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Hydrogenation of α,β-Unsaturated Carbonyl Compounds Using Recyclable Water-Soluble Fe^{II}/EDTA Complex Catalyst

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Abstract Hydrogenation of unsaturated carbonyl compounds like cinnamaldehyde and citral was studied in a biphasic media using water-soluble Fe^{II}/EDTA as a catalyst. It was observed that olefinic bond was selectively hydrogenated over the carbonyl group. Different reaction parameters like temperature, pressure, catalyst concentration were optimized for better selectivity of hydrocinnamaldehyde/dihydrocitronellal. The catalyst was further extended to hydrogenation of several other α,β-unsaturated carbonyl compounds.

Keywords Cinnamaldehyde · Citral · Biphasic catalysis · Hydrogenation reactions · EDTA

1 Introduction

Selective hydrogenation of α,β-unsaturated carbonyl compounds is an important reaction considering its extensive applications in the pharmaceutical and fine chemicals [1–3]. In recent years, much attention has been paid for selective hydrogenation of α,β-unsaturated aldehydes into unsaturated alcohols due to its applications in the synthesis of fine chemicals, perfumes and pharmaceuticals [4, 5]. Hydrocinnamaldehyde (HCAL) is also a hydrogenation product of cinnamaldehyde (CAL) and finds applications like as an intermediate for anti-viral pharmaceuticals, especially HIV protease inhibitors [6]. Citral is a substrate of keen interest to the fragrance and flavors industry. Its completely saturated aldehyde, dihydrocitronellal can be derived from citral hydrogenation via citronellal and is more stable than citral itself. Dihydrocitronellal could enhance the citrus effect of cologne; hence it is also one of the important fragrances. Earlier studies using various transition metal catalyzed hydrogenations for above substrates showed markedly different selectivity behavior in such reactions [7–9].

Biphasic catalysis is one of excellent technique which gives easy catalyst-product separation for reactions involving soluble transition metal complexes [10, 11]. It has been successfully used in many industrial processes for reactions like hydroformylation of propene, hydroisomerisation of butadiene and carbon-carbon bond formation [12, 13]. In the biphasic catalysis transition metal complex held in the aqueous phase by coordinating with appropriate water-soluble ligand and the organic phase contains reactants/products [10]. Selective reduction of unsaturated aldehydes to saturated aldehydes/alcohol or unsaturated alcohol, could be achieved by choosing the appropriate metal complexes as catalysts [7–9, 14, 15]. The applications of water-soluble transition metal complex catalysts in the biphasic hydrogenation have been extensively studied in recent years [16–19]. Water-soluble ruthenium complexes selectively reduces carbonyl group of α,β-unsaturated aldehydes [20–23]. Water-soluble rhodium and palladium complexes selectively catalyze the hydrogenation of carbon–carbon double bond to form saturated aldehydes [24–26]. It has been shown that water-soluble Ru/TPPTS complex selectively hydrogenate olefinic bond of cinnamaldehyde if certain parameters are controlled [27].

Recently Fe based complex catalysts have been reported for chemoselective hydrogenation of ketones [28] and nitroaromatics [29]. In continuation of our work in selective hydrogenations [30, 31] we herein report the hydrogenation

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of α,β-unsaturated carbonyl compounds including cinnamaldehyde and citral in a biphasic media for the first time using water-soluble Fe^{II}/EDTA complex catalyst.

2 Experimental

2.1 Materials

Cinnamaldehyde (Fluka), Citral and substrates (Aldrich), $FeSO_4 \cdot 7H_2O$ and Ethylenediaminetetraacetic acid disodium dihydrate i.e. $EDTA–Na_2 \cdot 2H_2O$ (S.D. Fine) were used as received. The reaction analysis was performed using GC (Chemito 1000), GCMS (Shimadzu QP-2010). High-pressure reactor of 100 mL and 400 mL capacity built in Hastalloy-C material was designed by M/S Amar equipments.

2.2 Typical Procedure for Hydrogenation of α,β-Unsaturated Carbonyl Compounds

In a 100 mL beaker, 28 mg (0.1 mmol) of $FeSO_4 \cdot 7H_2O$ and 186 mg (0.5 mmol) of $EDTA–Na_2 \cdot 2H_2O$ were dissolved in 50 mL water. This gives a clear light green color solution. To a high-pressure reactor of 400 mL capacity, α,β-unsaturated carbonyl compound (10 mmol) was added followed by addition of clear light green solution prepared above. The reactor was then pressurized to 400 psi of hydrogen and heated to 100 °C with an agitation speed of 900 rpm for 6 h. The reactor was cooled to room temperature, the remaining hydrogen was carefully vented. Ethyl acetate (2 × 25 mL) was added to the reactor and the reaction mixture was stirred for 15 min to extract the product. The aqueous layer containing the Fe/EDTA complex was recycled for the next run after phase separation. The combined extracts were dried over sodium sulfate and the solvent was evaporated in vacuo.

2.3 Products Analysis and Characterization

The products were analyzed using GC and compared with authentic standards. The quantitative analysis was performed using external standard method. The products were also confirmed by GC-MS.

Typical identification of some selected products by mass spectra (EI, 70 ev) are:

HCAL: $m/z = M^+$ 134 (70), 105 (30), 91 (100), 78 (20), 51 (25).
HCOL: $m/z = M^+$ 136 (24), 117 (100), 91 (85), 77 (23), 51 (15).
Scheme 2, III: $m/z = M^+$ 156 (40), 123 (30), 136 (90), 108 (35), 71 (100), 44 (65).
Table 3, entry 1: $m/z = M^+$ 98 (52), 69 (30), 55 (100), 42 (70).
Table 3, entry 2: $m/z = M^+$ 126 (45), 111 (20), 71 (100), 70 (40), 55 (50), 43 (52).
Table 3, entry 6: $m/z = M^+$ 116 (10), 88 (70), 71 (100), 60 (20), 43 (80), 29 (45).
Table 3, entry 8: $m/z = M^+$ 150 (35), 104 (60), 91 (100), 78 (20).

3 Results and Discussion

3.1 Chemoselective Hydrogenation of Cinnamaldehyde

Hydrogenation of unsaturated carbonyl compounds like cinnamaldehyde was studied in a biphasic media using water-soluble Fe^{II}/EDTA as a catalyst. In the present context, we preferred not to use any organic solvent, hence neat reactants were directly added to water phase containing Fe/EDTA complex. Since the reactants are liquid and immiscible in the aqueous phase, they form small droplets suspended in a continuous aqueous catalyst phase. This is also a typical example of biphasic catalysis wherein the catalyst phase acts as a continuous phase and the reactants form another phase in the form of suspended droplets [32]. Due to the elimination of the organic solvent phase, an increased concentration of reactants can be achieved leading to a higher reaction rate [33]. The products after reaction can be separated by simple phase separation or using extraction techniques. The hydrogenation of cinnamaldehyde (CAL) gives typical product profile as shown in Scheme 1. The results obtained for its hydrogenation are given in Table 1.

3.1.1 Influence of Catalyst

Screening of various first series transition metal salts as a catalyst precursor along with EDTA ligand for CAL hydrogenation was shown in Table 1 (entries 1–7). $FeSO_4$/EDTA was found to be best performing active catalyst and provides good conversion of CAL (99%) and selectivity towards HCAL (88%). The results obtained can be attributed to the stability constant of the Metal–EDTA complex (log K_{ML}).

The metal ion is bound to the ligand and the strength of this ligand can be estimated through the stability constant, log K_{ML} which is a function of the equilibrium concentration of the metal ion (M) and the ligand (L).

$$K_{ML} = \frac{C_{ML}}{C_M \, C_L}$$

The stability constants for Cu^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+},

Scheme 1 Hydrogenation of cinnamaldehyde

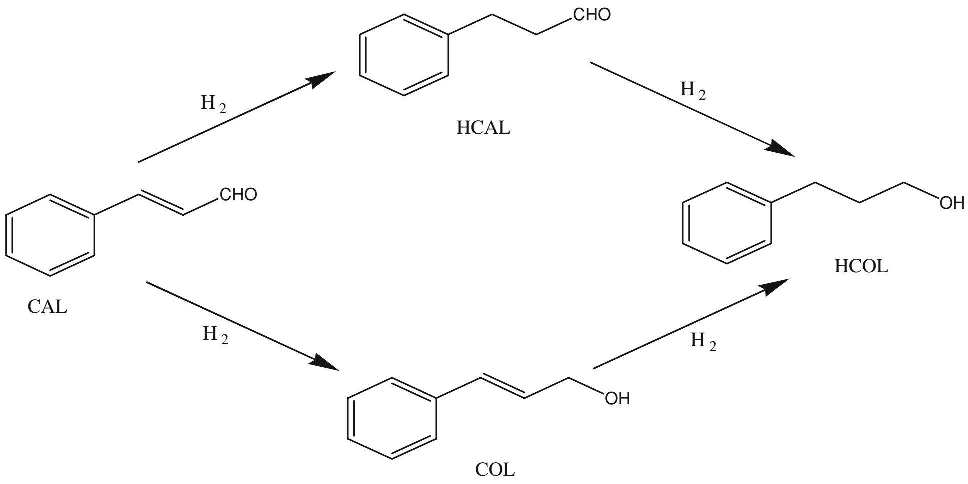


Table 1 Hydrogenation of cinnamaldehyde (CAL)[a]

Entry	Catalyst	Time (h)	Temp. (°C)	P H_2 (psi)	Conv.[f] (%)	Selectivity[f] (%)		
						HCAL	HCOL	COL
1	$CuSO_4 \cdot 5H_2O$	6	80	400	99	57	27	15
2	$MgSO_4 \cdot 7H_2O$	6	80	400	99	45	32	22
3	$MnSO_4 \cdot H_2O$	6	80	400	99	40	33	26
4	$ZnSO_4 \cdot 7H_2O$	6	80	400	99	62	22	15
5	$NiSO_4 \cdot 7H_2O$	6	80	400	99	48	30	21
6	$FeSO_4 \cdot 7H_2O$	6	80	400	99	88	9	2
7	$Fe(NO_3)_3 \cdot 9H_2O$	6	80	400	99	80	14	5
8	$FeSO_4 \cdot 7H_2O$	8	80	400	99	56	41	2
9	$FeSO_4 \cdot 7H_2O$	10	80	400	99	35	64	0
10	$FeSO_4 \cdot 7H_2O$	12	80	400	99	5	94	0
11	$FeSO_4 \cdot 7H_2O$	6	60	400	78	86	12	2
12	$FeSO_4 \cdot 7H_2O$	6	100	400	99	33	62	5
13	$FeSO_4 \cdot 7H_2O$	6	120	400	99	20	76	2
14	$FeSO_4 \cdot 7H_2O$	6	80	300	92	87	10	2
15	$FeSO_4 \cdot 7H_2O$	6	80	500	99	86	9	4
16[b]	$FeSO_4 \cdot 7H_2O$	6	80	400	46	78	20	2
17[c]	$FeSO_4 \cdot 7H_2O$	12	80	400	62	75	15	10
18[d]	$FeSO_4 \cdot 7H_2O$	6	80	400	99	87	9	3
19[e]	$FeSO_4 \cdot 7H_2O$	6	80	400	95	85	10	5
20	$Fe(NO_3)_3 \cdot 9H_2O$	8 + 1	80	400	99	94	5	1
21	10% Pd/C	3	80	300	99	92	6	1

[a] In 400 mL reactor, CAL 10 mmol, catalyst 1 mol%, EDTA–Na_2 5 mol%, water 50 mL, 900 rpm

[b] Without ligand

[c] Biphasic condition (toluene 50 mL:water 50 mL)

[d] 2 mol% of catalyst

[e] 3rd recycle

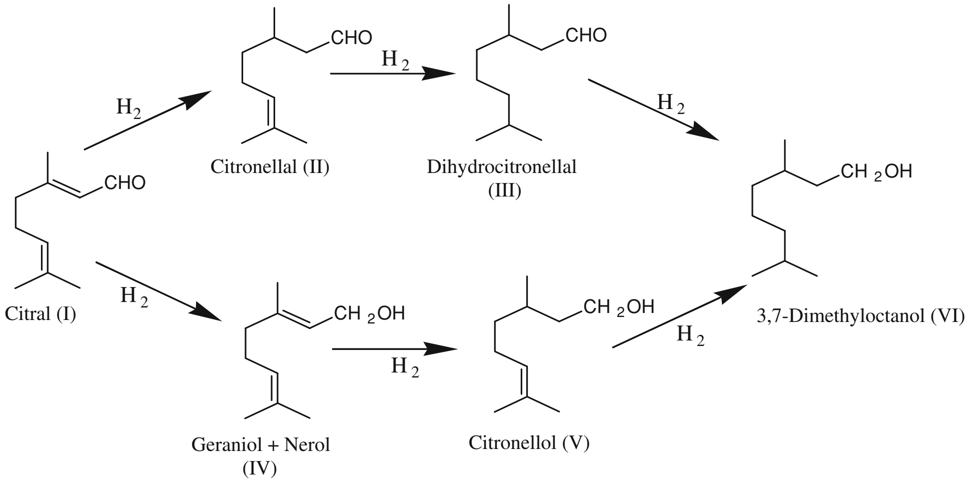
[f] Analyzed by GC and confirmed by GC-MS with precision of ± 2

Ni^{2+}, Fe^{2+} complexes with EDTA as a ligand are 18.80, 8.79, 13.87, 16.50, 18.62, 14.32 respectively [34]. It can be seen that the complexes having a too low or too high value of log K_{ML}, shows the deviation in the selectivity. However, Fe^{+2}/EDTA complex having the average value of stability constant 14.32 shows good selectivity towards HCAL. This might be due to that the complexes of Mg and Mn are not that stable enough for incoming hydrogen also the complexes of Cu, Zn, Ni are highly stable and might not have easy access for hydrogen.

The reaction time for hydrogenation of CAL was optimized as shown in Table 1 (entries 6, 8–10). Reaction time plays an important role and it was observed that when reaction time was increased from 6 to 12 h, HCOL was obtained as the only product due to further hydrogenation of HCAL. The HCAL can be selectively obtained by reducing the reaction time.

When reaction was performed in presence of catalyst precursor, $FeSO_4$, alone i.e. without addition of ligand EDTA, it gave lower conversion of CAL (46%) and 78%

Scheme 2 Hydrogenation of citral



selectivity towards HCAL (entry 16). When reaction was carried out under typical biphasic condition (entry 17) using $FeSO_4$/EDTA complex catalyst in aqueous phase with toluene as a organic phase, it gave poor performance like entry 16. When catalyst concentration was doubled i.e. 2 mol%, the 99% conversion was obtained alongwith 85% selectivity towards HCAL (entry 18). The catalyst was also recyclable retaining good activity and selectivity (entry 19). The catalyst $Fe(NO_3)_3 \cdot 9H_2O$/EDTA can gave 99% conversion of CAL and highest selectivity of 94% towards HCAL with alteration in reactions procedure i.e. hydrogenation for 8 h and further stirring for 1 h at 80 °C without hydrogen atmosphere (entry 20) [35]. The efficiency of Fe/EDTA catalyst system was compared with conventional heterogeneous Pd/C catalyst and found to give comparable results (entry 21). Although performance is comparable in this case, it should be noted that Fe/EDTA is an inexpensive alternative for Pd and which is a goal of current work.

3.1.2 Influence of Temperature

Hydrogenation of CAL was carried out at different temperatures in the range of 60–120 °C (entries 6, 11–13). Optimum results were obtained at 80 °C and temperature lower than 80 °C gave lower conversion of CAL. Selectivity change from HCAL to HCOL happens at higher temperatures i.e. 100 and 120 °C. Hence, temperature is one of the decisive factors in the selective hydrogenation due to the nature of competing consecutive reactions.

3.1.3 Influence of Pressure

Hydrogenation of CAL was studied at different hydrogen pressures, 300–500 psi (entries 6, 14, 15). Comparable results were obtained in all cases showing that selectivity is irrespective of hydrogen pressure.

3.2 Chemoselective Hydrogenation of Citral

Citral possesses one conjugated and one isolated olefinic bond, hence is an ideal substrate for study. Hydrogenation of citral (**I**) was carried out in a similar manner as that of CAL. Typical reactions products involved in the hydrogenation of citral is shown in Scheme 2 and the hydrogenation results were summarized in Table 2.

3.2.1 Influence of Catalyst

The catalyst screening results showed that, $FeSO_4 \cdot 7H_2O$, in combination with $EDTA–Na_2 \cdot 2H_2O$ was found to gave better activity and selectivity towards dihydrocitronellol (**III**). Reaction time for hydrogenation of **I** was optimized as shown in Table 2 (entries 6, 8–10). Increase in the reaction time, increases selectivity towards **III** and prolonged reaction time (9 h) gave 3,7-dimethyloctanol (**VI**) with 82% selectivity. However, **III** can be selectively obtained by reduction in reaction time to 6 h. The catalyst system was found to be recyclable without any appreciable loss in activity and selectivity (entry 16).

3.2.2 Influence of Temperature

Hydrogenation of **I** was carried out at four different temperatures, 80–120 °C (entries 6, 11–13). At lower temperatures high selectivity towards citronellal (**II**) was observed but with lower conversion of **I**. At higher temperature (120 °C) increased selectivity up to 82% towards **III** was observed with high conversion of **I**. This represents selectivity is highly dependant on temperature parameter.

3.2.3 Influence of Pressure

Hydrogenation of **I** was studied at different hydrogen pressures, 300–500 psi (entries 6, 14, 15). Again results

Table 2 Hydrogenation of citral (**I**)[a]

Entry	Catalyst	Time (h)	Temp. (°C)	*P* H_2 (psi)	Conv.[c] (%)	Selectivity[c] (%)			
						II	III	IV + V	VI
1	$CuSO_4 \cdot 5H_2O$	6	120	400	86	34	53	8	5
2	$MgSO_4 \cdot 7H_2O$	6	120	400	75	32	32	15	20
3	$MnSO_4 \cdot H_2O$	6	120	400	71	27	40	16	17
4	$ZnSO_4 \cdot 7H_2O$	6	120	400	78	28	42	12	18
5	$NiSO_4 \cdot 7H_2O$	6	120	400	66	25	30	20	25
6	$FeSO_4 \cdot 7H_2O$	6	120	400	99	10	82	3	5
7	$Fe(NO_3)_3 \cdot 9H_2O$	6	120	400	89	12	78	4	6
8	$FeSO_4 \cdot 7H_2O$	7	120	400	99	8	62	3	27
9	$FeSO_4 \cdot 7H_2O$	8	120	400	99	3	44	2	51
10	$FeSO_4 \cdot 7H_2O$	9	120	400	99	0	15	3	82
11	$FeSO_4 \cdot 7H_2O$	6	80	400	52	66	12	14	8
12	$FeSO_4 \cdot 7H_2O$	6	90	400	68	52	28	11	9
13	$FeSO_4 \cdot 7H_2O$	6	100	400	80	31	54	6	9
14	$FeSO_4 \cdot 7H_2O$	6	120	300	85	12	80	4	4
15	$FeSO_4 \cdot 7H_2O$	6	120	500	99	11	80	4	5
16[b]	$FeSO_4 \cdot 7H_2O$	6	120	400	99	10	82	4	4

[a] In 100 mL reactor, citral 5 mmol, catalyst 1 mol%, EDTA–Na_2 5 mol%, water 20 mL, 900 rpm

[b] 3rd recycle

[c] Analyzed by GC and confirmed by GC-MS with precision of ±2

showed that selectivity is not dependant of hydrogen pressure. However, at lower pressure (300 psi) low conversion of **I** (85%) was observed.

3.3 Hydrogenation of Various α,β Unsaturated Aldehydes

A variety of other α,β-unsaturated carbonyl compounds were selectively hydrogenated to their corresponding saturated analogues in biphasic media indicates general applicability of the present catalyst system. α,β-Unsaturated carbonyl compounds were hydrogenated at 100 °C gave optimized results (see Table 3 and Scheme 3).

Cyclohex-2-enone and 4,4-dimethylcyclohex-2-enone on hydrogenation gave high selectivity and high yield towards saturated cyclic ketones (entry 1 and 2). 3-Methyl substituted cyclic enones were found to give lower yields of 3-methyl substituted cyclic ketones due to lower conversion (entry 3 and 4).

α,β-unsaturated esters such as methyl, ethyl, *n*-butyl acrylate were successfully hydrogenated (entry 5). Propionic acid was found to be the major product in hydrogenation of methyl acrylate and ethyl acrylate. The probable reason may be the miscibility of these substrates in water resulting in completely homogeneous system, which favors the hydrolysis of ester to acid. However, *n*-butyl acrylate is immiscible in water and forms biphasic system resulting in *n*-butylpropionate in 88% yield. Similarly ethyl crotonate was hydrogenated to give ethyl butyrate in 49% yield (entry 6).

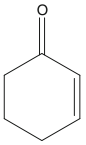
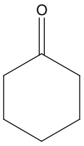
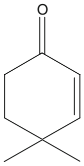
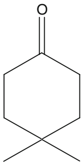
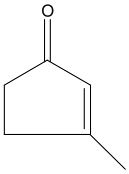
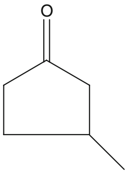
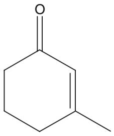
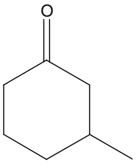
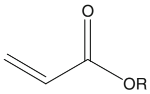
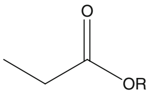
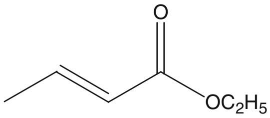
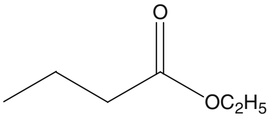
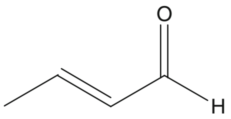
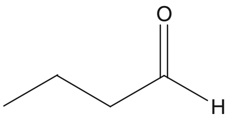
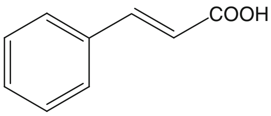
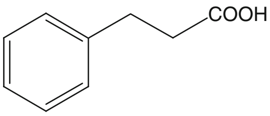
Selective hydrogenation of crotonaldehyde was also carried out using Fe/EDTA catalyst system. The reaction was performed for 3 h to give *n*-butanal as the product in 68% yield however, when reaction was performed for 6 h, it gave completely hydrogenated *n*-butanol as the only product. Cinnamic acid at 140 °C (>m.p.) results in biphasic system under hydrogenation condition to give 25% yield of hydrocinnamic acid.

3.4 Mechanism

$FeSO_4$ and EDTA–Na_2 in situ forms an equimolar octahedral complex I having stability constant (log K_{ML}) 14.32, however, increasing Fe:EDTA ratio increases the stability of the complex [34]. The reaction mechanism proposed for this transformation is given in the Scheme 4.

Fe–EDTA complex I coordinate with molecular hydrogen through bridged oxygen atoms resulting the complex II. Bridged oxygen atoms are more labile than chelates formed by two nitrogen atoms of EDTA molecule [36, 37]. Labile bridged oxygen atoms can give access to the incoming reactants i.e. α,β-unsaturated carbonyl compounds on the central Fe atom, which results in a π-complex III with α,β-unsaturated compound [38, 39]. The π-complex then gets

Table 3 Selective hydrogenation of various α,β-unsaturated carbonyl compounds[a]

Entry	Substrate	Conversion[a] (%)	Product[b]	Yield[b] (%)
1		99		95
2		85		80
3		25		20
4		29		22
5				
	R = –CH_3	95	R = H	90
	R = –C_2H_5	91	R = H	86
	R = –C_4H_9	92	R = –C_4H_9	88
6		55		49
7[c]		90		68
8[d]		26		25

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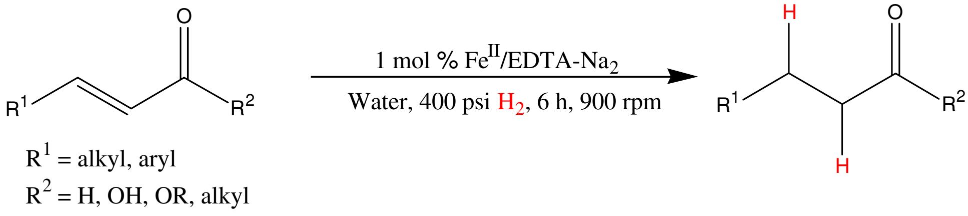
[a] Procedure as given in experimental section

[b] Analyzed by GC and confirmed by GC-MS with precision of ±2

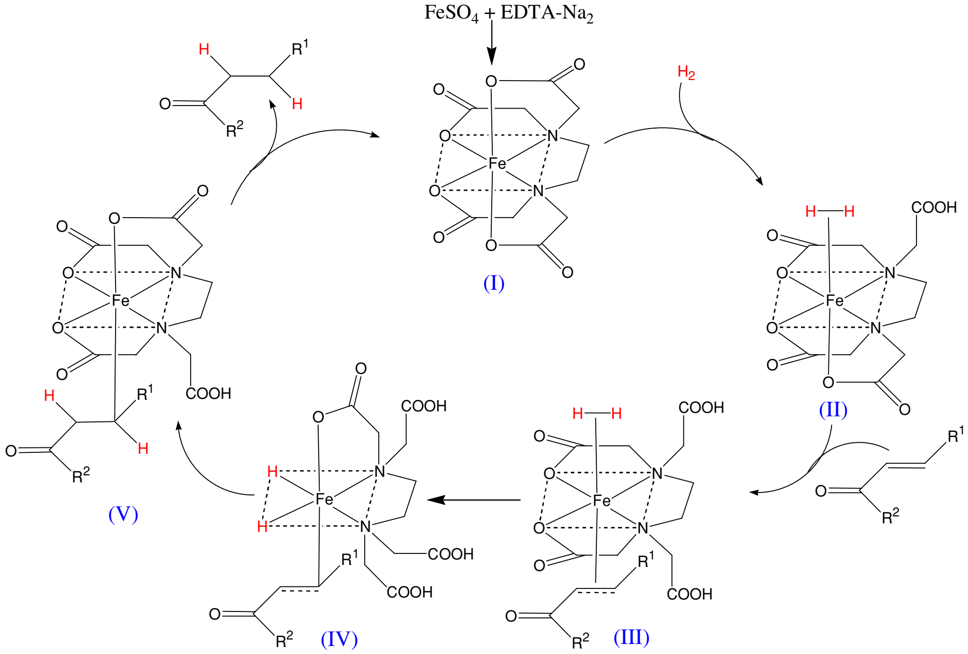
[c] 3 h

[d] At 140 °C

Scheme 3 Hydrogenation of α,β-unsaturated carbonyl compounds



Scheme 4 Mechanism



transformed into a σ-complex IV by forming Fe–C bond and hydrogen transfer occurs across the α,β carbon–carbon bond as shown in V. Saturated α,β-unsaturated compound is released giving back the Fe–EDTA octahedral complex I which completes the catalytic cycle.

4 Conclusions

Hydrogenation of cinnamaldehyde and citral were studied in biphasic media for the first time using Fe/EDTA catalyst system and is an efficient alternative to noble metal (Rh, Pd, Pt, Ru) based catalysts. Olefin bond in α,β-unsaturated compound was hydrogenated prior to the carbonyl group. The present catalyst system uses environmentally benign water as solvent and commercially available non-toxic EDTA as ligand. It also tolerates the use of any other organic solvent and is recyclable after simple phase separation. The catalyst system has wider applicability in the selective hydrogenation of various α,β-unsaturated compounds to corresponding saturated analogues.

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