

Electronic Supporting Information (ESI)

**Tunable acid-base bifunctional catalytic activity of FeOOH in an orthogonal
tandem reaction**

D. Vernekar and D. Jagadeesan*

Physical and Materials Chemistry Division

CSIR National Chemical Laboratory

Dr. Homi Bhabha Road

Pune – 411 008.

*Email: d.jagadeesan@ncl.res.in

Telephone: +91-020-2590 3046 Fax: +91-020-25902636.

ESI-1: Experimental section

a) Synthesis method of polymorphs of FeOOH

Materials and Methods

The iron salts used for the synthesis of FeOOH polymorphs were Ferric Nitrate $\text{Fe}(\text{NO}_3)_3$ (Molychem), Ferric Chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (Molychem), Ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) (Fluka). The alkali hydroxides used were Potassium hydroxide (KOH) (Alfa-Aesar) and Sodium hydroxide (NaOH) (Sd-fine). H_2O_2 (Merck) was used as an oxidizing agent for the synthesis of δ FeOOH. For the catalysis reaction, Benzaldehyde dimethyl acetal and Nitromethane were obtained from Sigma Aldrich. For the Acidity and Basicity measurements, indicators mentioned in the table along n-butylamine and trichloroacetic acid were obtained from TCI Chemicals. All solutions needed for titration were prepared in dry benzene. All chemicals were used without further purification.

Synthesis of α -FeOOH.¹

Ferrihydrite was precipitated by adding 18mL of 5M KOH to 10 mL of 1M $\text{Fe}(\text{NO}_3)_3$ solution. The suspension obtained was diluted to 200mL with distilled water and held in a closed polypropylene bottle at 70 °C for 60 h. During this time the voluminous red brown ferrihydrite suspension transforms into a compact yellow precipitate of α -FeOOH which was filtered, washed and dried at 50 °C.

Synthesis of β -FeOOH.¹

500 mL of 0.1M FeCl_3 solution was held in a closed vessel at 70 °C for 48 h. During this period there was a change in pH from 2.3 to 1 and a compact yellow precipitate was obtained which was filtered and washed with distilled water and dried at 60 °C. This gave β -FeOOH

with 6 % Chloride. To obtain 4 % Chloride in the β -FeOOH channels 0.05M FeCl₃ solution was taken in the synthesis protocol.

Synthesis of β -FeOOH(OH⁻ Exchanged).²

β -FeOOH(6At% Cl⁻) was stirred in 100mL of 0.2M aq. Aq. NH₃ solution for 2h to ion-exchange counter anion with OH⁻. The solid was centrifuged and washed with distilled water and dried at 60 °C.

Synthesis of γ -FeOOH.³

4g FeCl₂.4H₂O was dissolved in distilled water. To this 1M 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 FeOOH which were separated by filtration and washed with ethyl alcohol and distilled water several times and dried at 60 °C.

Synthesis of δ -FeOOH.¹

5M NaOH solution was added dropwise to 150 mL of 0.1 M FeCl₂ solution till pH reached 8. To this 20mL of 30% H₂O₂ was added in one lot. Upon addition of the oxidizing agent the green suspension rapidly turned reddish brown. The product was centrifuged, washed with distilled water and dried at 40 °C.

Catalysis Reaction.

A reaction mixture composed of 3mmol Benzaldehyde dimethylacetal, 2mL CH₃NO₂ and 3mmol distilled water were taken in a 25 mL RBF. 0.1g of the polymorph was added. The reaction mixture was refluxed under N₂ atmosphere for 48h with stirring. Control Experiments were carried out by either changing the reaction duration (12h, 24h, 48h,) or by changing the temperature (80 °C, 105 °C) keeping other parameters uniform.

Pyridine Adsorption.

To identify the presence of Brønsted Acid and Lewis acid sites on FeOOH, pyridine adsorption was done by placing the polymorphs in a desiccator concentrated with pyridine vapour for 48 h. The samples were then evacuated at 100 °C to remove physically adsorbed Pyridine and were pressed into KBr pellets for FT-IR analysis. To confirm the role of acidic sites on γ -FeOOH the Deacetylation-Henry reaction was performed by adding pyridine (0.37mmol) externally to the reaction mixture containing 3 mmol benzaldehyde dimethylacetal, 2 mL CH₃NO₂ and 3 mmol of distilled water at the start of the reaction along with 0.1 g of γ -FeOOH. The reaction was run at 105 °C under N₂ atmosphere for 48 h. The catalyst was separated by centrifugation.

Recyclability Experiment.

The catalyst used for the reaction was separated by centrifugation and repeatedly washed with methanol to remove the adsorbed organic species and then dried at 60 °C. The dried catalyst was used for the next cycle. The ratio of the reactant molecule to the weight of the catalyst was kept constant.

Materials Characterization.

X-Ray Diffractions measurements were made using Phillips PAN analytical diffractometer for Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Infrared Spectroscopy measurements were done using Bruker FT-IR. The samples were analyzed as KBr pellets. Scanning Electron Microscopy (SEM) were obtained using Quanta 200-3D ESEM microscope. The specimens were prepared by dropping a well-dispersed suspension of the sample in isopropyl alcohol onto a silicon wafer. Once isopropyl alcohol had evaporated, gold was sputtered on the surface for better sample conductivity during SEM analysis. Transmission electron microscopy (TEM)

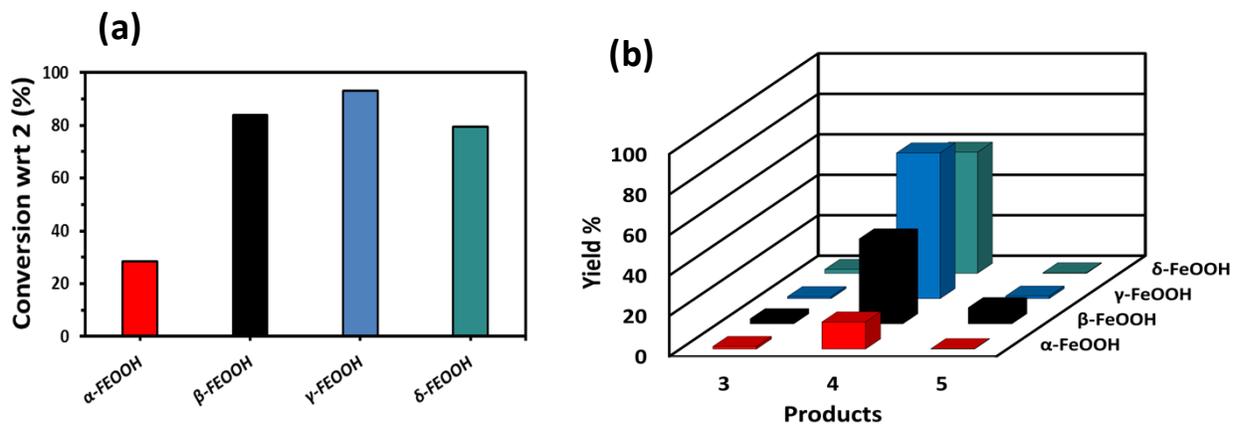
images were obtained using FEI Tecnai-20ST electron microscope. Specimens of the samples were prepared by drop-casting well-dispersed isopropyl particle suspensions onto a carbon coated copper grids. The Surface area measurements were performed using Quantachrome Autosorb-iQ gas sorption device.

b) Characterization of catalysts (titrations)⁴

S.No	Indicators	pK _a	Colour	
			Basic (B)	Acidic (BH ⁺)
1.	Neutral red	+6.8	Yellow	Red
2.	Phenylazonaphthylamine	+4.0	Yellow	Red
3.	p-Dimethylaminoazobenzene	+3.3	Yellow	Red
4.	Benzeneazo-diphenylamine	+1.5	Yellow	Purple
5.	Dicinnamalacetone	-3.0	Yellow	Red

The acidity and basicity at various acid base strengths were measured by performing titrations using n-butylamine and trichloroacetic acid respectively using a series of indicators mentioned in the table. Since all FeOOH are coloured we used Silica-Alumina and Aluminium oxide as a reference. The indicator colour change was monitored on the white solid. In a typical experiment to determine acidity, 0.1g of silica alumina was taken along with 0.015g of the polymorph in a closed conical flask. 5mL of the standard indicator solution in dry benzene was added and allowed the adsorption process to take place. The solid was then titrated with 0.1N n-butylamine solution in dry benzene. The neutralization is followed by noting the gradual disappearance of the indicator colour on the white solid. The end point was taken at the point when the entire white solid regained its original colour. The basicity measurements were done using Aluminum oxide as reference and trichloroacetic acid as a titrant.

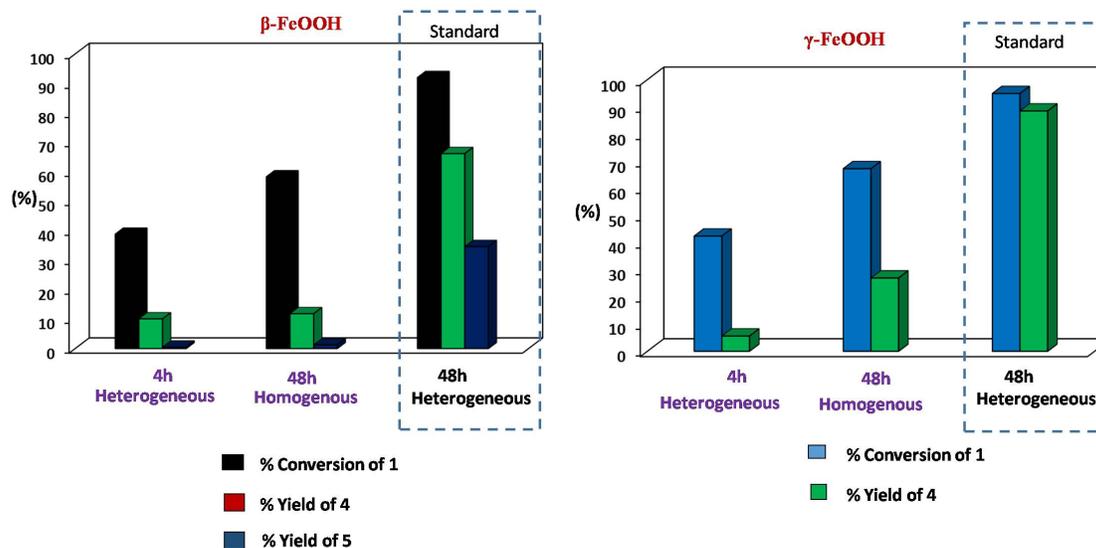
ESI 2: Catalytic activity of polymorphs of FeOOH in Henry reaction starting from 2



The catalytic activity of the polymorphs of FeOOH for in Henry reaction starting from 2 is plotted. Figure a) shows the conversion (%) and b) shows the selectivity of products 3, 4 and 5.

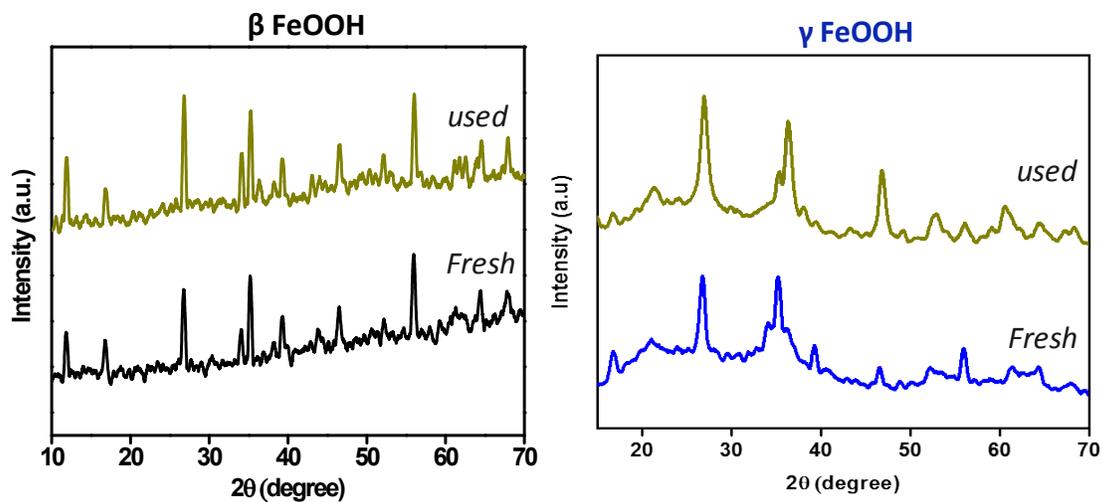
ESI 3: Heterogeneous catalytic activity of β and γ FeOOH

We carried out the reaction in the presence of β and γ -FeOOH separately initially for 4h during which 40-50% conversion w.r.t **1** was observed. Following this, we separated the catalyst and continued to carry out the reaction for another 44 h. The data is plotted below.

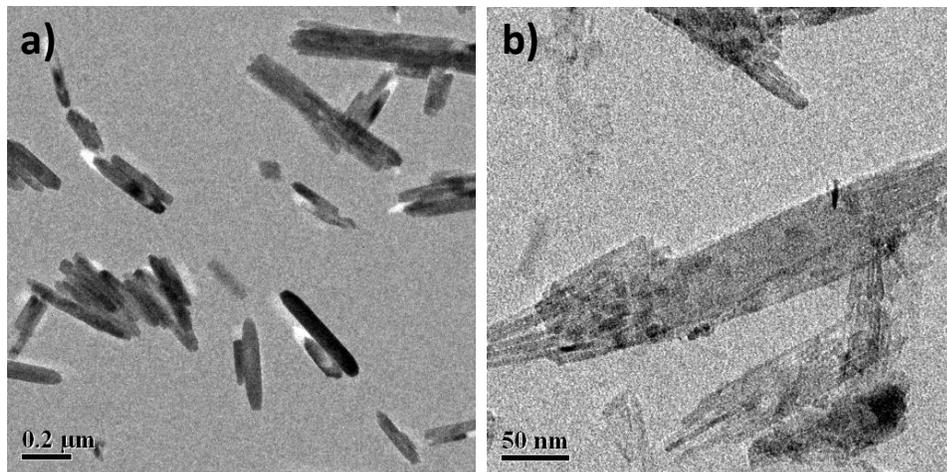


It is observed that at the end of 44 h, the conversion of reaction w.r.t **1** increased in case of β and γ -FeOOH. However, **2** was the only product that was formed in the absence of the catalyst. For comparison, the standard reaction, where FeOOH heterogeneous catalyst was present throughout 48 h is also presented. The figure confirms that formation of products **4** in case of γ FeOOH and **4** and **5** in case of β FeOOH are catalyzed by heterogeneous FeOOH.

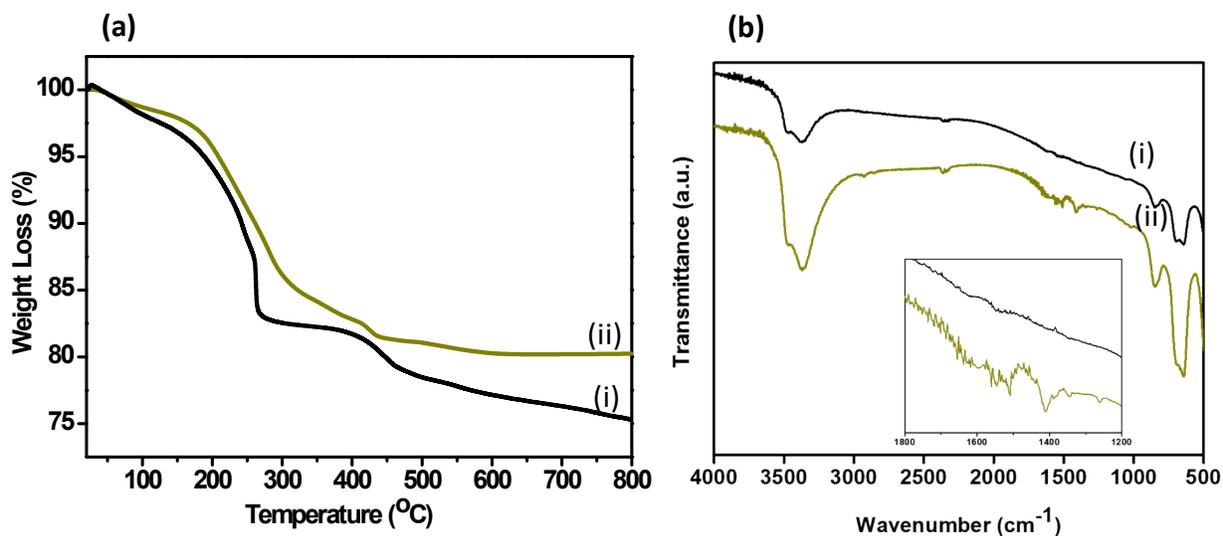
ESI 4: XRD patterns of fresh and the used catalysts (after 5 cycles) β FeOOH and γ FeOOH.



ESI 5: TEM data of used samples of β and γ FeOOH



ESI 6: IR and TGA data of fresh and used β FeOOH



In Figure a) TGA of fresh (trace i) and used (ii) samples of β FeOOH are shown. The extent of weight loss in the temperature region 250 – 400 °C is less by 1.8 % in the case of used β FeOOH sample indicating loss of Cl⁻ ion. In Figure b), FT-IR spectra of fresh (trace ii) and used (trace i) of β FeOOH samples are shown. The new absorption stretch in the region 1200 to 1800 cm⁻¹ in the inset can be ascribed to C=C stretching frequency which could be due to adsorbed organic molecules such as **4**.

References

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