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Water-promoted surface basicity in FeO(OH) for the synthesis of pseudoionones (PS) and their analogues



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ABSTRACT

Use of Iron oxyhydroxide (γ -FeO(OH)) as a robust catalyst for the synthesis of important intermediates like pseudoionones and their analogues through the C-C bond formation reactions like knoevenagel and aldol condensation is explored. These motifs are the building blocks for the construction of the sesquiterpenes as well as the diterpenes such as retinoic acid, Vitamin A etc. Iron oxyhydroxide (γ -FeO (OH)) was synthesized and well characterized using XRD, FT-IR, TEM, XPS and adsorption studies to establish the catalytic activity. A thorough investigation on the nature of basic sites and the role of water as a promoter was explored based on dye adsorption, *in situ* methanol dissociation and CO₂ adsorption studies. The catalyst also showed a wide range of substrate scope with active methylene groups involving various functional groups such as cyanides, esters and acetophenones along with its stability and reproducibility.

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1. Introduction

Pseudoionones (PS) are special monoterpenoids used in the synthesis of industrially important chemical intermediates such as α -, β - and γ -ionones [1]. PS are synthesized in large scale by aldol condensation between citral and acetone in the presence of a base (Scheme 1) [2]. The product yields vary between 50 and 80% depending upon the reaction conditions and the catalysts used. Heterogeneous base catalysts such as alkaline metal oxides [3], basic zeolites [4], and Mg-Al hydrotalcites [5] are preferred over homogeneous bases due to non-toxicity, non-corrosion, minimal waste and recyclability. Recently, LiOH-H₂O [6], aluminophosphates (ALPO) [7], anionic clays [8], choline hydroxide/MgO [9], KF-Al₂O₃ [10] and Mg-Al mixed oxides containing rare earth elements [11] have been shown to catalyze the synthesis of PS. Among various catalysts, hydrotalcites are quite interesting as the studies on the reconstructed hydrotalcites (Mg₆Al₂(OH)₁₈·4H₂O) showed that a combination of O²⁻ (Lewis basic) and intercalated OH⁻ anions (Brønsted base) provide a high activity [12]. The presence of charge-compensating Brønsted base (OH⁻ ions) in the Mg-Al hydrotalcite matrix was shown to increase the selectivity of PS from 60% to >90% as compared to the catalysts with just O^{2-} sites. Unfortunately, these intercalated OH⁻ ions have a tendency to leach away into the solvent due to their non-covalent bonding, leading to a severe loss in the activity. Taking a cue from this work, we wanted to explore the use of Iron oxyhydroxides FeO(OH) as a catalyst for the synthesis of PS. FeO(OH) are metastable intermediates during the synthesis of iron oxides from its hydroxide gel precursors. It naturally contains abundant concentration of potential Brønsted basic sites such as -0^- and Lewis basic sites such as O²⁻ in the crystal structure (Scheme 2a). [13] Most importantly, the basic sites $(0^- \& 0^{2-})$ are chemically bonded to the metal and occur in close proximity to O²⁻ sites of FeO(OH) crystal. The structure is therefore suitable for a high and stable activity in the synthesis of PS [14]. For the first time, we report the use of FeO (OH) as stable and highly active catalyst for the synthesis of PS. In addition to that, we also provide an overwhelming evidence that H₂O promotes the catalytic activity of FeO(OH).

2. Experimental section

2.1. Materials & methods

Ferrous chloride ($FeCl_2 \cdot 4H_2O$) and Sodium hydroxide (NaOH) were purchased from Thomas-Baker. Citral and other active methylene substrates were obtained from Sigma-Aldrich.



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Scheme 1. Flowchart showing the synthesis of ionones from citral via pseudoionones [15]



Scheme 2. (a) Crystal structure of γ -FeO(OH). (b) The three coordination modes of OH on FeO(OH) surface.

Analytical grade acetone was obtained from Merck. Methanol, ethyl acetate, petroleum ether and silica gel (100–230–400 mesh) were obtained from Chem Labs, India.

2.1.1. General experimental procedure for the preparation of γ -FeO (OH)

4 g FeCl₂·4H₂O was dissolved in distilled water. To this 1 M NaOH was added until the pH of the solution reached 6.5–6.8. After reaching this pH, greenish black deposits were formed. Oxygen was bubbled through this solution for 20 min to obtain orange deposits i.e. γ -FeO(OH) which were separated by filtration and washed with ethyl alcohol and distilled water several times and dried at 60 °C. All the other control catalysts (CaO, MgO, CeO₂,

AlPO, Al_2O_3) were prepared using standard preparation methods from literature.

2.1.2. General experimental procedure for the synthesis of PS

In a 50 mL round bottom flask citral (0.152 g, 1 mmol) and acetone (0.116 g, 2 mmol) were taken along with specially dried 1,4dioxane (5 mL) as a solvent H_2O (1 mL) was used as an additive, the catalyst amount was fixed at 0.100 g. The round bottom flask was connected to a water cooled Liebig condenser which was tightly sealed at the other end to prevent any evaporation. The reaction mixture was heated up to 100 °C (reflux) in an oil bath. The reaction was monitored by using thin layer chromatography. After the completion of the reaction, reaction mixture was filtered, water removed using anhydrous MgSO₄ and the mixture was analyzed by Gas Chromatograph equipped with Mass Detector and/or isolated using column chromatography and confirmed by ¹H NMR.

2.1.3. In situ CO₂-IR & methanol dissociation studies

In situ CO₂/MeOH adsorption/dissociation Infrared Spectroscopy measurements were done using PerkinElmer 2000 Frontier FT-IR equipped with Praying Mantis[™] assembly using MCT (HgCdTe) detector. CO₂/MeOH were injected into the port from which the injected molecule was driven under nitrogen flow (50 mL/min) and adsorbed on the sample. The samples were then analyzed using the spectrum software and compared with the blank measurements.

2.1.4. Fluorescence studies using Rhodamine 6G

In a 10 mL volumetric flask, 0.002 M Rhodamine 6G solution was prepared in distilled water. 4 mL of this solution was taken and 10 mg of γ -FeO(OH) was added and the resultant mixture was stirred for 6 h at room temperature. The catalyst was then removed and the resultant filtrate was subjected to fluorescence measurements at the excitation wavelength of 500 nm and emission wavelength centered around 562 nm. The fluorescence emission spectra of Rh-6G were analyzed using PTI Quanta MasterTM steady state spectrofluorometer. The resultant FeO(OH)-Rh-6G complex was obtained by thoroughly drying over Buchi rotavap and its FT-IR was recorded and compared with bare FeO(OH) and Rh-6G solids. To quantify the amount of Rh-6G adsorbed in dioxane-water mixtures, four different solutions constituting various ratios of dioxane: water were prepared (10 mL). 20 mg of Rh-6G was dissolved in each of these and 40 mg of FeO(OH) was dispersed in 5 mL of the above prepared Rh-6G solutions and stirred at room temperature for 1 h. The fluorescence measurements were done after removing FeO(OH) and immediately quantified based on the calibration plots for the various solution mixtures.

2.1.5. FeO(OH) activation studies, hot filtration, & recyclability test

 γ -FeO(OH) activation studies were performed by taking a two neck round bottom flask containing 100 mg FeO(OH), 5 mL 1,4dioxane and 1 mL water. One neck of the flask was attached to the liebeg condenser and the other was sealed using a rubber septum. The reaction mixture was refluxed for 2 h. After 2 h of reflux, acetone and citral were introduced in the flask simultaneously using a syringe though the rubber septum. Aliquots were removed hourly and analyzed using GC–MS. For Hot filtration test, the reaction was carried out normally but in a two neck round bottom flask. The reaction was stopped after 4 h and the catalyst was filtered using a syringe filter and the supernatant liquid was further allowed to reflux without any catalyst. Recycle studies were performed by washing the filtered catalyst with 1,4-dioxane and MeOH after every cycle (12 h reaction) and then dried to be used for next cycle.

2.1.6. Material characterization

X-ray diffraction measurements were made using Phillips PAN analytical diffractometer with Cu-K α radiation (λ = 1.5406 Å). Transmission electron microscopy (TEM) images were obtained using FEI Tecnai-20ST electron microscope. Specimens of the samples were prepared by drop-casting well-dispersed isopropyl particle suspensions onto a carbon coated copper grid. The surface area measurements were performed using Quantachrome Autosorb-iQ gas sorption device. The binding energies of the elements on the catalyst were analyzed by X-ray photoelectron spectroscopy (Thermo Fisher Scientific Instruments UK, Model K ALPHA+) with

an X-Ray Source- Al K α (Monchromatic) with 6 mA beam current and 12 kV.

2.1.7. Analysis of catalysis reaction products

The catalysis reaction was monitored and quantified using Shimadzu GC–MS QP 2010 Ultra using Restek FFAP/HP-5 columns with the ion source temperature maintained at 210 °C. The injection and interface temperature were set at 220 °C. The carrier gas used was Helium. The column ramping was 20 °C/min starting from 30 °C till 210 °C with 40 min hold at the final temperature. The catalysis reaction involving different substrates were monitored on TLC (Thin Layer Chromatography) and the products were isolated using column chromatography and confirmed by ¹H NMR.

3. Results and discussion

3.1. Material characterization

The crystal structure of FeO(OH) sample was studied using Xray Diffraction pattern and was found to be consistent with the reported pattern of γ -FeO(OH) (JCPDS card no 73-2326) [16] (Fig. 1a). It has an orthorhombic structure with arrays of closepacked anions (O²⁻/OH⁻) stacked along the [1 5 0] direction and Fe³⁺ ions occupying the octahedral interstices (Scheme 2a). FT-IR spectra (Fig. 1b) showed a broad absorption band in the range of 3350–3400 cm⁻¹ due to O-H stretching characteristic of the FeO (OH) polymorph. Bands in the wave number regions of 620– 680 cm⁻¹ are due to Fe-O symmetric stretching. Characteristic bands in 750–1000 cm⁻¹ are due to —OH bending and stretching vibrations [17].

The surface composition of FeO(OH) was studied using X-ray Photoelectron Spectroscopy (XPS). Deconvoluted O1s XPS spectra (Fig. 1c) confirmed contributions due to three kinds of oxygen



Fig. 1. (a) XRD pattern of γ -FeO(OH). (b) Infrared Spectra of γ -FeO(OH). (c) Deconvoluted O1s XPS spectra. (d) Fe 2p XPS spectra of FeO(OH).

species a) oxygen involved in Fe-O-Fe (529.9 eV) b) the surface hydroxyl groups Fe-OH (531.3 eV) and c) chemisorbed and physisorbed water (532.3 eV) [18,19]. The XPS signal of Fe2p (Fig. 1d) showed two peaks due to Fe2p_{3/2} and Fe2p_{1/2} at 710.6 eV and 724.1 eV respectively. Weak satellite peaks attributed to Fe(III) ions owing to the energy transfer processes of the excited core electrons were observed around 718.0 eV due to Fe2p_{3/2} and at 732.8 eV due to Fe2p_{1/2}. The structure of γ -FeO(OH) was further probed using Thermogravimetric Analyzer (Fig. S1). The thermal decomposition profile of γ -FeO(OH) indicated weight loss due to dehydration in the low temperature region (150-250 °C) and transformation of the phase to α - Fe₂O₃ at higher temperatures (250 °C onwards) [20]. BET surface area of γ -FeO(OH) was 247 $m^2 g^{-1}$ with a pore volume of 0.58 cc g^{-1} and a pore radius of 15.8 Å (Fig. S1b). The observed hysteresis showed typical type IV characteristics which could be due to interparticle spaces.

Microstructure of γ -FeO(OH) was studied using TEM which showed rod-shaped crystals of 250–500 nm in length and 20– 50 nm in diameter (Fig. 2a, b & c). Frequently, the rods occurred in stacks as shown in the regions (I), (II) and (III) of Fig. 2a. In Fig. 2b, a magnified image of stack of rods (I) can be seen. Fig. 2c shows the high-resolution TEM image of a nanorod with clearly visible lattice fringes. The spacing between the fringes 0.33, 0.26 and 0.16 Å correspond to the (1 2 0), (0 3 1) and (1 5 1) planes of γ -FeO(OH) respectively. The electron diffraction pattern of an isolated stack of FeO(OH) indicated the single crystalline nature of the sample which could be indexed to the planes of γ -FeO(OH) (Fig. 2d).

3.2. Knoevenagel condensation

PS was synthesized by condensation of citral with acetone (and other active methylene compounds). To prevent citral from selfcondensation, the acetone and other active methylene compounds were taken twice (2 mmol) as much as citral (1 mmol). The reaction setup was sealed to prevent the formation of the oxidation product nerolic acid. A blank control experiment that involved refluxing of all the reactants for 12 h in the absence of γ -FeO (OH) catalyst (Table S2, entries 1, 2 and 3), did not show the formation of PS in solvents such as CH₃OH, CH₂Cl₂ and 1,4-dioxane at their reflux temperature respectively. Neither was any activity observed even in the presence of γ -FeO(OH) in solvents such as CH₃OH and CH₂Cl₂ (Table S2, entries 4, 5 & 6). However, the presence of γ -FeO(OH) in 1.4- dioxane showed a marginal conversion of 25%. Interestingly, when 1 mL of H₂O was added to 5 mL of 1.4dioxane solvent containing γ -FeO(OH), the conversion of the substrate increased to 96% with 100% selectivity to PS. In the absence of the catalyst, a mixture of dioxane-H₂O (5:1) as solvent showed only 12% conversion under identical reaction conditions (Table S2, entry 9). Thus, γ -FeO(OH) in the presence of H₂O was essential to achieve a high conversion of citral to PS.

We compared the reaction rates due to γ -FeO(OH) with other well-known solid bases both in the presence and the absence of water (Fig. 3a). In the presence of conventional solid bases the reaction rates remained below 0.012 mmol L⁻¹h⁻¹ even when water was used. In other words, H₂O caused a marginal decrease in the rates of the reactions when CaO, MgO, AlPO, Al₂O₃ or CeO₂



Fig. 2. (a) TEM image of γ-FeO(OH) rods. (b) High magnification TEM image of (I), encircled in Fig. 2a c) High resolution TEM images of rods in region (I) & d) Electron diffraction pattern.



Fig 3. (a) Rate of the reaction for the various catalysts screened in the presence and absence of water for the synthesis of the PS. Reaction Conditions: citral (0.152 g, 1 mmol), acetone (0.116 g, 2 mmol), specially dried 1,4-Dioxane (5 mL), H₂O (1 mL), time (12 h), reflux, sealed conditions. (b) Plot of TON Vs duration of reaction in the presence of γ -FeO(OH) with and without H₂O.

were used as catalysts. Interestingly, in the presence of water, γ -FeO(OH) showed an impressive four-fold increase in the rate of the reaction making it the most active catalyst. Turnover number (TON) gives the number of reactant molecules converted per minute per catalytic active site present on 1 g of γ -FeO(OH) under given the reaction conditions. The number of sites was calculated based on the concentration of surface –OH groups on FeO(OH) using O1s XPS spectra. The change in the TON of the reaction in the presence of γ -FeO(OH) at the end of 1, 4 and 6 h were compared with the reactions carried out in the absence of water. At the end of 1 h, TON of γ -FeO(OH) gave a value of just 15 mmol g⁻¹ in the presence of H₂O (Fig. 3b). The TON of the reaction increased with time to 161 and 258 mmol g^{-1} after 4 h and 6 h respectively. Interestingly, at the end of 4 h the increase in TON was 10-fold when the reaction was carried out in the presence of H₂O as compared to 2-fold in the absence of water. This indicated that active sites were generated on the surface of the γ -FeO(OH) by H₂O during the course of the reaction. However, generation of the active sites gradually flattened off after 4 h. A time-dependent plot of catalyst performance in the presence and absence of water is presented in Fig. 4 (trace i & iii). The dotted line shows the conversion trend in an experiment when the catalyst was filtered off under hot conditions after 6 h of reaction (Fig. 4, trace ii). Absence of further conversion indicated that there was no leaching of ions from the catalyst making a homogeneous contribution to catalysis under the reaction conditions.

The role of water as an activating agent was studied by allowing FeO(OH) to stir in dioxane-water mixture for 2 h at reflux temperature and then introducing the reactants (Fig. 4, trace iv). Interest-



Fig. 4. Study of effect of H_2O on the activation of γ -FeO(OH) (i) in the absence of water (ii) hot filtration test: flat line represents no further progress in reaction after the removal of the catalyst (iii) in the presence of water (iv) reactants introduced after 2 h of stirring FeO(OH) in dioxane-water mixture.

ingly, the conversion trends showed an improved spike with 60% conversion after just 2 h of adding the reactants. On the other hand, almost 7 h was needed to attain this conversion value, when the reactants were present from the beginning i.e. 0 h. The observation strongly suggests that H₂O plays a crucial role in activating γ -FeO (OH) by deprotonating surface —OH to form —O⁻. A surface concentration of O⁻ groups builds up over a period of 2 h which makes γ -FeO(OH) a more efficient catalyst in the condensation reaction. Water appeared to have no such promoting effect in the catalytic activity of other solid bases indicating operation of a different nature of active site on γ -FeO(OH).

3.3. Active sites

3.3.1. Basicity in FeO(OH) and role of H₂O

Our previous studies have shown that surface -OH groups on metal oxyhdroxides have a strong role in the acid-base catalyzed reactions [14,21]. To further probe the activity of surface hydroxyl groups, we studied the changes in FT-IR absorption spectra of -OH vibrations due to interactions with CO₂ molecule. It has been shown that interaction with CO₂ can alter the O-H stretching frequencies of FeO(OH) samples upto 150–175 cm⁻¹ [22]. The difference spectra (Trace iii in Fig. 5 a, b) was obtained by subtracting the absorption bands of neat γ -FeO(OH) sample from that of the CO₂-adsorbed FeO(OH). The anti-symmetric and symmetric modes of the C–O stretching region of carbonate & (bi) carbonate species were formed on the surface of FeO(OH). Interaction of CO₂ with surface –OH and its deprotonated –O⁻ groups resulted in strong bands at 1512 cm⁻¹ and 1314 cm⁻¹ corresponding to the above modes respectively (Fig. 5b) [22]. This observation confirmed the basicity of the O⁻ sites on the surface. Further, FeO(OH) surface may have three kinds of hydroxo groups 1) singly (= FeOH, -OH) 2) doubly (\equiv Fe₂OH, μ -OH) and 3) triply coordinated (\equiv Fe₃OH, μ_3 -OH) (Scheme 2) [23]. From the plot in Fig. 5a, one can infer the nature of the surface -OH groups depending on the site at which the carbonate & (bi) carbonate species are coordinated. At a triply coordinated site (\equiv Fe₃OH, μ_3 -OH) and at doubly coordinated site (\equiv Fe₂OH, μ -OH), the absorption bands appear at 3597 cm⁻¹ and 3627 cm⁻¹ respectively [22,23]. The single coordinated (=FeOH, -OH) species which usually shows bands above 3650 cm⁻¹ was reasonably intense in our sample suggesting its presence in large number as compared to species with other coordination modes. Due to the difference in the coordination number of the underlying Fe atoms, the surface hydroxyl groups that are bonded to it exhibits difference in basicity and hence difference in reactivity. Past literature reports based on adsorption and charging studies indicate double coordinated hydroxyl groups to be inert, whereas single and triple coordinated species are reactive with highest reactivity for single coordinated species in proton



Fig 5. Infrared Spectra of (i) neat FeO(OH) (ii) CO₂ adsorbed on FeO(OH) and (iii) their difference spectra (a) changes in the hydroxyl group stretch (b) changes in the C–O stretch.

adsorption measured by pressure jump relaxation methods [24,25]. The presence of all three types of surface —OH groups explains the catalytic activity of γ -FeOOH. For example, studies on (0 0 1) plane of γ -FeO(OH) had shown equal numbers of single and triply coordinated hydroxyls whereas, (0 1 0) plane contained doubly coordinated surface hydroxyls exclusively [17]. Thus, the deprotonated surface hydroxyl groups show exceedingly high conversion as compared to other metal oxide catalysts.

$$FeO(OH) + H_2O \rightleftharpoons FeO(O^-) + H_3O^+$$
(1)

Since the pK_a of water ($pK_a = 14$) is higher than the protons on FeO(OH) ($pK_a > 10$), it can deprotonate FeO(OH) to give FeOO⁻ according to Eq. (1) [17]. The Brønsted basicity was investigated by means of methanol deprotonation followed by *in situ* Infrared Spectroscopy (Fig. 6) Earlier studies on hydroxylated MgO show that MeOH interacts with the surface basic sites forming monodentate methoxy and bidentate methoxy species at 1115 cm⁻¹ and 1092 cm⁻¹, whereas molecularly adsorbed methanol involving H-bonding gives an absorption band at 1064 cm⁻¹. [26] The various interactions with FeO(OH) surface can be visualized in Fig. 6c. In



Fig 6. *In situ* FT-IR spectra obtained by subtracting MeOH adsorbed FeO(OH) and neat FeO(OH) spectra (a) in the absence of water (b) in the presence of water. Trace (i) (ii) & (iii) denote scans taken after 5 min, 15 min & 25 min respectively. (c) Vibration modes of MeOH dissociation on FeO(OH) surface: Molecularly adsorbed species (1064 cm⁻¹), Bidentate methoxy species (1092 cm⁻¹) and Monodentate methoxy species (1115 cm⁻¹). (d) Relative MeOH dissociation on FeO(OH) in the presence and absence of water w. r.t molecularly adsorbed MeOH.

Fig. 6a & b, we observe the bands centered at 1064 cm^{-1} and 1115 cm⁻¹ indicating molecularly adsorbed MeOH and the formation of monodentate methoxy species on FeO(OH) surface. The formation of monodentate methoxy species on FeO(OH) is a clear indication of the presence of basic sites O^{-} [26,27]. Incidentally, these bands were more intense in the absence of water (Fig. 6a). The competitive interaction between MeOH and H₂O with surface hydroxyl groups is probably responsible for the phenomenon. Band at 1092 cm⁻¹ due to bidentate methoxy species was not predominant except at the initial 5 min scan in the absence of water Fig. 6a (i). However, this band disappeared with time because of weak bidentate methoxy interaction with the surface. To quantify the effect of water on basicity, the relative ratio of peak intensities of monodentate methoxy and molecularly adsorbed MeOH in the absence and presence of water were calculated (Fig. 6d). The average value gave the measure of methanol dissociation on FeO(OH). We invariably observed that the value was higher (0.85) for the system in the presence of H_2O than in the absence of H_2O (0.45). This shows that H₂O helps to increase the number of monodentate methoxy species by increasing the O⁻ species on the FeO(OH) surface.

To support the conclusion that H_2O promotes the *in situ* formation of FeOO⁻, we carried out the adsorption of a positively charged dye Rhodamine 6G (Rh-6G) Fig. 7a. This dye is known to adsorb on a negatively charged surfaces e.g. on the deprotonated OH on graphene which can be monitored using florescence spectroscopy [28]. The details are presented in the experimental section.

The \equiv FeOO⁻ species is a negatively charged surface and hence has an affinity to adsorb a positively charged Rh-6G (Fig. 7c). The supernatant solution in FeO(OH)-Rh-6G after removing the FeO (OH) from the solution showed a marked lower florescence as compared to the standard solution. This indicates that the surface of FeO(OH) has negative charge due to the presence of FeOO⁻ (Fig. 7b) and hence the concentration of Rh-6G in the solution decreased as seen by the lower fluorescence (red trace, Fig. 7c). Fig. 7e show a comparative plot of FeO(OH) and FeO(OH)-Rh-6G complex. One noticeable change is the shift in OH stretching frequency of FeO(OH)-Rh-6G complex from 3134 cm⁻¹ in pure FeO (OH) to 3172 cm⁻¹. This red shift can be attributed to the interaction of the deprotonated surface hydroxyl groups with the positively charged nitrogen of Rh-6G similar to that, reported for graphene oxide-Rh-6G complex [28]. A comparision of FT-IR bands



Fig 7. (a) Structure of Rhodamine –6C. (b) Interaction between FeO(OH) and Rh-6C. (c) Fluorescence spectrum for Rh-6G and FeO(OH)-Rh-6G (Excitation-500 nm) in water. (d) Quantification of amount of dye adsorbed on FeO(OH) in various dioxane: water mixtures. (e) FTIR spectra for FeO(OH) and FeO(OH)-Rh-6G complex. (f) FT-IR spectra for Rh-6G and FeO(OH)-Rh-6G complex.

in the fingerprint region of Rh-6G and FeO(OH)-Rh-6G is shown in Fig. 7f. The bands of Rh-6G showed a slight blue shift in the FeO (OH)-Rh-6G complex further confirming a strong interaction between the positively charged nitrogen of the dye and the negatively charged $FeO(O^{-})$ species as shown in Fig. 7b. The dye adsorption on FeO(OH) was also studied using a similar fluorescence experiment in different dioxane-water compositions matching the solvent conditions. The dye concentration in the supernatant decreased from 0.03 mmol to 0.01 mmol as water content increased (Fig. S3) indicating that Rh-6G adsorbs more on FeO (OH) in excess water conditions due to formation of $FeO(O^{-})$. The amount of Rh-6G adsorbed on FeO(OH) in the dioxane water mixtures was quantified and the results are shown in Fig. 7d. The Rh-6G adsorption values showed an increasing trend with increase in water content. For example, 0.29 mmol of Rh-6G was adsorbed per g of FeO(OH) at 4.5:0.5 dioxane-water ratio. This value reached 0.76 mmol/g of FeO(OH) at 1:1 dioxane-water ratio. Thus, it is confirmed that surface -OH group gets deprotonated in the presence of H₂O to form the O⁻ sites responsible for adsorption of Rh-6G.

In order to verify if externally added H_2O promoted the catalytic activity in FeO(OH) by introducing additional surface —OH groups, the FeO(OH) sample was stirred in water for 6 and 12 h. After the stipulated time the solid was filtered and dried. Previous studies on interaction of FeO(OH) with salt water had shown the formation of Fe(OH)₃ and [Fe(OH)]⁺² on FeO(OH) surface [29]. IR transmittance levels of the dried samples between 3670 cm⁻¹ and 2458 cm⁻¹ corresponding to the surface hydroxyl groups and physisorbed water were studied. Interestingly, these bands remained consistent with that of bare sample untreated with H_2O (Fig. S4). Thus, H_2O does not promote activity in FeO(OH) by increasing the number of surface hydroxyl groups on FeO(OH) within the duration of the reaction.

3.4. Substrate scope

To understand the efficiency of the activity of γ -FeO(OH), we tested it for the Knoevenagel condensation reactions of various active methylene group compounds to synthesize PS, their analogues and other products. All the reactions were carried out using specially dried 1,4-dioxane as a solvent with 1 mL of externally added water. The reaction of acetone with the citral (Table 1, entry 1) gave the aldol condensation product with 84% isolated yield in 12 h. Encouraged by this, we used substituted acetophenones with various functional groups exerting -I and -R effects to condense with citral. It was observed that the para substituted -Cl group in 4-chloroacetophenone on reaction with citral gave an isolated yield of 72% due to higher -I as well as -R effect (Table 1, entry 2). In comparison, 3-bromoacetophenone gave a 68% yield (Table 1, entry 3) of the condensation product. The activating -NO₂ group in 4-nitro acetophenone gave 74% yield of condensation product (Table 1, entry 4). Further extension of the catalyst activity testing was carried out to study Knoevenagel condensation reactions with compounds having active methylene groups. Firstly, malononitrile on reaction with citral yields 82% condensation product in (Table 1, entry 5). Ethylcyanoacetate on reaction with citral gave the condensation product in 74% yield (Table 1, entry 6). Similarly, the Knoevenagel condensation reaction of citral was further studied for nitroethane and nitromethane having active methylene groups which yields up to 70% and 75% condensation product respectively (Table 1, entry 7& 8) under similar reaction conditions.

3.5. Catalyst recycle study

The efficiency of γ -FeO(OH) catalyst was established by its recycle studies (Fig. 8). After completion of the first run, the catalyst was separated by filtration, washed several times with 1,4-

Table 1

Condensation reactions of Citral with active methylene compounds using $\gamma\text{-FeO}(\text{OH})$ as catalyst.



Reaction conditions: citral (0.152 g, 1 mmol), Reactant b (2 mmol), 1,4-Dioxane (5 mL), H_2O (1 mL), time (12 h), reflux 1,4-Dioxane was dried over molecular sieves and then used. Products isolated by column chromatography and confirmed by ¹H NMR.



Fig. 8. Recyclability of γ -FeO(OH) for PS synthesis.

dioxane and dried at 100 °C and then used for eight subsequent runs. Fig. 8 shows that the citral conversion was stable (96–92%) even after five recycles with minor losses. The selectivity of PS dropped down from 100 to 83% after 8th recycle due to competitive formation of Nerolic acid. Also, the X-ray diffraction pattern of the catalyst appeared stable after 8th recycle under the reaction conditions with minor changes (Fig. S5).

In a plausible mechanism shown in Scheme 3, the first step involves the deprotonation of the surface hydroxyl groups of FeO (OH) to give FeOO⁻ using water. These FeOO⁻ species act as base centers to abstract the proton from active methylene compounds



Scheme 3. Plausible reaction mechanism for the synthesis of the Pseudoionones and their analogues.

(Step 2), thus paving way for the attack of the formed carbanion to the carbonyl group of citral (Step 3). Loss of water molecule assisted by FeOO⁻ finally yields the pseudoionone (Step 5).

4. Conclusions

This work demonstrates for the first time the use of FeO(OH) as an environmental friendly, cost effective base catalyst for transformation of citral to PS and its analogues. Combined presence of Brønsted basic O⁻ and Lewis basic O²⁻ is effective for PS synthesis. In situ CO₂ adsorption studies confirmed the presence of singly, double and triply coordinated hydroxyl groups with the active singly coordinated species in abundance. Experimental evidences clearly showed that, externally added water promoted formation of Brønsted basic O⁻ sites on FeO(OH) by deprotonating the surface hydroxyl goups. This O⁻ was responsible for drastic improvement in activity. The basicity on FeO(OH) obtained by water activation is chemically different from those present on other solid bases explored in literature for PS synthesis. Our studies also indicated, this basicity (O⁻) was superior and easily controllable based on water content in the system. The material also exhibited a decent substrate scope and we went on to isolate PS and its analogues which were hitherto not reported.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.08.026.

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