuous growth of thiophenol oxidation was takes place, reaching a maximum conversion value of 99.58% of thiophenol to H_2O_2 molar ratio at 2:6. The oxidation did not change much with increase in ratio from 2:6 to 2:10. However, a decrease in thiophenol selectivity occurred for 10 mmol oxidant value up to 97.7% .This decrease in thiophenol can be due to the increased formation of water in the reaction mixture, resulting in lowering of solubility, and/or to over-oxidation reactions of thiophenol to the byproducts at higher oxidant ratio. Therefore, 6 mmol oxidant was optimized for the further oxidation reaction.

Effect of solvent:

The various solvents like ethanol (EtOH), methanol (MeOH), acetonitrile (ACN) and dichloromethane (DCM) were used for the reaction at reflux temperature under optimized conditions shown in the fig. 7. The reaction of oxidative coupling of thiophenol was carried out without solvent, gave very low conversion (18%). The results indicated that, choice of solvent can have a significant effect on the performance of a reaction.



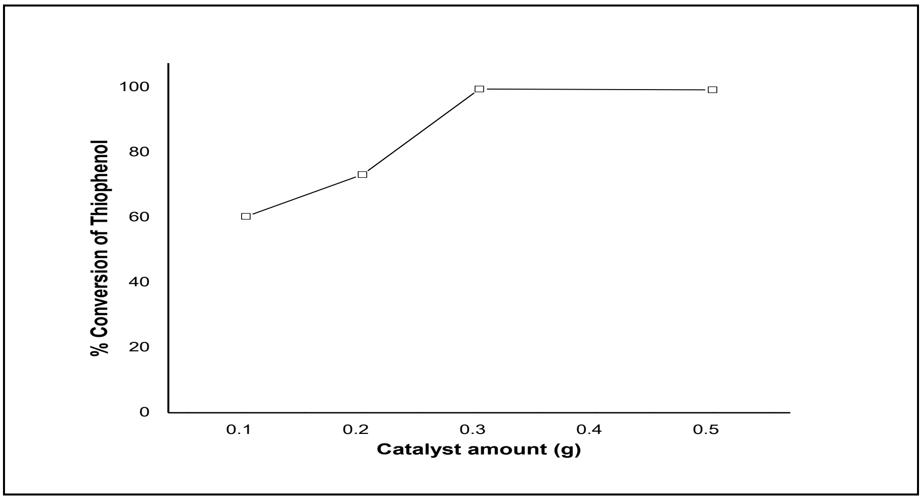
Reaction condition: thiophenol/oxidant- 2/6mmol, Solvent-10ml, Catalyst-0.3g. Temp.-80°C

Fig 7: Effect of solvent on oxidative coupling of thiophenol

The order of effect of solvent over the conversion of thiophenol were observed in the range of ACN > DCM > EtOH > MeOH > without solvent. Among all the solvents, the polar aprotic acetonitrile solvent gave better conversion as well as selectivity of about ~100%. In case of other solvents, the decrease in conversion value was due to the low solubility of hydrogen peroxide in a nonpolar solvent as a result of which the reaction could not proceed. This facilitates the adsorption of reactions on the catalyst surface and increases the conversion. Therefore further reaction was carried out by using acetonitrile as solvent.

Effect of catalyst amount:

The effect of the amount of the catalyst on the oxidative coupling of thiophenol was studied in the range of 0.1, 0.2, 0.3 and 0.5g of the catalyst given in the fig. 8 under optimized reaction conditions. It was observed that with the increase of catalyst amount the conversion of thiophenol increases. This may presumably due to the availability of more active sites of the catalyst.



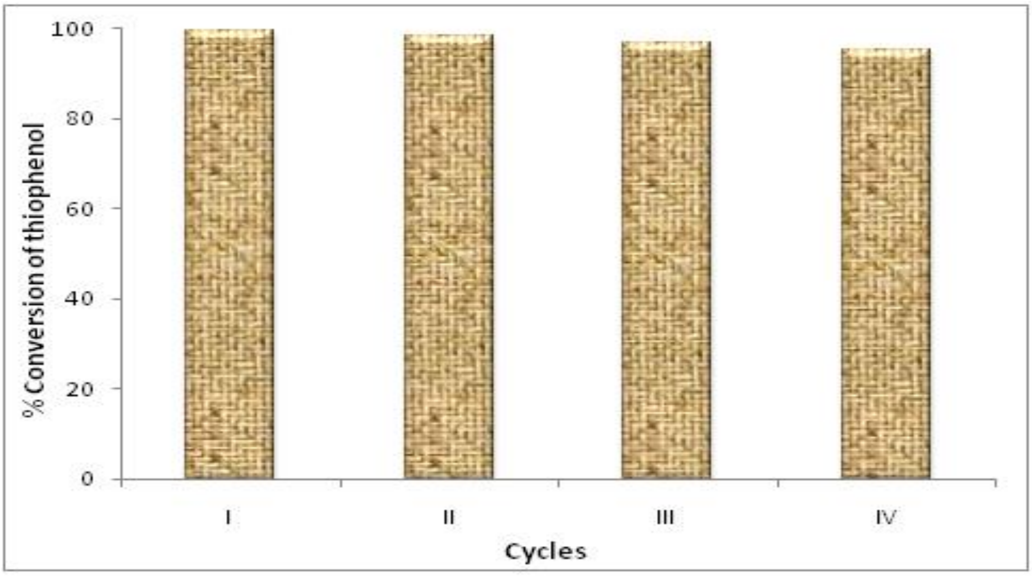
Reaction condition: thiophenol/oxidant- 2/6mmol, ACN-10ml, Temp.-80^{0}C.

Fig 8: Effect of catalyst amount on oxidative coupling of thiophenol

With increasing catalyst amount from 0.1g and 0.2g, reaction gave low conversion of thiophenol up to 60.37% and 73.25% respectively. Further increasing the amount of catalyst to 0.3g improved the thiophenol conversion to 99.58%. On increasing the catalyst concentration the number of active sites available for the reaction increases which favors the easy adsorption and desorption of reactants and products and hence increases the catalytic activity. However further increasing the catalyst amount to 0.5g the thiophenol conversion and selectivity of diphenyl disulfide product remain nearly same; which suggests that large amount of catalyst was not needed to improve the reaction product. Therefore 0.3g catalyst amount was selected for the further studies of oxidative coupling of thiophenol reaction.

Reusability:

For the recycling studies, the catalyst was separated from the reaction mixture after completion of reaction by filtration, washed with acetone, heated at 500°C for 6h, and subjected to the next catalytic run, with same molar ratio of the substrate under the optimized reaction conditions. The results were shown in the fig.9.



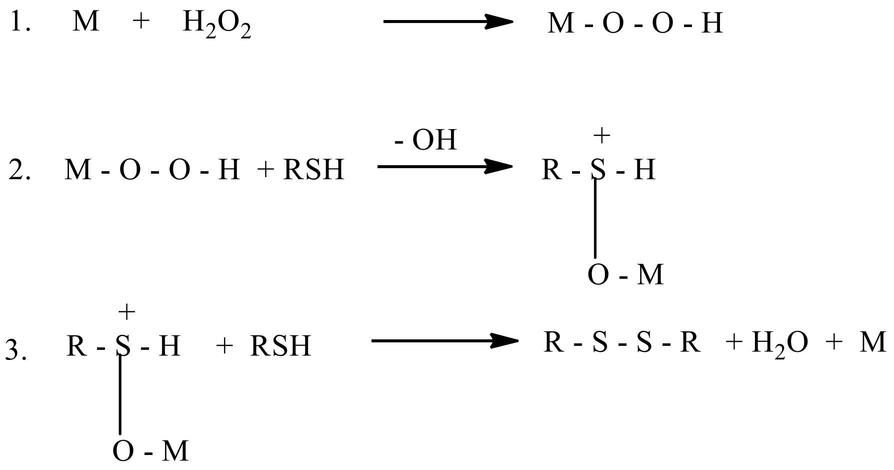
Reaction condition: thiophenol/oxidant- 2/6mmol, ACN-10ml, Catalyst-0.3g, Temp.-80°C

Fig 9: Reusability of the catalysts on oxidative coupling of thiophenol

After successive recycle and reuse of Fe/CeO$_2$ catalyst, it showed that slight decrease in conversion of thiophenol takes place but selectivity of corresponding disulfide product remains same. From the data it was clear that, recycled catalyst was gave good stability. Thus the catalyst was recycled four times without significant loss of activity.

Proposed mechanism:

The plausible mechanism for oxidative coupling of thiophenol was shown in fig.10. In this reaction, H_2O_2 formed peroxy species with active sites of catalysts. Then these species further react with thiophenol molecule to form an intermediate [37]. This intermediate coupled with another molecule of thiophenol leads to RSSR and H_2O. This might be due to the strong acidity of the Fe/CeO$_2$ catalysts.



$$1.\quad M + H_2O_2 \longrightarrow M-O-O-H$$

$$2.\quad M-O-O-H + RSH \xrightarrow{-OH} R-\overset{+}{\underset{\underset{O-M}{|}}{S}}-H$$

$$3.\quad R-\overset{+}{\underset{\underset{O-M}{|}}{S}}-H + RSH \longrightarrow R-S-S-R + H_2O + M$$

(Where, M - Fe/CeO$_2$)

Fig 10: Mechanism of oxidative coupling of thiophenol

CONCLUSION

Hydrothermally prepared pure CeO$_2$ and various wt. % loading of Fe/CeO$_2$ catalysts exhibits nanocrystalline nature. The catalysts revealed good agreement between the particle size obtained from FESEM and XRD data. Formation of mesoporous material was confirmed by BET surface area technique. The appropriate acidity of 0.8 wt. % Fe/CeO$_2$ catalyst was helpful for the excellent catalytic performance. From optimized reaction condition, it was observed that by choosing an appropriate combination of solvent and green oxidant for the reaction, to achieve not only high conversion of thiophenol (99.58%) but also the high selectivity for disulfide formation (100%). The catalyst can be easily recycled three times without any loss to confirm its reusability and stability. Easy product recovery and recycling efficiency of catalyst along with high conversion and selectivity may be useful for the synthesis of different substituted thiophenol under eco-friendly conditions.

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Conflicts of Interest: "The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper."

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