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## Chemo- and regioselective head-to-tail heterodimerization of vinylarenes with 1,1-diphenylethene over heterogeneous catalyst (Sn $\beta$ zeolite)

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**In the presence of Sn $\beta$  zeolite, vinylarenes undergo the highly chemo- and regioselective head-to-tail heterodimerization with 1,1-diphenylethene to form the corresponding alkenes in good to excellent yields. The scope of the reaction was explored by various vinylarenes with 1,1-diphenylethene. However, the substrates having strong electron-withdrawing groups failed to react with 1,1-diphenylethene under the present catalytic conditions. Moreover, Sn $\beta$  zeolite is recyclable and can be reused without significant loss in its catalytic activity.**

### Introduction

The development of catalytic C-H bond activation followed by C-C bond formation reactions has been one of the most challenging and active area of research in modern synthetic organic chemistry owing to their significant impact on the both academic and industrial research.<sup>1</sup> In particular, dimerization of alkenes is an important transformation (industrial process) for generating higher alkenes from abundant and inexpensive petrochemical feedstocks, which find extensive applications as industrial intermediates, as a source of new kinds of polymers, lubricants, detergents and many other useful chemicals.<sup>2,3</sup> The dimerization of alkenes gives the longer chain alkenes through head-to-head (h-h), head-to-tail (h-t) and tail-to-tail (t-t) dimerization.<sup>4</sup> Especially, the dimerization (head-to-tail (h-t) and tail-to-tail (t-t)) can be considered as the more attractive transformation since a new allylic carbon stereogenic centre is formed. In fact, several natural products and valuable pharmacologically important compounds, such as Naproxen, Nafenopin and Dimentindene, Warfarin derivative Phenprocoumon<sup>5</sup> contains this chemical structure.<sup>5</sup> Consequently, the dimerization of alkenes has received significant attention among the scientific community.<sup>6-10</sup>

Generally, 1,1-diarylethenes give the indan products in the presence of Lewis acids.<sup>11-15</sup> However, recently, W.-M. Dai et al developed an efficient head-to-tail heterodimerization of vinylarenes with 1,1-diarylethenes under homogenous catalytic conditions.<sup>16</sup> But, this homogeneous catalytic system has disadvantages related to the recovery and reuse of catalyst.<sup>16</sup> Therefore, there is a strong demand for developing methodologies for head-to-tail heterodimerization of alkenes under heterogeneous catalytic conditions in which the catalyst can be easily recoverable and reused without significant loss in their catalytic activity.

In recent years, environmental and economical considerations have raised strong interest to redesign commercially important processes to avoid the use of harmful substances and the generation of toxic waste. In this respect there is no doubt that heterogeneous catalysts can play a key role in the development of environmentally benign processes in petroleum chemistry and in the production of chemicals. Heterogeneous catalysts have many advantages over homogeneous ones such as low cost, tolerance to a wide range of temperatures and pressures, easy and inexpensive removal from the reaction mixture by simple filtration or centrifugation, easy and safe disposal, safe storage, long lifetimes, increased eco-friendliness, regenerability and reusability. Moreover, application of the inorganic solid acids, especially zeolite materials have wide spread applications both in petroleum and fine chemical industries due to their unique physical and chemical properties, such as uniform channel size, large internal surface area, unique molecular shape selectivity, strong acidity and good thermal/hydrothermal stability. In continuation of our efforts toward the development of novel and eco-friendly synthetic protocols using zeolites,<sup>17</sup> herein we report a highly chemo- and regioselective head-to-tail heterodimerization of vinylarenes with 1,1-diphenylethene over heterogeneous catalyst (Sn $\beta$  zeolite). However, to the best of our knowledge, hitherto there has been no report for the head-to-tail heterodimerization of vinylarenes with 1,1-diphenylethene using a reusable, heterogeneous catalyst.

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## Experimental

### Reagents and Materials

Zeolite  $\beta$  in ammonia form ( $\text{NH}_4\beta$ ) with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 38$  was purchased from Alfa Aesar. Vinyl arenes, 1,1-diphenylethene and metal precursors were purchased from Sigma-Aldrich.

### Preparation of Catalyst

The  $\text{NH}_4\beta$  zeolite was calcined at 500 °C for 10 h to obtain H $\beta$  zeolite. Metal modified zeolite H $\beta$  was prepared by wet impregnation using the metal precursors ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot \text{XH}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) with 10 weight percentage. Zeolite H $\beta$  was added to the aqueous solution of corresponding metal salt (The ratio of weight of the zeolite to the volume of distilled water used to dissolve the metal salt was 1:3), which was then placed on a hot plate with stirring at 80 °C to remove the excess water. The prepared solid mass was dried for 12 h at 100 °C and calcined at 450 °C for 6 h in the presence of static airflow before using it for the reaction.

### General procedure for the head to tail heterodimerization of vinylarenes with 1,1-diphenylethene

Vinylarene (2 mmol), 1,1-diphenylethene (2.5 mmol) and 10% Sn $\beta$  zeolite (100 mg) were added to 1 mL of 1,2-dichloroethane (DCE) in a 15 mL of sealed vial and the reaction mixture was allowed to stir at 100 °C. After disappearance of the vinylarene (monitored by TLC) or after an appropriate time, the reaction mixture was cooled to room temperature, diluted with DCM. The catalyst was separated by filtration and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel using *n*-hexane-ethyl acetate as eluent to give desired products. All the products were identified on the basis of  $^1\text{H}$  and  $\text{C}^{13}$  NMR spectral data.

### Characterization of catalysts

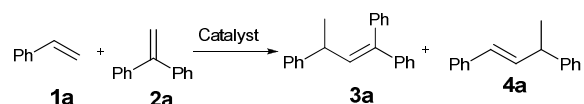
All the samples were systematically characterized by different spectroscopic techniques. The XRD patterns of the samples were obtained on a Regaku miniflux X-ray Diffractometer using Ni filtered  $\text{CuK}\alpha$  radiation at  $2\theta = 2\text{--}80^\circ$  with a scanning rate of  $2^\circ \text{min}^{-1}$  and the beam voltage and currents of 30 kV and 15 mA, respectively. FT-IR (Carry 660, Agilent Technologies) spectra were obtained in the range of  $1300\text{--}1700 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$  and 64 scans. The experiments were performed *in situ* using a purpose-made IR cell connected to a conventional vacuum-adsorption apparatus. The sample powders were pressed into self-supporting wafers (density  $\sim 40 \text{ mg/cm}^3$ ) under a pressure of  $10^5 \text{ Pa}$ . After that, the samples were introduced in the IR cell. Firstly, the samples were pre-treated by heating them in dynamic vacuum at a rate of  $10^\circ \text{C/min}$  up to 400 °C and maintained at the same temperature for 1 h. After cooling down to 150 °C the spectrum was collected in the DRIFT mode. Then the samples were exposed to pyridine until surface saturation and the spectrum was

recorded. The DRIFT spectra after pyridine treatment were subtracted from the spectra of the untreated catalyst to obtain the peaks only due to pyridine-acid interaction. Finally, the spectra were quantified with the Kubelka–Munk function. The temperature programmed desorption (TPD) of ammonia of H $\beta$  and metal modified  $\beta$  zeolites samples were measured using an Auto Chem 2910 (Micromeritics, USA). In a typical method about 0.1 g of calcined sample was degassed at 200 °C for 3 h in helium at a flow rate of  $30 \text{ mL min}^{-1}$ . After degassing the sample was saturated with 10%  $\text{NH}_3$  (balance helium) at 60 °C, at a flow rate of  $50 \text{ mL min}^{-1}$  and subsequently flushed with helium gas at 60 °C for 1 h. The TPD measurements were carried out from 60 °C to 700 °C at a ramping rate of  $10^\circ \text{C min}^{-1}$ . The amount of desorbed  $\text{NH}_3$  was calculated using GRAMS/32 software. The products were identified by NMR spectra using a Bruker VX NMR FT-300 or Varian Unity 500 spectrometers instrument in  $\text{CDCl}_3$ . Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) downfield from TMS. ESI mass spectra were obtained by using Micromass Quattro LC mass spectrometer and High-resolution mass spectra obtained by using ESI-QTOF mass spectrometry.

## Results and discussion

### Catalyst screening

**Table 1** Optimization study for the head-to-tail heterodimerization of styrene with 1,1-diphenylethene<sup>a,b</sup>



Entry	Catalyst	Conversion 1a (%) <sup>b</sup>	3a Yield (%) <sup>c</sup>	4a Yield (%) <sup>c</sup>
1	NaY	15	8	4
2	HY	20	11	7
3	HMCM-41	21	13	6
4	HZSM-5 (40)	16	10	5
5	Montmorillonite K10	23	15	7
6	H-Mordenite	26	16	8
7	H $\beta$	72	57	15
8	Absence of catalyst	00	00	00
9	10% Sn $\beta$	99	90	9
10	10% Fe $\beta$	28	20	6
11	10% Co $\beta$	25	18	7
12	10% Cr $\beta$	36	24	10
13	10% W $\beta$	43	30	11
14	10% Ni $\beta$	52	42	9
15	10% Mo $\beta$	76	63	11

<sup>a</sup> Reaction conditions: **1a** (2 mmol), **2a** (2.5 mmol), Catalyst (100 mg), 1,2-dichloroethane (DCE) (1 mL), 100 °C, 15 h, sealed vial. <sup>b</sup> Conversion of **1a** was based on GC. <sup>c</sup> Isolated yields.

Initially, we investigated the suitable reaction conditions for head-to-tail heterodimerization of vinylarenes with 1,1-diphenylethene using styrene (**1a**) and 1,1-diphenylethene (**2a**) as a model system (Table 1). In order to choose the best

catalyst, the reaction was carried out over various zeolites, MCM-41 and montmorillonite K10 at 100 °C in sealed vial for 15 h in DCE (Table 1, entries, 1-7). Among the catalysts examined, H $\beta$  zeolite showed the higher catalytic activity and furnished the **3a** in 57 % yield, along with 15% yield of homodimer **4a** (Table 1, entry 7). Although extensively investigated for many zeolitic structures, metal modified zeolite  $\beta$  has not been yet widely explored.<sup>18</sup> It is well acknowledged that the metal modification in zeolites manipulates the total acidity, acid site strength and nature of acid sites.<sup>19</sup> In an attempt to improve the yield of **3a**, we studied the head-to-tail heterodimerization of styrene with 1,1-diphenylethene over various metal modified zeolite  $\beta$  catalysts under similar reaction conditions (Table 1, entries 9-15) and the results revealed that Sn $\beta$  is the most effective catalyst over others (Table 1, entry 9). Influence of the both solvent and catalyst amount were also studied under similar reaction conditions over Sn $\beta$  (see the ESI Table S1 and S2). As can be seen from above obtained results, the optimized reaction conditions to get the highest yield for this reaction are 2:2.5 mole ratio of styrene to 1,1-diphenylethene in 1,2-dichloroethane (DCE) (1 mL) at 100 °C over 10% Sn beta zeolite (Table 1, entry 9).

**Table 2** The heterodimerization of vinylarenes (**1a-1m**) with 1,1-diphenylethene (**2b**) over 10% Sn $\beta$  zeolite<sup>a,b</sup>

Entry	Olefin	R	Product	Yield (%)
1	<b>1a</b>	Ph	<b>3a</b>	90
2	<b>1b</b>	4-MeOC <sub>6</sub> H <sub>4</sub>	<b>3b</b>	00 <sup>c</sup>
3	<b>1c</b>	3-MeC <sub>6</sub> H <sub>4</sub>	<b>3c</b>	80
4	<b>1d</b>	4-MeC <sub>6</sub> H <sub>4</sub>	<b>3d</b>	86
5	<b>1e</b>	2,4-DiMeC <sub>6</sub> H <sub>3</sub>	<b>3e</b>	80
6	<b>1f</b>	4-tert-Butyl C <sub>6</sub> H <sub>4</sub>	<b>3f</b>	84
7	<b>1g</b>	4-FC <sub>6</sub> H <sub>4</sub>	<b>3g</b>	75
8	<b>1h</b>	4-ClC <sub>6</sub> H <sub>4</sub>	<b>3h</b>	76
9	<b>1i</b>	4-BrC <sub>6</sub> H <sub>4</sub>	<b>3i</b>	70
10 <sup>d</sup>	<b>1j</b>	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>3j</b>	-
11 <sup>d</sup>	<b>1k</b>	4-COOHC <sub>6</sub> H <sub>4</sub>	<b>3k</b>	-
12 <sup>d</sup>	<b>1l</b>	C <sub>5</sub> H <sub>5</sub> N	<b>3l</b>	-
13 <sup>d</sup>	<b>1m</b>	n-C <sub>8</sub> H <sub>16</sub>	<b>3m</b>	-

<sup>a</sup> Reaction conditions: **1a-1m** (2 mmol), **2a** (2.5 mmol), 10% Sn $\beta$  (100 mg), 1,2-dichloroethane (DCE) (1 mL), 100 °C, 15 h, sealed vial. <sup>b</sup> Isolated yields. <sup>c</sup> Polymerization products. <sup>d</sup> No conversion of substrate was observed.

Having the optimized conditions in hand, the scope and limitations of the present catalytic system was explored by reaction of various vinylarenes with 1,1-diphenylethene and the results are summarized in Table 2. The <sup>1</sup>H NMR spectra of all products indicated that only the E isomers were formed. Alkyl substituted styrenes **1c-1f** reacted smoothly to furnish

the corresponding trisubstituted alkenes **3c-3f** in 80-86% yields, respectively, without forming respective homodimers (Table 2, entries 3-6). In case of 4-methoxystyrene (**1b**), the polymerization pathway became dominant and a complex mixture of unidentified products were obtained (Table 2, entry 2). The reaction of 4-halo-styrenes **1g-1i** with 1,1-diphenylethene proceeded efficiently to afford the relevant products **3g-3i** in 70-76% yields (Table 2, entries 7-9), along with a substantial amounts of corresponding homodimers (16-22%). Unfortunately, the substrates 3-nitrostyrene (**1j**), 4-vinylbenzoic acid (**1k**), 2-vinylpyridine (**1l**) and 1-octene (**1m**) did not react under the present reaction conditions (Table 2, entries 10-13).

To determine the strength of acidity of the samples, temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) has been performed on the H $\beta$  and metal modified  $\beta$  zeolites (Fig. 1). The total amount of acidity measured by NH<sub>3</sub>-TPD for the H $\beta$  and metal modified zeolite  $\beta$  catalysts are represented in Table 3. As can be seen in Fig. 1, the presence of weak acid sites are responsible for high conversion of styrene (Sn $\beta$ , Mo $\beta$  and H $\beta$ ), whereas other metal modified beta zeolites have strong to medium acid sites which gave less conversion of styrene. Among the modified H $\beta$  zeolites, Sn $\beta$  was found to be most active catalyst probably due to more number of weak acidic sites present on the catalyst surface (see the ESI Table S4).

**Table 3** Acidity of H $\beta$  and metal modified zeolites<sup>a</sup>

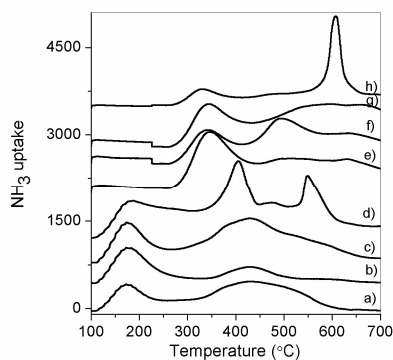
Catalysts	Acidity (mmol of NH <sub>3</sub> g <sup>-1</sup> )	Acidity (B/L ratio) <sup>a</sup>
H $\beta$	0.47	1.13
10% Sn $\beta$	1.04	0.20
10% Co $\beta$	1.73	0.58
10% Cr $\beta$	1.31	0.54
10% Fe $\beta$	1.59	0.44
10% Mo $\beta$	1.40	0.25
10% Ni $\beta$	1.66	0.78
10% W $\beta$	1.40	0.37

<sup>a</sup> Relative ratio of Bronsted to Lewis acidity measured by pyridine adsorbed FT-IR spectra

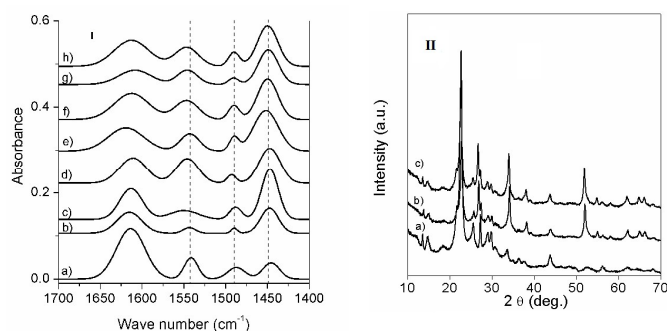
The Pyridine adsorbed H $\beta$  and modified H $\beta$  samples are analyzed by FT-IR spectroscopy to distinguish the Brønsted and Lewis acid sites present on the catalyst surface. The interaction of pyridine with the Brønsted and Lewis acid sites gives rise to bending vibrations at 1540 and 1450 cm<sup>-1</sup>, respectively and a vibrational band at 1490.4 cm<sup>-1</sup> is attributed to pyridine adsorbed on both Bronsted and Lewis acid sites. The relative ratio of peak intensities corresponding to Bronsted and Lewis acid sites is measured and the results are reported in Table 3. It is evident from Table 3 that the Sn $\beta$  showed a lowest B/L ratio (0.20) (than the H $\beta$  and other metal modified beta zeolites) gave better yield of the corresponding product (**3a**) compared to other catalysts. Although H $\beta$  possessed a higher B/L ratio, the TPD of NH<sub>3</sub> results exemplified that the presence of higher number of weak acid sites compared to other metal

modified H $\beta$  zeolites could be a possible reason for the higher conversion of styrene over H $\beta$  catalyst.

The XRD patterns of H $\beta$  and Sn $\beta$  showed similar patterns (Fig. 2, II), except a prominent peak at  $2\theta = 51.7^\circ$  which is attributed to SnO<sub>2</sub> phase (ICDD# 88-0287) and this phase remain unchanged even after reuse, which indicates the stability of the catalyst.



**Figure 1** NH<sub>3</sub>-TPD profiles of a) H $\beta$  b) Sn $\beta$  c) Mo $\beta$  d) Ni $\beta$  e) W $\beta$  f) Cr $\beta$  g) Fe $\beta$  h) Co $\beta$



**Figure 2** I) Pyridine FT-IR spectra of a) H $\beta$  b) Sn $\beta$  c) Mo $\beta$  d) W $\beta$  e) Ni $\beta$  f) Cr $\beta$  g) Fe $\beta$  h) Co $\beta$ . II) XRD pattern of a) H $\beta$  b) Sn $\beta$  c) reused Sn $\beta$

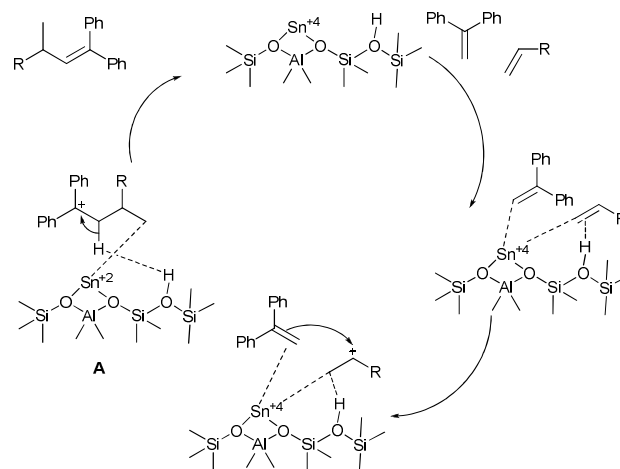
**Table 4** The head-to-tail heterodimerization of styrene with 1,1-diphenylethene over Sn $\beta$  zeolite-reusability of the catalyst<sup>a,b</sup>

Entry	Cycle	<b>3a</b> Yield (%) <sup>c</sup>	<b>4a</b> Yield (%) <sup>b</sup>
1	First	90	9
2	Second	91	7
3	Third	90	8
4	Fourth	89	9
6	Fifth	88	10

<sup>a</sup> Reaction conditions: **1a** (2 mmol), **2a** (2.5 mmol), 10% Sn $\beta$  (100 mg), 1,2-dichloroethane (DCE) (1 mL), 100 °C, 15 h, sealed vial. <sup>b</sup> Isolated yields.

The reusability of the catalyst is one of the most significant properties for the industrial applications and environmental considerations. The catalyst (Sn $\beta$  zeolite) was easily separated from the reaction mixture by simple filtration. Further, recycling of catalyst was carried out by performing the reaction of styrene with 1,1-diphenylethene under standard reaction conditions and the reused catalyst showed consistent

activity even after fifth reuse (Table 4). The catalyst was highly crystalline before and after the reaction, which was confirmed by XRD (Figure 1). There was no leaching of aluminium or silicon from zeolite (H $\beta$ ) and confirmed by elemental analysis. A plausible reaction mechanism is illustrated in Scheme 1. It is assumed that the Lewis acidic sites of Sn $\beta$  zeolite brings the olefin molecules closer by coordinating with the  $\pi$  electrons of the olefins. Once the olefin molecules are adsorbed and coordinated to acidic sites (both Lewis and Bronsted) of Sn $\beta$  zeolite, polarization of the C=C bond by Bronsted acidic site of zeolite generating an electrophilic center, which subsequently reacts with another olefin to give the corresponding dimer via intermediate (A).



**Scheme 1** Plausible mechanism for the formation of substituted olefins over Sn $\beta$  zeolite

## Conclusions

In conclusion, we have developed a convenient Sn $\beta$  zeolite catalyzed protocol for the highly chemo- and regioselective head-to-tail heterodimerization of vinylarenes with 1,1-diphenylethene under mild conditions. The scope and limitations of this process are demonstrated with various vinylarenes and 1,1-diphenylethene. However, the substrates (alkenes) having strong electron-withdrawing groups were unsuccessful with this catalytic system. Notable advantages offered by this strategy are use of non-hazardous and reusable catalyst, higher yields of the desired products, simple work-up procedure, which make this catalytic system an attractive and useful alternative to the existing method.

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## Chemo- and regioselective head-to-tail heterodimerization of vinylarenes with 1,1-diphenylethene over heterogeneous catalyst (Sn $\beta$ zeolite)

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Highly chemo- and regioselective heterodimerization of vinylarenes with 1,1-diphenylethene to form the corresponding alkenes using heterogeneous catalyst (Sn $\beta$  zeolite) is reported for the first time.

