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Solvent free selective isomerization of *p*-diethylbenzene to *m*-diethylbenzene using modified Hβ zeolites

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ABSTRACT

Solvent free and selective isomerization of *p*-diethylbenzene (*p*-DEB) to *m*-diethylbenzene (*m*-DEB) was carried out using metal modified zeolite Hβ at high temperature. The metal modification of Hβ catalyst was carried out by using typical Lewis acidic cations Al^{3+}, Fe^{3+}, Ti^{4+}, Sn^{4+} and Sb^{3+}. The catalysts were characterized by XRD, FE-SEM, HR-TEM, FT-IR, N_2-desorption (BET), ICP-AES, NH_3-TPD, pyridine-IR, and TGA techniques for structure, morphology, acidity and stability. Particle size of the crystallites was determined by HR-TEM and the size was in the range of 15 - 35 nm. At 250°C, Al-Hβ, Fe-Hβ and Ti-Hβ catalysts showed 69 - 75% conversion of *p*-DEB with 43 - 51% selectivity towards *m*-DEB. This process is a greener alternative to the classical $AlCl_3$ process. Further, such an isomerization would make the styrene manufacture more economic. Copyright © 2014 VBRI press.

Keywords: Zeolite Hβ; diethylbenzene; isomerization; heterogeneous catalysis; cation exchange.

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Introduction

The isomerization of substituted aromatic compounds to the desired isomers is very important in specialty chemical production. One of the objectives is to convert undesirable regioisomer formed in a reaction to the desired regioisomer. Acid catalyzed isomerizations of disubstituted benzenes, such as xylenes **[1]**, dichlorobenzenes **[2]**, chlorotoluenes **[3]**, diisopropylbenzenes **[4]**, mixed dihalobenzenes **[5]**, diethylbenzenes **[6]**, haloethylbenzens **[7]**, alkyl phenols **[8]**, t-butyltoluenes **[9]**, terphenyls **[10]**, and trihalobenzenes **[11]**, have been reported.

m-Diethylbenzene (*m*-DEB) is an important intermediate for fine chemicals. It is oxidized by air to diethylbenzene hydroperoxide, which is useful in the production of *m*-ethylphenol. *m*-Ethylphenol is valuable in the preparation of additives for lubricating oils, and it is a stabilizer for rubber, synthetic resins, and oils **[12]**. Other valuable intermediates which can be obtained from *m*-diethylbenzene are *m*-divinylbenzene and *m*-ethylvinylbenzene which are obtained by thermal dehydrogenation of *m*-DEB **[13]**. *m*-Divinylbenzene (*m*-DVB) is a reactive monomer and is a cross-linking agent for copolymers such as ion exchange resins. It is also used as a viscosity modifier of lubricating oil **[14]**.

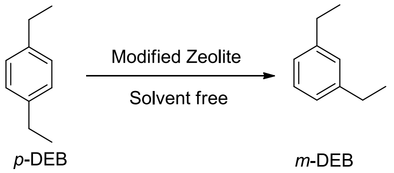
Currently, *m*-DEB is produced commercially by alkylation of benzene or ethylbenzene with ethylene over a homogeneous catalyst $AlCl_3$ **[15, 16]**. It can be also produced over the catalysts like BF_3-HF **[17, 18]**. The high activity of $AlCl_3$ and BF_3-HF produces a mixture of DEB isomers. These catalysts, being very active and homogeneous, pose problems like corrosion of reactor, involvement of a neutralization step generating huge waste, and loss of catalyst, which make this process less attractive.

Considering these issues, efforts have been made to produce *m*-DEB by ethylation of benzene or ethyl benzene over heterogeneous catalysts like mixed metal oxides **[19, 20]** and modified ZSM-5 **[21, 22]**. In these processes the conversion of benzene or ethyl benzene is kept below 50% and the selectivity of *m*-DEB is reported to be in the range of 20-25%. Further, in these processes always a mixture with undesirable by-products is formed. As an alternative to the alkylation, Olah reported the preparation of *m*-DEB by the isomerization of *p*-DEB using $AlCl_3$ as a homogeneous catalyst **[6]**. This process also has limitations as given above. The process also suffers from formation of by-products like triethylbenzene and polyalkylated products.

On the background of these drawbacks of homogeneous catalysts, the isomerization of *p*-DEB to *m*-DEB has been attempted using heterogeneous catalysts. Bolten has described a process for the isomerization using zeolite Y **[23]**. The equilibrium product distribution at 170°C after 6h is about 3.9% *meta,* 73% *para,* 0.7% *ortho* isomers of DEB. Ethylbenzene and high boilers are also formed in about 11.9% and 10.5% yield, respectively. When the reaction is continued for 100h, the conversion of *p*-DEB increases, but selectivity of *m*-DEB remained very low (about 32%) and disproportionation products increase significantly.

Review of the pertinent literature shows that there exists a need to develop an efficient process for the preparation of *m*-DEB. Particularly we felt that there is a need to focus on the rearrangement of easily available *p*-DEB to *m*-DEB, using a heterogeneous solid acid catalyst; in order to achieve more conversion of *p*-DEB and high selectivity towards the *m*-isomer. *p*-DEB is an easily avaialble by-product in the manufacture of ethylbvenzene.

Zeolites are solid acid catalysts which can be modified in a variety of ways to tailor their activity profile. Zeolites are extensively used in petrochemical industry to carry out different types of catalytic reactions such as cracking, isomerization, alkylation, etc. Zeolites have many advantages such as, superior thermal stability, scope for modification, reusability, etc.



Scheme 1. Isomerization of *p*-DEB in the presence of modified Hβ catalyst.

In continuation with our ongoing research on heteroheneous acid catalysts **[24, 25]**, herein, we report a simple, efficient, and solvent-free selective isomerization of *p*-DEB to *m*-DEB in the presence of transition metal modified zeolites Hβ **(Scheme 1)**.

Conversion of *p*-DEB, which is a cheap by-product of styrene manufacture, into industrially important *m*-DEB is commercially important. The process is a greener and efficient alternative to the classical processes using homogeneous catalyst. To the best of our knowledge, no such solvent free, solid acid catalyzed, process has been reported for the isomerization of *p*-DEB to *m*-DEB.

Experimental

Materials

Zeolite Hβ (Si/Al 32) was procured from M/s Sud-Chemie India. All metal salts were of A.R. grade and were procured from M/s S. D. Fine Chemicals Ltd., Mumbai. DEB isomers and ethylbenzene were obtained from local market, analyzed and purified before use. The purity of DEB was about 98%.

General procedure for catalyst preparation

Anhydrous metal chloride (15 g) was dissolved in deionized water (60 mL). The solution was cooled to room temperature and Hβ (10 g) was added over a period of 10 min; (in case of $SbCl_3$, $TiCl_4$ and $SnCl_3$, 10 mL conc. HCl was added to the water prior to addition of Hβ to clear the turbidity). The resulting slurry was stirred at room temperature (28 °C) for 5 h. The catalyst was filtered through a glass fritted funnel (G-2), washed with deionized water (2 X 60 mL) till free from Cl^- ions. The paste was spread in a glass petri dish and dried in an electric oven in air for 2 h at 80°C. Calcination of the catalyst was done in an electric furnace in air at 300°C with a heating rate of 60°C h^{-1}. Thus, a series of catalysts (M-Hβ, M = Metal) was prepared by exchanging Al^{3+}, Fe^{3+}, Ti^{4+}, Sn^{4+} and Sb^{3+} cations with Hβ. The catalysts were preserved in a desiccator and used after activation at 120°C for 12 h in an oven.

Catalyst characterization

NH_3-TPD measurements were done on a Micromeritics TPD/TPR AutoChem II 2920 V3.03 instrument. The samples were activated at 550°C for 30 min in a flow of helium (30 mL/min) and then saturated with ammonia at 50°C (10% NH_3 in He and desorption at 30°C/min to 550°C).

Nitrogen adsorption-desorption isotherms were obtained on a Micromeritics ASAP 2010 apparatus. Before measurement, the samples were degassed at 350°C for 4h under vacuum. The specific surface area and pore volume were calculated by the BET and BJH methods, respectively, with a value of P/P_0 lower than 0.98. The FT-IR spectra were recorded using a Shimadzu 3800 FT-IR spectrophotometer. For pyridine-IR pyridine was adsorbed at room temperature and desorption was carried out at 150°C under high vacuum for 30 min. The metal content of the catalyst was determined by ICP-AES using a Varian Vista AX ICP-AES spectrometer. Powder XRD patterns were recorded using a JEOL JDX-8030 X-ray diffractometer equipped with Cu *Kα* source operated at 40 kV and 40 mA with a scan rate of 2°/min. The morphology and crystal size of the catalysts were observed by FE-SEM. The samples were coated with gold to create contrast. EDAX was done using JEOL JSM7600F electron microscope. HR-TEM images were obtained on a JEOL JEM 2110, a scanning transmission research electron microscope with field emission intermediate voltage (200 kV) and magnification of up to 8,000,000×.

General procedure for isomerization of p-DEB to m-DEB

The reaction was carried out in a 100 mL hastelloy made, high pressure reactor; equipped with an agitator, a digital pressure gauge, and a temperature probe (M/s Amar Equipment Ltd., India). The reactor was dried under a flow of dry nitrogen gas. *p*-DEB (20g, 149 mmol) was charged and a freshly calcined catalyst (2.0 g, 10% w/w) was added. The in-built pressure was in the range of about 150-350 psi at the set temperatures. The temperature and pressure in the reactor were continuously recorded. After the specified time, the reactor was allowed to cool to room temperature and then further cooled in ice-cooled water. The reaction mixture was filtered through a glass fritted funnel and analyzed by GC (Perkin Elmer Clarus 480 series gas chromatograph) equipped with FID, capillary column Carbowax 32 M-type, 25m × 0.53 mm, 1.0 m film thickness, carrier gas N_2, 60–280°C, 10°C min^{-1}.

Results and discussion

Catalysts characterization

The modified catalysts were characterized with respect to its acidity (TPD-NH_3, pyridine-IR), surface area, average pore diameter, total pore volume (BET analysis), metal percent (ICP analysis), morphology (FE-SEM, HR-TEM), crystallanity (XRD), and IR-spectroscopy (FT-IR).

TPD-NH_3 method was used to determine the acidity of the catalysts. The TPD-NH_3 thermograms are shown in **Fig. 1.** The amount of NH_3 desorbed at 50°C-550°C corresponded to the total number of acid centres in the samples. The catalysts showed similar profiles with maxima around 150°C. However, the curve intensities of Al-Hβ, Fe-Hβ and Ti-Hβ were higher than those of Sn-Hβ and Sb-Hβ, indicating strong acidity of Al-Hβ, Fe-Hβ and Ti-Hβ; the acidity of Hβ was low, comparable to that of Sn-Hβ and Sb-Hβ. Thus, after the metal cation exchange, the acidity of the zeolite catalysts increased and the order of acidity was Hβ < Sb-Hβ < Sn-Hβ < Ti-Hβ < Fe-Hβ < Al-Hβ.

The strength of Lewis acid sites was compared using pyridine-IR. The FT-IR spectra of the catalysts in the region of 1700-1400 cm^{-1} are given in the supplementary data **S1**. The bands due to Lewis acid sites (1446 cm^{-1} and 1600 cm^{-1}) are stronger in the catalysts modified with Al, Fe, and Ti than those in the spectra of catalysts modified with Sn and Sb.

To check the thermal stability, Al-Hβ300 was analyzed by TGA. About 5% loss in mass was observed up to 300°C, indicating that the catalyst was stable at the working temperature. (TGA Spectra are provided in supplementary data **S2**).

The catalysts were characterized by BET method for surface area, average pore diameter, and pore volume (**Table 1**). Surface area of the catalysts was observed to be 152.3 - 475.9 m^2/g, average pore diameter in the range of 23.6 - 33.7 nm, and total pore volume in the range of 0.358 - 0.823 cm^3/g. The metal modification had an obvious effect on surface area (S_{BET}). As the metal cation size increased the surface area (S_{BET}) of the catalyst decreased; surface area of Sn-Hβ and Sb-Hβ (152.3 m^2/g and 206.4 m^2/g respectively), being much lower than that of Hβ (Table 1, entry 5, 6 Vs 1).

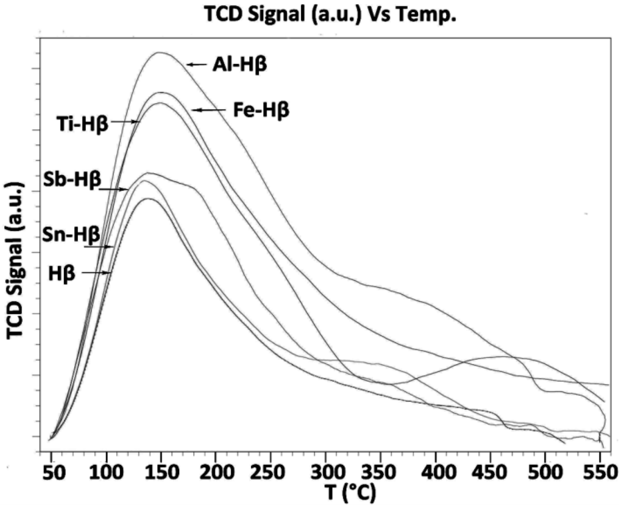


Fig. 1. NH_3-TPD thermograms of metal modified Hβ.

On the other hand, the surface area of the catalysts containing small size metal cations Al, Fe and Ti decreased slightly as compared to that of Hβ (**Table 1**, entry 1-4). The N_2 adsorption-desorption isotherms of the modified catalysts are provided in supplementary data **S3**. They showed a typical profile of crystalline microporous material. It is reported, and confirmed from the TPD-NH_3 results, that after metal exchange the acidity of the catalyst increases; however surface area decreases **[26]**.

Thus, the modified zeolite catalysts had microporous system with increased acidity as compare to Hβ. ICP-AES analysis showed that the quantity of metal exchanged was in the range of 6.3% - 8.4% w/w.

XRD patterns of the catalysts are given in **Fig. 2.** The characteristic peaks of Hβ were at 7.5° and 22.5° due to planes d_{100} and d_{302} respectively **[27]**.

Table 1. Characterization of the ion-exchanged Hβ catalysts.

Sr. No.	Catalyst	Metal content (%)^a	Surface area S_{BET} (m^2/g)^b	Average pore diameter (nm)^c	Total pore volume (cm^3/g)^c	Acidity (TPD) (μmole NH_3/g)^d
1	Hβ	-	475.9	23.6	0.823	498.2
2	Al-Hβ	8.3	405.4	25.6	0.733	1285.6
3	Fe-Hβ	8.1	397.1	24.8	0.764	1033.4
4	Ti-Hβ	7.3	387.2	25.5	0.765	960.6
5	Sn-Hβ	6.7	206.4	29.3	0.512	548.7
6	Sb-Hβ	8.4	152.3	33.7	0.358	594.7

[a] Calculated from ICP technique, [b] Calculated from BET technique,
[c] Calculated from BJH Adsorption, [d] Determined by NH_3-TPD.

Broad peak at 7.5° is the characteristic peak of the faulted structure, while the sharp peak at 22.5° is due to the tetragonal and monoclinic symmetry structure of Hβ. The XRD indicated that the basic structure of Hβ has not changed after the cation exchange. The crystallanity of Hβ was also maintained after the modification. The average diameter of the crystallites was estimated by Scherrer equation, using the value of the half-height width (B = 0.63°) of the most intense peak (2θ = 22.4°), and found to be around 11 nm **[28, 29]**. Similar observation has been reported by Camblor **[30]**.

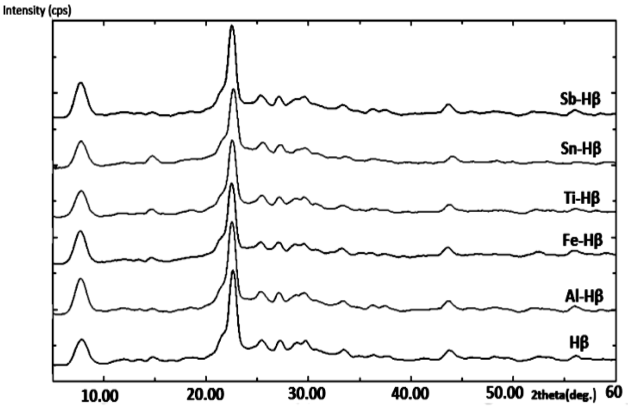


Fig. 2. XRD patterns of Hβ and metal modified Hβ catalysts.

FE-SEM image of Al-Hβ is shown in **Fig. 3.** The metal exchange did not change the morphology and crystal size of the catalysts. The catalyst particles were small in size, spheroidal, and were of uniform diameter of around 35-80 nm. The catalyst assemblies were closely packed and no cracks were observed on the grain surfaces. The surface was rough. The metal content was determined by EDAX, and found to match with that obtained from ICP analysis (Supplementary Data **S4**).

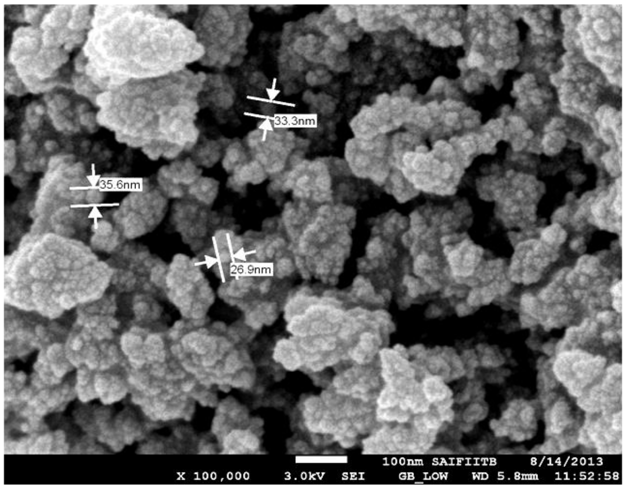


Fig. 3. FE-SEM image of Al-Hβ

HR-TEM micrograph of Al-Hβ catalyst is shown in **Fig. 4**. A fine ordered pattern of the microporous structure was observed. The morphology of the catalyst was similar to that of Hβ **[29]**.

The crystalline size of the catalyst was in the range of 15-35 nm, close to that estimated from XRD. Electron diffraction pattern along several zone axes confirmed the -crystallanity the catalysts. These micrographs confirm the presence of 12-membered ring pores in an array of 4-, 5-, and 6-membered rings in the structure.

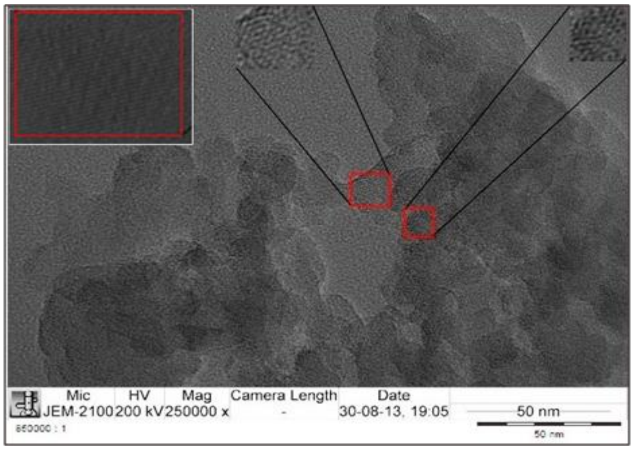


Fig. 4. HR-TEM image of Al-Hβ catalyst

The IR spectra of the catalysts are given in supplementary data **S5**. The typical bands of Hβ were observed at 1240-1200 cm^{-1} (external asymmetric stretching), 1100-1050 cm^{-1} (internal asymmetric stretching) and 800-750 cm^{-1} (symmetric stretching of TO_4, T = Si, Al) **[31]**. The framework structure of zeolite was confirmed by peaks at 580-570 cm^{-1} (double 6-membered ring vibrations) and 510-490 cm^{-1} (double 4-membered ring vibrations). The band at 460 cm^{-1} was assigned to the T-O bending. These observations corroborated with XRD analysis.

Isomerization of p-DEB

We prepared metal modified Hβ catalysts by treating Hβ with aqueous solutions of metals salts; the metal cations being Al^{3+}, Fe^{3+}, Ti^{4+}, Sb^{3+} and Sn^{4+}. The selection of the metals was done on the basis of the following consideration. The metals are typical Lewis acids. They were selected on the basis of our earlier results with these metals **[24, 25]**. Al and Ti are strong Lewis acids. Fe and Sb are weak Lewis acids under classical conditions; however, they show unusual high acidity when supported on clays and zeolites **[32, 33]**. We have earlier reported the unusual high catalytic activity of Sb for the first time **[34]**. Though Sn is a soft cation, in supported form, in many reactions, it drives the reactions through radical mechanism. It is known that calcination has profound effect on the catalytic species formed on the surface of the catalyst **[35]**. The catalysts were calcined at 300°C and dried at 120°C for 12h before the use.

The isomerization of *p*-DEB was carried out in the presence of the catalysts at 200°C, 250°C, and 300°C, and the built-in pressure in the range of 150psi - 350psi. The reaction was carried out at 250°C in the presence of all the catalysts including Hβ (10% catalyst loading) (**Table 2**). Al-Hβ, Fe-Hβ, and Ti-Hβ catalysts were more active than Sn-Hβ and Sb-Hβ. The conversion of *p*-DEB in the case of te former catalysts was in the range of 69-75% and the *m*-

DEB selectivity 43-51%. The selectivity of *m*-DEB achieved is higher as compared to the earlier reports **[23]**. The other two catalysts were much less effective. In all the cases *o*-DEB was formed in very small amount (0.2–1.9%). Unmodified Hβ was much less active and gave conversion of *p*-DEB up to 10.2%, with selectivity of *m*-DEB 8.8% (**Table 2**, entry 1). The isomerization was also carried out at 300°C for 6h using all the catalysts (Supplementary Data **S6**).

Table 2. Isomerization of *p*-DEB at 250°C in the presence of different metal modified Hβ catalysts.[a]

Sr. No.	Catalyst	Conv. of *p*-DEB (%)	Selectivity (%)				
			p-DEB	*m*-DEB	o-DEB	EB	High boilers [b]
1	Hβ	10.2	89.7	8.8	0.2	0.9	0.4
2	Al-Hβ	69.3	30.5	51.5	1.5	9.7	6.8
3	Fe-Hβ	75.5	24.3	48.1	1.6	16	10
4	Ti-Hβ	71.9	27.9	43.6	1.9	16.3	10.3
5	Sn-Hβ	14.5	85.4	10.8	0.7	2.3	0.8
6	Sb-Hβ	13.8	86.1	10.6	0.6	2.1	0.6

[a] Reaction conditions *p*-DEB (20 g), catalyst (2 g), time (6 h), temp (250°C)[b] . Amount of high boilers was determined by mass balance.

At this temperature, using Al-Hβ the conversion of *p*-DEB increased significantly from 69.3% to 91.1%, but the selectivity towards *m*-DEB decreased from 51.5 % to 32%. Further, the amount of disproportionation products increased. To compare the effect of the metals, the isomerization was carried out at 200°C (**Table 3**). At this reaction temperature the conversion of *p*-DEB significantly decreased; however, the trend among te metals remained the same. Thus, 250°C was the best temperature to study this reaction. Results obtained with Al-Hβ at different temperature are given in **Fig. 5.**

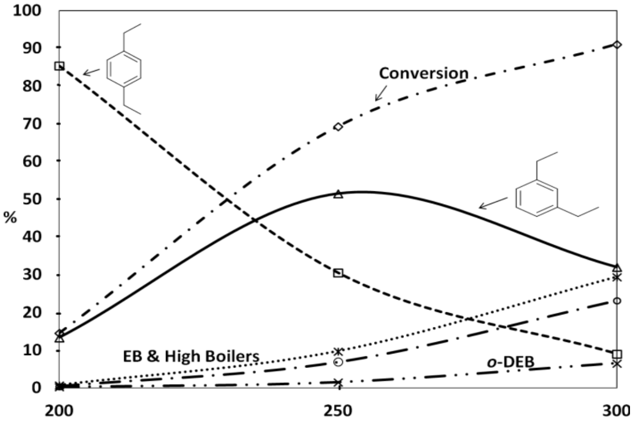


Fig. 5. Effect of reaction temperature on the isomerization of *p*-DEB in the presence of Al-Hβ catalyst.

Using the most active catalysts Al-Hβ, Fe-Hβ, and Ti-Hβ the reaction was carried out at 250°C and monitored with respect to time (**Table 4**, **Fig. 6** for Al-Hβ, see supplementary data for Fe-Hβ, and Ti-Hβ). Among the three catalysts Al-Hβ was the best one. It was noted that at 6h the conversion was satisfactory and the *m*-DEB selectivity was the highest; however, on increasing the time to 8h the conversion increased, but the selectivity decreased. Hence, increasing the time beyond 6h was not beneficial. It was further noted that with time the disproportionation of *p*-DEB increased leading to formation of EB and high boilers; the disproportionation products were high at 8h. Similar trend was observed in the case of Fe-Hβ and Ti-Hβ. Using Fe-Hβ, maximum selectivity of *m*-DEB of 48.1% was observed at 6h. Beyond this, the selectivity decreased, along with increase in the disproportionation products (Supplementary Data **S7**).

Table 3. Isomerization of *p*-DEB at 200°C in the presence of different metal modified Hβ catalysts [a]

Sr. No.	Catalyst	Conv. Of *p*-DEB (%)	Selectivity (%)				
			p-DEB	*m*-DEB	o-DEB	EB	High boilers[b]
1	Al-Hβ	14.5	85.4	13.3	0.2	0.7	0.4
2	Fe-Hβ	15.2	84.7	10.1	0.5	2.8	1.9
3	Ti-Hβ	13.6	86.3	9.1	0.5	2.6	1.5
4	Sn-Hβ	3.3	96.6	2.6	0.1	0.5	0.2
5	Sb-Hβ	2.8	97.1	2.3	0.1	0.3	0.2

[a]Reaction conditions: *p*-DEB (20 g), catalyst (2 g), temperature (200°C), time (6 h.) [b] Amount of high boilers was determined by mass balance.

Table 4. Effect of reaction time on the isomerization of *p*-DEB in the presence of Al-Hβ catalyst.[a]

Sr. No	Time (h)	Conv. of *p*-DEB (%)	Selectivity (%)				
			p-DEB	*m*-DEB	*o*-DEB	EB	High boilers [b]
1	0	0	99.8	0.2	0	0	0
2	2	26.1	73.7	21.8	0.9	2.7	0.9
3	4	55.6	44.2	42.3	1.1	7.5	4.9
4	6	69.3	30.5	51.5	1.5	9.7	6.8
5	8	82.6	17.2	46.5	1.8	20.1	14.4

[a] Reaction conditions: *p*-DEB (20 g), Al-Hβ (2 g), T (250°C).
[b] Amount of high boilers was determined by mass balance.

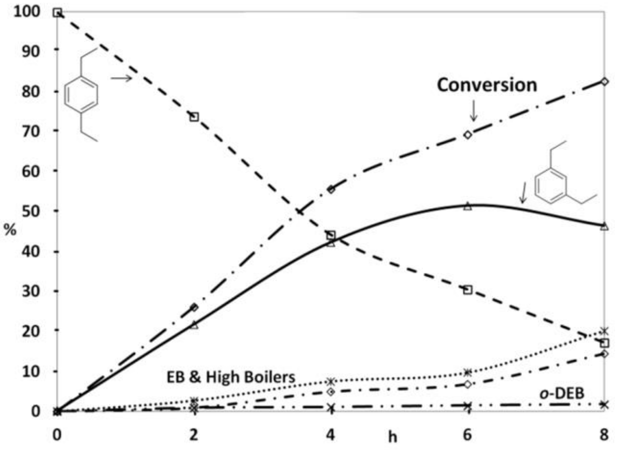


Fig. 6. Effect of reaction time on the isomerization of *p*-DEB in the presence of Al-Hβ catalyst at 250°C.

Using Ti-Hβ catalyst, 43.6% selectivity of *m*-DEB was obtained at 6 h (Supplementary Data **S8**); continuation of the reaction leads to decrease in the selectivity of *m*-DEB and increase in the by-products.

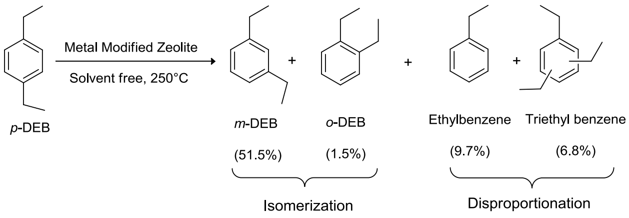
The isomerization was carried out using two promising catalysts Al-Hβ and Fe-Hβ, with 10 wt % and 20 wt % loading (**Table 5**). In both the cases, it was observed that *p*-DEB conversion increased on increasing the quantity of catalyst; on the other hand, the selectivity towards *m*-DEB deteriorated due to formation of increased amount of ethyl benzene and high boilers. Thus, 10 wt% catalyst loading was found to be optimum.

Table 5. Effect of the quantity of catalyst on the isomerization of *p*-DEB.[a]

Catalyst	Cat. (wt %)	Conv. Of *p*-DEB (%)	Selectivity (%)			
			p-DEB	*m*-DEB	o-DEB	EB
Al-Hβ	10	69.3	30.5	51.5	1.5	9.7
Al-Hβ	20	83.5	16.4	39.4	3.2	23.5
Fe-Hβ	10	75.5	24.4	48.1	1.5	16
Fe-Hβ	20	84.6	15.3	38.5	4.1	24.3

[a] Reaction conditions: *p*-DEB (20 g), Temp (250°C), time (6 h)
[b] Amount of high boilers was determined by mass balance

The formation of all the products may be rationalized on the basis of Lewis acid catalyzed intermolecular mechanism involving dealkylation followed by thermodynamically favourable realkylation **[36]** (**Scheme 2**). Al-Hβ, Fe-Hβ and Ti-Hβ are more Lewis acidic than Sn-Hβ and Sb-Hβ; and hence they were more active than the latter group. The correlation between selectivity of *m*-DEB and amount of the disproportionation products (EB + High boilers) formed at 250°C is shown in **Fig. 7.**



Scheme 2. Rearrangement of *p*-DEB.

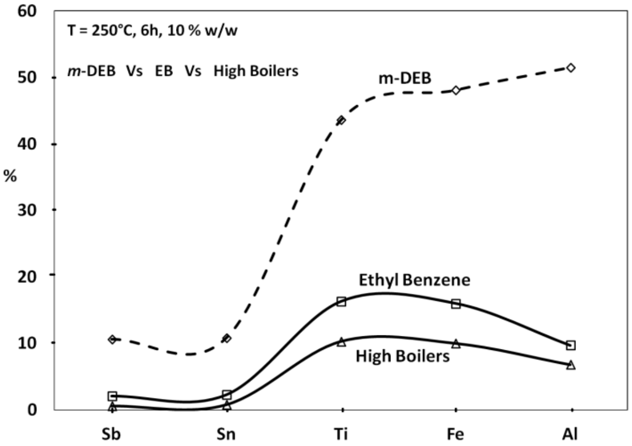


Fig. 7. Correlation between selectivity of *m*-DEB and disproportionated products formed at 250^{o}C, in the presence of different modified catalysts.

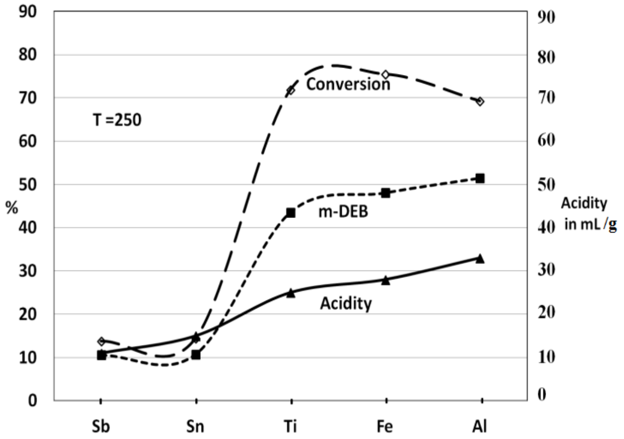


Fig. 8. Correlation between acidity of the catalyst with conversion of *p*-DEB and selectivity of *m*-DEB at 250°C.

Thus, *m*-DEB selectivity was parallel to the quantity of disproportionation products formed. This supported the intermolecular dealkylation-realkylation mechanism. Interestingly, with Al-Hβ the formation of ethyl benzene and high boilers was low, even though the conversion of *p*-DEB was high. Sn-Hβ and Sb-Hβ catalysts showed less selectivity towards *m*-DEB, and the formation of ethyl benzene and high boilers was also less.

A reason for the large difference in the selectivity of *m*-DEB would be the difference in the acidity of the metal modified catalysts. The most active catalysts Al-Hβ, Fe-Hβ, and Ti-Hβ were more acidic than the less active catalysts, Sn-Hβ and Sb-Hβ. Acidity of the catalyst has an important effect on the isomerisation, through dealkylation-realkylation mechanism. Increase in the acidity of the catalyst increased the conversion of *p*-DEB and also the selectivity of *m*-DEB **(Fig. 8).** The most interesting observation was the significant effect of the metal on the reaction. In the case of most active catalysts Al-Hβ, Fe-Hβ, and Ti-Hβ the acidity increased considerably as compared to Hβ, and at the same time surface area did not decrease much. On the other hand, in the case of Sn-Hβ and Sb-Hβ catalysts the acidity slightly increased as compared to Hβ; however, the surface area decreased considerably (**Table 1**). The deceased surface area may be the main reason for their low activity.

Conclusion

In conclusion, Hβ modified by cation exchange in aqueous solution with acidic metal cations Al^{3+}, Fe^{3+}, Ti^{4+}, Sn^{4+} and Sb^{3+} and activated at 300°C are effective for the isomerisation of *p*-DEB to *m*-DEB in the absence of solvent. At 250°C, Al-Hβ, Fe-Hβ, Ti-Hβ were the best catalyst which showed conversion of *p*-DEB of 69% -75% with 43% - 51% selectivity towards *m*-DEB. The conversion and selectivity are the highest reported so far using any heterogeneous solid acid catalyst. The activity of the catalysts could be correlated with the acidity and surface area of the catalyst; the reaction required strong Lewis acidity ang large surface area.The process provides an effective and greener alternative to the traditional process of preparation of *m*-DEB using homogeneous catalysts. The feed *p*-DEB is a by-product of styrene manufacture and is commercially available. Thus, the process is a value addition to the styrene manufacturing.

Acknowledgements
We are thankful to M/s Sud - Chemie India Pvt. Ltd., Vadodara, India, for supplying Hβ zeolite. MSE is thankful to the UGC, New Delhi (India), for providing a fellowship under SAP.

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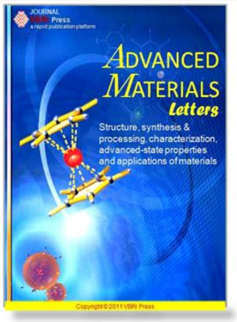

Electronic Supplementary Information

Solvent free selective isomerization of p-diethylbenzene to m-diethylbenzene using metal modified Hβ zeolites

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1) General Information

All chemicals and reagents were procured from local markets and from commercial suppliers. Zeolite Hβ was obtained from M/s Sud-Chemie India. The isomerization of *p*-DEB was performed in a 100 mL hastelloy made, high pressure reactor (autoclave); equipped with agitator, digital pressure gauge, and temperature probe (M/s Amar Equipment Ltd., India). The catalysts were characterized with respect to acidity (TPD-NH_3, Pyridine-IR), pore volume, surface area, pore diameter (BET analysis), amount of metal percent (ICP analysis), morphology (FE-SEM, HR-TEM), crystanality (XRD), IR-spectroscopy (FT-IR) and stability (TGA). All products are well known compounds and identified by appropriate technique such as GC, GC-MS and were compared with previously reported data. Mass spectra were obtained on Shimadzu GC-MS (QP 2010) (Rtx-17, 30 m × 25mmID, film thickness 0.25 μm) (column flow- 2 mL/min, 80 °C to 240 °C at 10°/min. rise) instrument.

2) Catalysts characterization data

The FT-IR spectra were recorded using a Shimadzu 3800 FT-IR spectrophotometer. Pyridine was adsorbed over the calcined catalysts at room temperature, followed by desorption of pyridine at 150°C under high vacuum for 30 min. The FT-IR spectra of pyridine adsorbed modified Hβ catalysts and Hβ in the region of 1700-1400 cm^{-1} is shown in **Fig. S1**. The bands related to Lewis acid sites (1446 cm^{-1} and 1600 cm^{-1}) are stronger in Hβ catalysts modified with Al, Fe, and Ti than those in the modified with Sn and Sb.

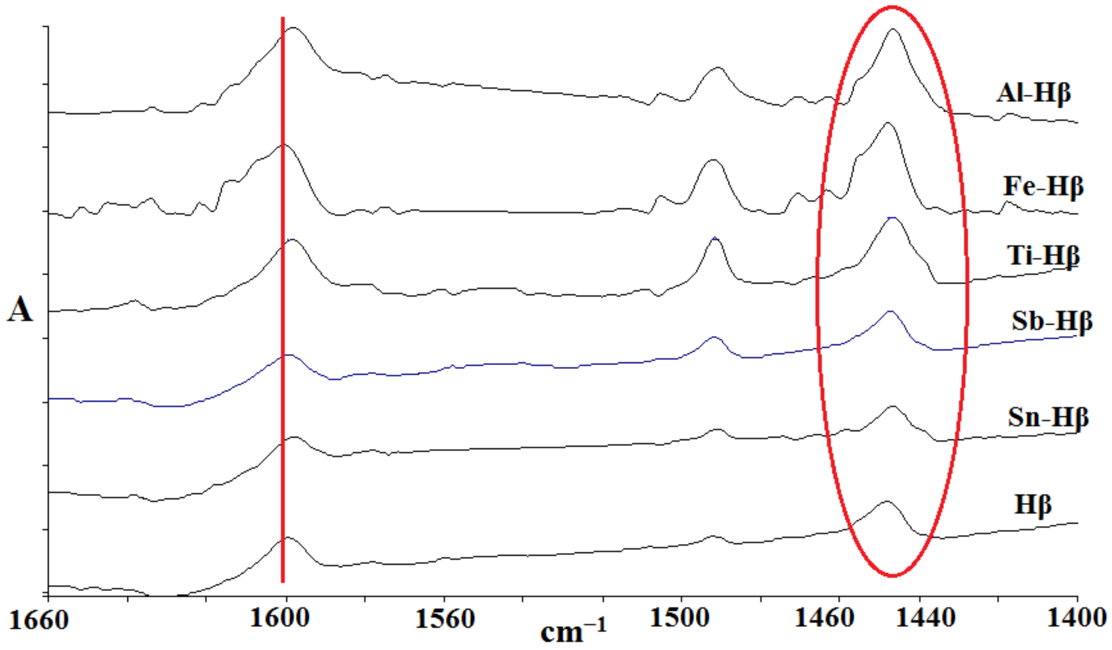

Fig. S1. FT-IR spectra of pyridine adsorbed on modified Hβ at 150°C.

In order to check the thermal stability, Al-Hβ300 catalyst was characterized by TGA. It was recorded on Perkin Elmer STA-6000 instrument with temperature range from 30°C to 800°C and a ramp 10°C/min. About 5% loss in weight was observed up to 300°C. Thus, the catalyst was stable at the working temperature (**Fig. S2**).

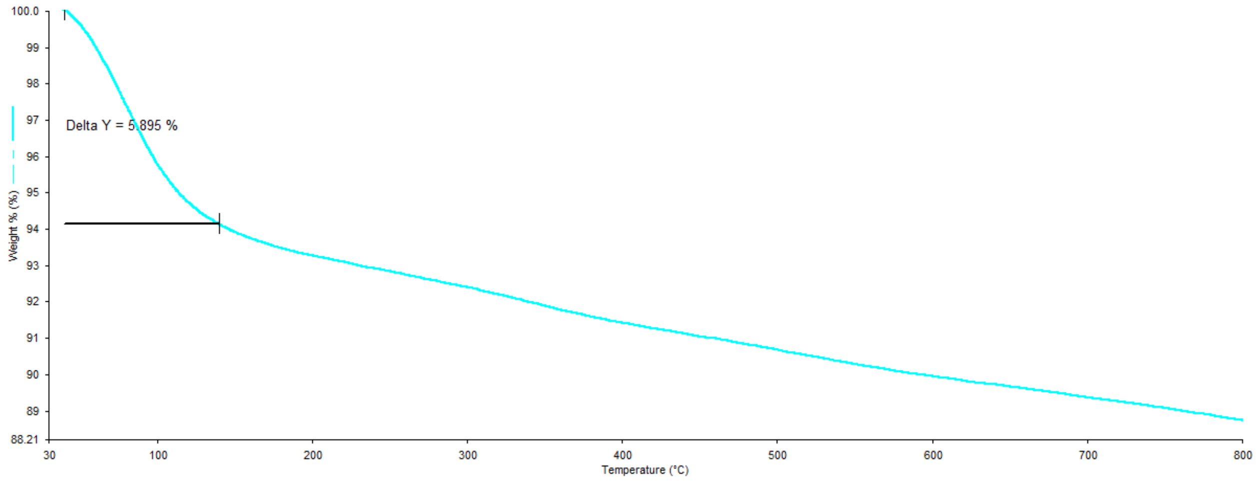

Fig. S2. TGA of Al-Hβ300

Nitrogen adsorption-desorption isotherms were obtained on a Micromeritics ASAP 2010 apparatus. Before measurement, the samples were degassed at 350 °C for 4 h under vacuum. The specific surface area and pore volume were calculated by the BET and BJH methods, respectively, with a value of P/P^0 lower than 0.98 (**Fig. S3**). TPD measurements were done on a Micromeritics TPD/TPR AutoChem II 2920 V3.03 instrument. The sample was activated at 550°C for 30 min in a flow of helium (30 mL/min) and then saturated with ammonia at 50°C (10% NH_3 in He and desorption at 30°C/min to 550°C).

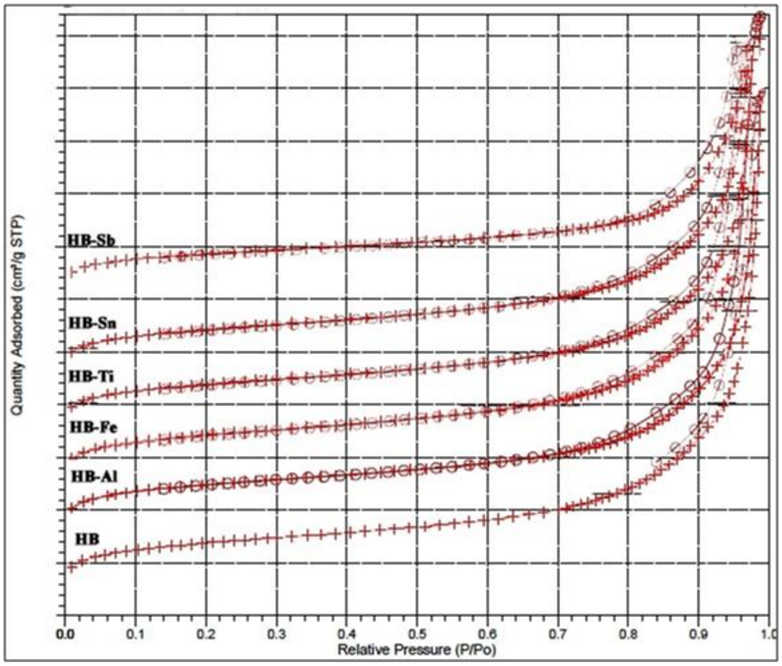

Fig. S3. N_2 adsorption–desorption isotherms of the catalysts

The samples were coated with gold to create contrast. Energy Dispersive X-ray Analysis (EDAX) was done using JEOL JSM7600F electron microscope. The metal content determined by EDAX method matched with the ICP analysis (**Fig. S4a, S4b**).

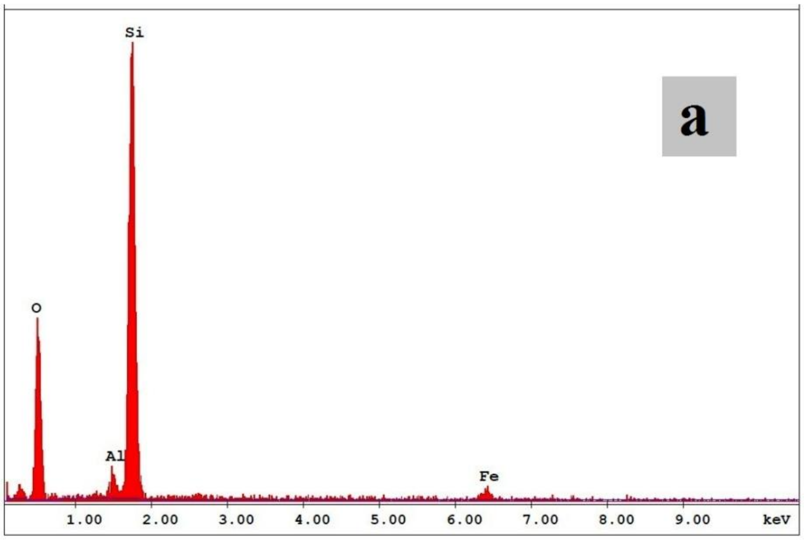

Fig. S4a. EDX image of Fe-Hβ

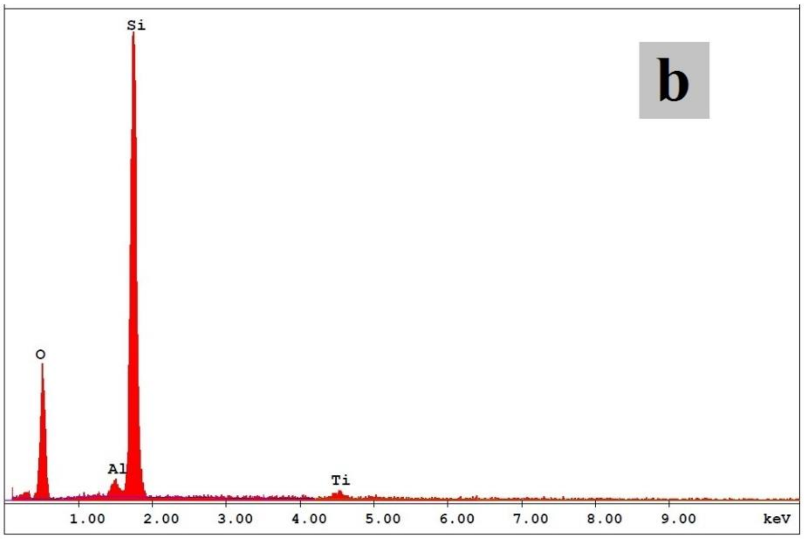

Fig. S4b. EDX image of Ti-Hβ

The FT-IR was recorded using a Shimadzu 3800 FT-IR spectrophotometer. The metal content of the catalyst was determined by ICP-AES using a Varian Vista AX ICP-AES spectrometer. The IR spectra of the catalysts show several typical bands (**Fig. S5**.). The bands in the region of 1240 - 1200 cm^{-1}, 1100 - 1050 cm^{-1} and 800 - 750 cm^{-1} are due to the external asymmetric stretching, internal asymmetric stretching, and symmetric stretching of TO_4 (T = Si, Al), respectively.[1] The double 6-membered ring and double 4-membered ring vibrations observed respectively at 580 - 570 cm^{-1} and 510 - 490 cm^{-1} indicate the framework structure of zeolite. The band at around 460 cm^{-1} is assigned to the T-O bending. These observations are in agreement with the XRD data.

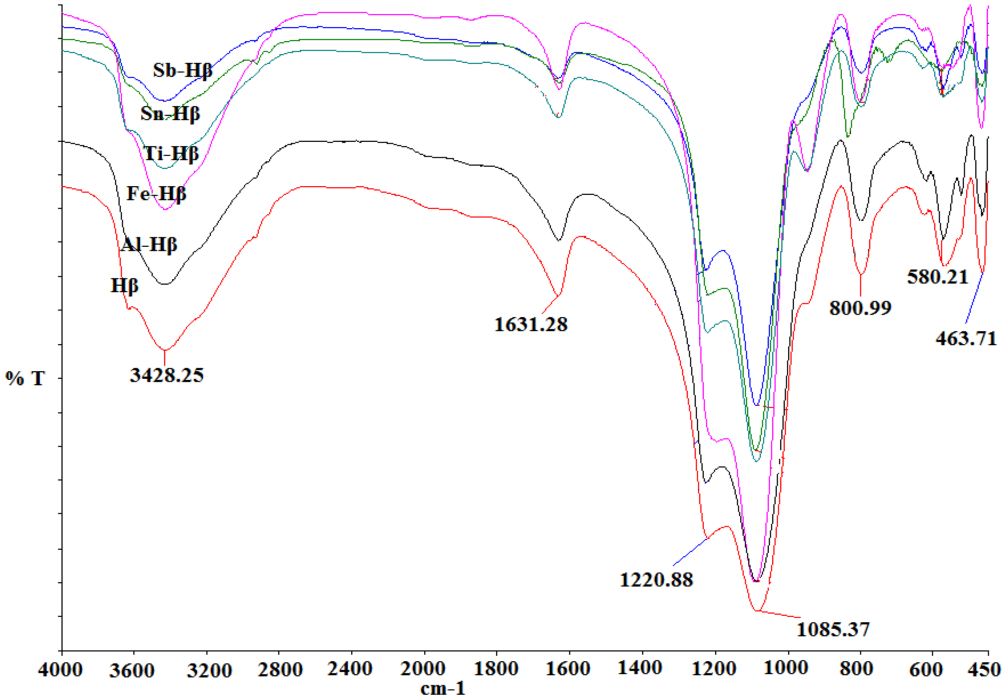

Fig. S5. FT-IR spectra of Hβ and metal modified Hβ catalysts.

3) Experimental Results

The isomerization was carried out at 300 °C for 6h using all the catalysts. At this temperature, all the catalysts showed the significant increase in the *p*-DEB conversion, but selectivity towards *m*-DEB decreased rapidly. Further, the amount of disproportionation products also increased (**Fig. S6**.).

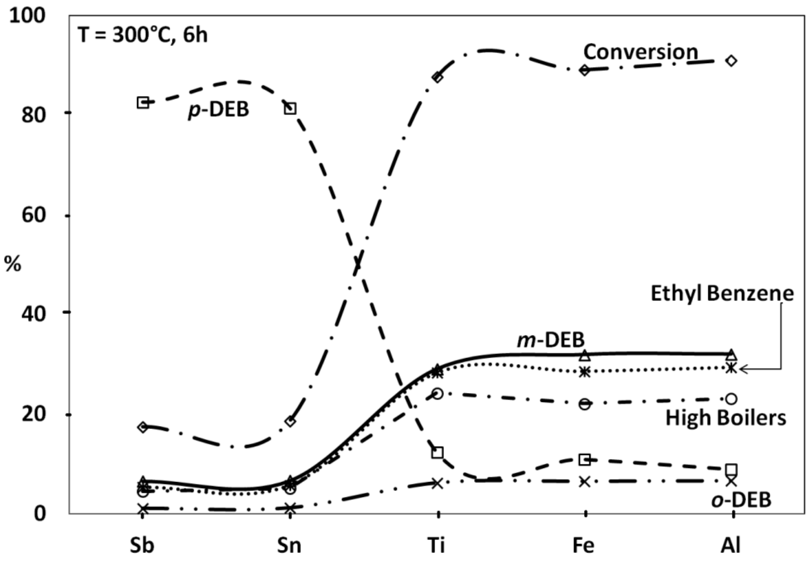

Fig. S6. Effect of reaction temperature (300°C) on the isomerization of *p*-DEB in the presence of modified Hβ.

Isomerization of *p*-DEB reaction was monitored in presence of Al-Hβ, Fe-Hβ, and Ti-Hβ catalysts with respect to time up to 8 h at 250°C. Results obtained with reaction monitoring in presence of Fe-Hβ and Ti-Hβ can be discussed with the help of **Fig.S7** and **Fig.S8**. The isomerization reaction proceeds very smoothly with increased catalyst acidity. There was substantial increase in the conversion of *p*-DEB with time and the conversion was optimum at 8h. However, *m*-DEB selectivity gradually increased upto 6 h, same time ethyl benzene and high boilers were also obtained because of dealkylation and realkylation. Beyond that though the conversion of *p*-DEB continued to increase but selectivity of *m*-DEB started decreasing, along with marginal increase in disproportionation products. Maximum selectivity of *m*-DEB was obtained upto 48.1% after 6 h (**Fig. S7**). Beyond that, selectivity of *m*-DEB started fall down, along with increase in the disproportionation products. Using Ti-Hβ catalyst, 43.6% electivity of *m*-DEB was obtained at 6 h (**Fig.S8**); continuation of reaction ends up into decrease in selectivity of *m*-DEB and increase in byproducts.

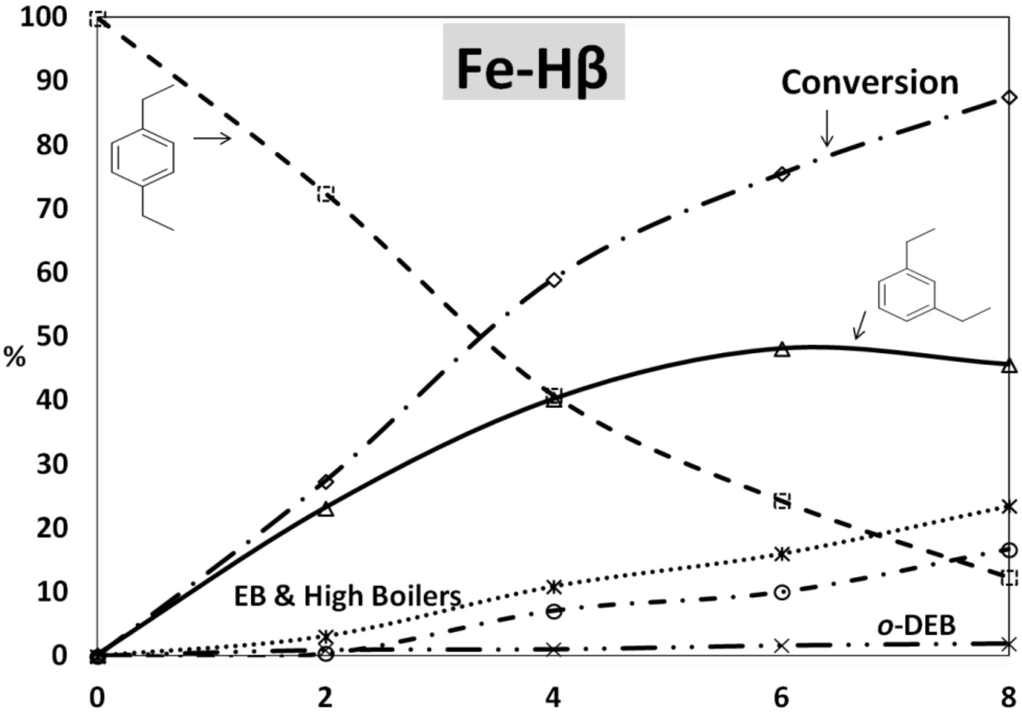

Fig. S7. Effect of reaction time on the isomerization of *p*-DEB in the presence of Fe-Hβ catalyst at 250°C

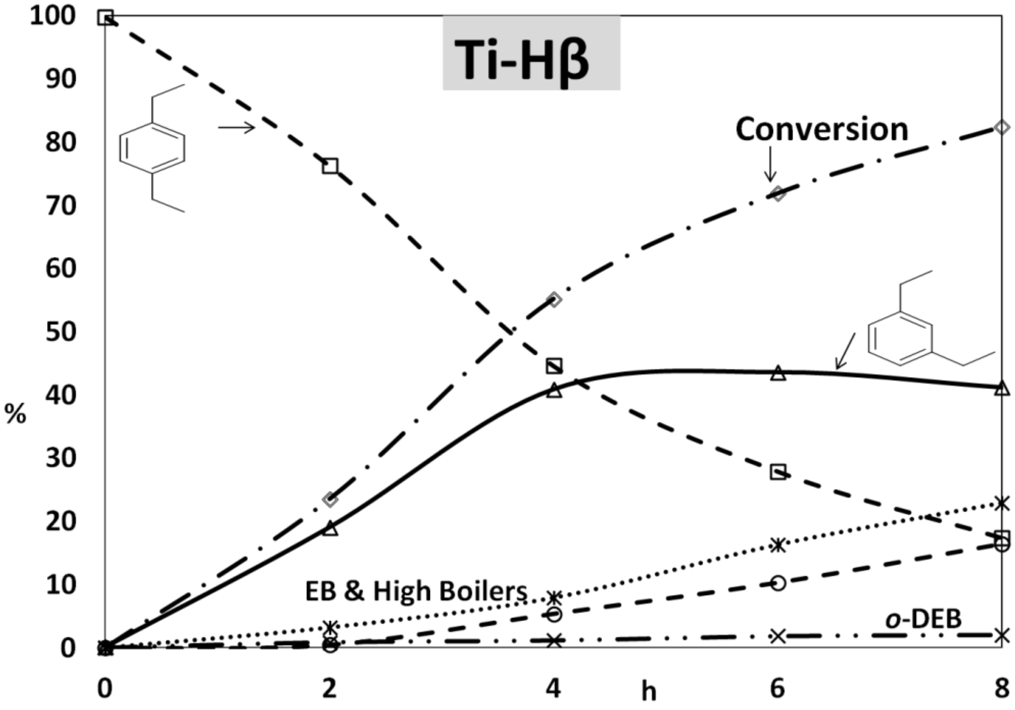

Fig. S8. Effect of reaction time on the isomerization of *p*-DEB in the presence of Ti-Hβ catalyst at 250°C

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