

The ‘single-pot’ synthesis of C_{2n+2} -aldol derivatives from C_n -alkenes using multi-functional catalyst

Vivek K. Srivastava, Sumeet K. Sharma, Ram S. Shukla, Raksh V. Jasra *

Silicates and Catalysis Discipline, Central Salt and Marine Chemicals Research Institute (CSMCRI), G.B. Marg, Bhavnagar 364 002, Gujarat, India

Received 12 December 2005; received in revised form 9 March 2006; accepted 20 March 2006

Available online 28 March 2006

Abstract

A multi-functional catalyst [HF/HT], by impregnation/intercalation of inorganic metal complex, $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ [HF] on a solid base hydrotalcite; $(\text{Mg}_{1-x}\text{Al}_x(\text{OH}_2))^{x+} ((\text{CO}_3^{2-})_{x/n} \cdot m\text{H}_2\text{O})$ [HT] having hydroformylation, aldol condensation and hydrogenation activity is reported for synthesis of C_{2n+2} -aldol derivatives from C_n -alkenes in single pot. The effect of the, HT/HF weight ratio, Mg/Al molar ratio of HT and aldol condensation temperature (T_2) at a fixed hydroformylation temperature (T_1) is studied for single pot synthesis of C_8 aldol derivatives from propylene using [HF/HT] catalyst system under varied reaction parameters. The selectivity of 2-ethylhexanal is observed to increase from 7% to 48% by increasing the HT (Mg/Al = 3.5) to HF ratio from 1 to 10. The selectivity of 2-ethylhexanol increased from 11% to 21% on increasing the Mg/Al molar ratio of HT from 1.5 to 3.5 in the multi-functional catalyst system at aldol condensation temperature (T_2) 250 °C.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Aldol reaction; Hydroformylation; Hydrogenation; Multi-functional catalyst; Single pot; Hydrotalcite

1. Introduction

Synthesis of C_{2n+2} aldehydes/alcohols from C_n alkenes is a multi-step process involving hydroformylation of an alkene for the production of aldehyde using Rh or Co based catalysts [1–3]; followed by aldol condensation of aldehyde with stoichiometric amounts of liquid base like KOH or NaOH [4,5]; and finally hydrogenation of unsaturated aldol derivatives using Ni or Cu catalytic systems [6–9]. For example, nearly 60% of total *n*-butanal synthesized commercially by hydroformylation of propylene is converted to C_8 alcohol employing the aldol condensation of *n*-butanal followed by hydrogenation of condensation product [1]. Similarly, synthesis of 2,2,4-trimethyl-1,3-pentanediol which is a useful intermediate for the production of polyesters and resins, is done by homo-aldol condensation of isobutanal produced by propylene hydroformylation [10,11].

Besides being multi-step synthesis, the existing processes for the synthesis of C_{2n+2} aldehydes/alcohols from C_n alkenes are both environmentally and economically inefficient and have other drawbacks like use of hazardous liquid base such as KOH or NaOH in large stoichiometric amount. Alkali metal hydroxides require large amount of water for the neutralization and washing after the completion of reaction, for the disposal of spent KOH/NaOH. It is estimated that approximately 1–1.5 tons of spent liquid base is being generated for every 10 tons of product formed in the homogeneous aldol condensation [12].

To overcome these drawbacks, a novel concept of using a multi-functional catalyst [HF/HT], by impregnation/intercalation of inorganic metal complex, $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ [HF] on a solid base hydrotalcite; $(\text{Mg}_{1-x}\text{Al}_x(\text{OH}_2))^{x+} ((\text{CO}_3^{2-})_{x/n} \cdot m\text{H}_2\text{O})$ [HT] has been attempted [13] for carrying out hydroformylation, aldol condensation and hydrogenation in a single pot under varied reaction conditions for the first time for the synthesis of C_{2n+2} aldehydes/alcohols from C_n alkenes.

* Corresponding author. Tel.: +91 278 2471793; fax: +91 278 2567562.
E-mail address: rvjasra@csmcri.org (R.V. Jasra).

2. Experimental

Ethylene (99.5%), propylene (99.6%) and syn-gas (99.8%) were procured from Alchemie Gases & Chemicals Pvt. Ltd., India respectively. Liquid olefins were procured from Sigma–Aldrich, USA. The rhodium metal precursors $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, triphenylphosphine (PPh_3), sodium borohydride (NaBH_4), and formaldehyde (HCHO) were purchased from Sigma–Aldrich, USA for the synthesis of HF complex. The salts of magnesium ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminum ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium carbonate (Na_2CO_3), and sodium hydroxide (NaOH) were purchased from s.d. Fine Chemicals, India for synthesizing HT component of the multi-functional catalyst system. The double distilled milli-pore de-ionized water was always used wherever necessary.

The multi-functional catalyst system [HF/HT] was synthesized by the following procedure. 10 ml toluene solution of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ (500 mg) and PPh_3 (1050 mg) was poured into a flask containing 3.5 g HT of Mg/Al ratio = 3.5. The slurry was stirred for 32 h at room temperature under inert atmosphere. After 32 h, the toluene was removed under vacuum at room temperature. The final product was a dry free-flowing light yellow powder.

The powder X-ray diffraction patterns of the HF complex, HT and multi-functional catalyst [HF/HT(X)] of different Mg/Al ratio (X) were recorded with Phillips X'Pert MPD system equipped with XRK 900 reaction chamber, using Cu $\text{K}\alpha$ radiation ($\lambda = 1.54050 \text{ \AA}$). The P-XRD pattern of HT (Fig. 1) for each Mg/Al ratio showed sharp and symmetric peaks at lower diffraction angles ($2\theta = 10\text{--}25$) and broad asymmetric reflections at higher angles ($2\theta = 30\text{--}50$), which were characteristics of hydrotalcites like materials [14,15]. The sharp peaks of the HF complex

at $2\theta = 8.5$ and 20 were present in all the P-XRD spectra of the multi-functional complex. As the value of X increases from 1.5 to 3.5, there is a shift toward lower 2θ values 11.3 and 23.1 of the (003) and (006) planes respectively, of P-XRD patterns of the different HT(X) samples. This is in agreement with the concurrent decrease of the positive charge of the layers of HT. The same feature is obviously observed for the [HF/HT(X)] mixtures. Moreover, these latter patterns allow to conclude that no intercalation has taken place because the lines of the two phases (HT and HF) clearly appeared and there is no shift of the 001 peaks relatively to the parent samples.

The desired amount of the multi-functional catalyst system (700 mg) was added into the autoclave (100 ml EZE-Seal Stirred Reactor, Autoclave Engineers, USA) having 50 ml toluene as a solvent. The autoclave was flushed twice with nitrogen prior to introducing desired pressure (10 bar) of the propylene or 2 g (by weight), in case of liquid alkenes ($n = 4\text{--}10$). The reactor was then brought to $60 \text{ }^\circ\text{C}$ reaction temperature (T_1). Then CO (5 bar) and H_2 (15 bar) ($\text{CO}:\text{H}_2 = 1:3$) gases were introduced into the reactor. Then the reaction was initiated by starting the magnetic stirrer at 1000 rpm. The reaction was kept for 3 h at $60 \text{ }^\circ\text{C}$ temperature. After 3 h, the reaction temperature was raised to $T_2 \text{ }^\circ\text{C}$ (150 or $250 \text{ }^\circ\text{C}$) to initiate the aldol condensation and hydrogenation reactions for 9 h. During this time, the constant pressure of the reactor was maintained by supplying H_2 from reservoir. After the total reaction time, i.e., 12 h, the orange-red solution of the product mixture is subjected to GC (Shimadzu-17A, universal capillary column, 0.25 mm dia., 60 m length) and GC-MC (Shimadzu, Model – QP2010) analysis. The product distribution (% selectivity) of the each product was calculated by the following formula:

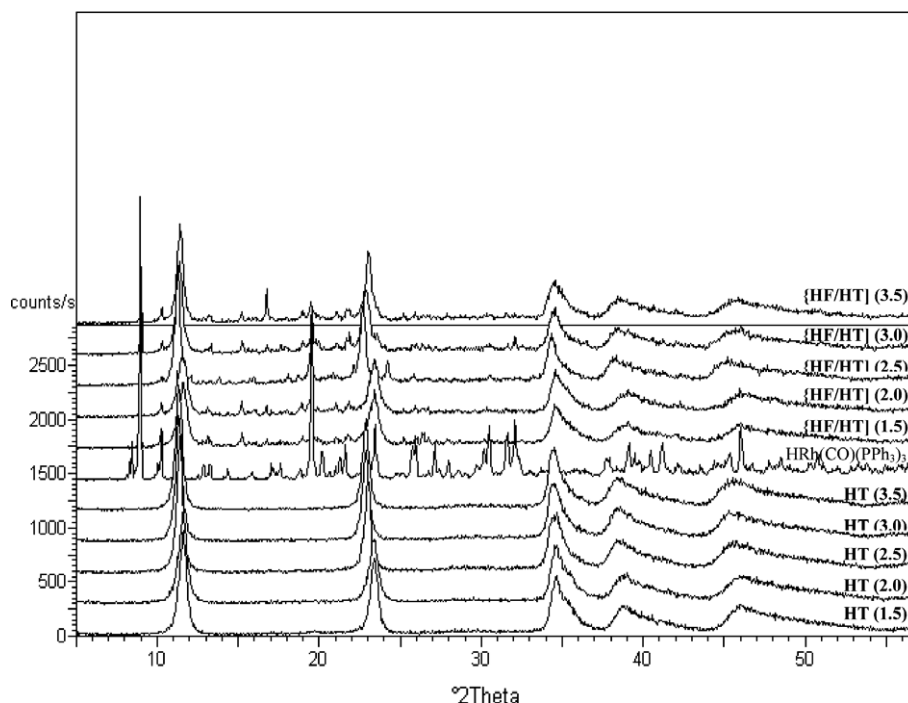


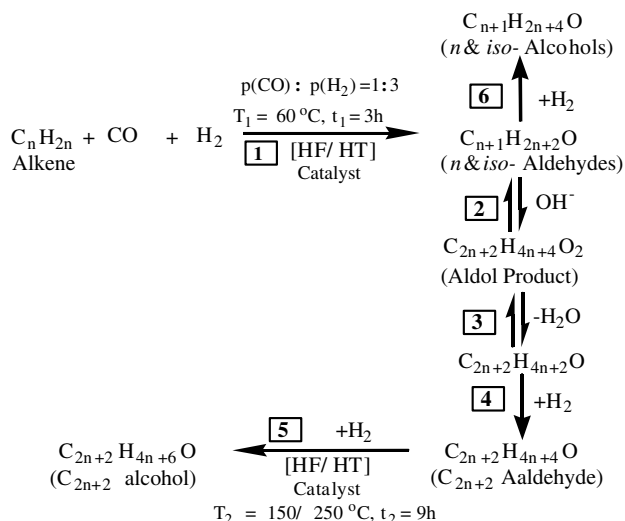
Fig. 1. P-XRD pattern of HF complex, HT and multi-functional catalyst [HF/HT(X)] system.

$$\begin{aligned}
& \%n\text{-Butanal} \\
& = \left(\frac{\text{moles of } n\text{-butanal}}{\text{moles of } (n\text{-butanal} + \text{iso-butanal} + n\text{-butanol} + \text{iso-butanol} + 2\text{-ethylhexenal} + 2\text{-ethylhexanol} + 2\text{-ethylhexanol})} \right) \times 100 \\
& \%iso\text{-Butanal} \\
& = \left(\frac{\text{moles of iso-butanal}}{\text{moles of } (n\text{-butanal} + \text{iso-butanal} + n\text{-butanol} + \text{iso-butanol} + 2\text{-ethylhexenal} + 2\text{-ethylhexanol} + 2\text{-ethylhexanol})} \right) \times 100 \\
& \%n\text{-Butanol} \\
& = \left(\frac{\text{moles of } n\text{-butanol}}{\text{moles of } (n\text{-butanal} + \text{iso-butanal} + n\text{-butanol} + \text{iso-butanol} + 2\text{-ethylhexenal} + 2\text{-ethylhexanol} + 2\text{-ethylhexanol})} \right) \times 100 \\
& \%iso\text{-Butanol} \\
& = \left(\frac{\text{moles of iso-butanol}}{\text{moles of } (n\text{-butanal} + \text{iso-butanal} + n\text{-butanol} + \text{iso-butanol} + 2\text{-ethylhexenal} + 2\text{-ethylhexanol} + 2\text{-ethylhexanol})} \right) \times 100 \\
& \%2\text{-Ethylhexenal} \\
& = \left(\frac{\text{moles of 2-ethylhexenal}}{\text{moles of } (n\text{-butanal} + \text{iso-butanal} + n\text{-butanol} + \text{iso-butanol} + 2\text{-ethylhexenal} + 2\text{-ethylhexanol} + 2\text{-ethylhexanol})} \right) \times 100 \\
& \%2\text{-Ethylhexanol} \\
& = \left(\frac{\text{moles of 2-ethylhexanol}}{\text{moles of } (n\text{-butanal} + \text{iso-butanal} + n\text{-butanol} + \text{iso-butanol} + 2\text{-ethylhexenal} + 2\text{-ethylhexanol} + 2\text{-ethylhexanol})} \right) \times 100 \\
& \%2\text{-Ethylhexanol} \\
& = \left(\frac{\text{moles of 2-ethylhexanol}}{\text{moles of } (n\text{-butanal} + \text{iso-butanal} + n\text{-butanol} + \text{iso-butanol} + 2\text{-ethylhexenal} + 2\text{-ethylhexanol} + 2\text{-ethylhexanol})} \right) \times 100
\end{aligned}$$

To ensure the reproducibility of the reaction, repeated experiments were carried out under identical reaction conditions. The results obtained, including conversions and selectivities were found in the range of 5% variation, confirming the reproducibility of the results.

3. Results and discussion

The role played by the multi-functional catalyst system [HF/HT] for each step involved in the synthesis of C_{2n+2} alcohol from C_n alkene in single pot is as depicted in



Scheme 1. The formation of C_{2n+2} alcohol from C_n alkene in single pot.

Scheme 1. The reaction is initiated by the formation of C_{n+1} aldehydes (n & iso) via hydroformylation reaction (Step 1) catalyzed by the HF complex of the multi-functional catalyst system. The HT component catalyzes the aldol condensation of n - C_{n+1} aldehyde to C_{2n+2} aldol derivatives and subsequently to C_{2n+2} unsaturated aldehyde after removal of one molecule of water (Steps 2 and 3). The HF complex of the multi-functional catalyst system under varied reaction conditions also catalyze the Steps 4 and 5, i.e., hydrogenation of C_{2n+2} unsaturated aldehyde to C_{2n+2} saturated aldehyde and subsequent reduction of C_{2n+2} saturated aldehyde to C_{2n+2} alcohol. The possible side reactions are the isomerization and hydrogenation of the C_n alkene, hydrogenation of C_{n+1} aldehydes to their corresponding alcohols (Step 6) and cross-aldol reaction of C_{n+1} aldehydes.

The activity of [HF/HT] multi-functional catalyst was initially investigated for the various C_n alkenes ($n = 2-10$) to observe the effect of chain length on the formation of C_{2n+2} aldol derivatives (Table 1). It was interesting to see that the selectivity of C_6 aldol derivatives prepared from ethylene was achieved up to 87% within 12 h reaction time. However, there was a gradual decrease in the selectivities of C_{2n+2} aldol derivatives on increasing the chain length of C_n alkenes. The decrease in the selectivity of C_{2n+2} aldol derivatives is due to the side reactions, i.e., isomerization and hydrogenation of higher alkenes (Run 5–7; Table 1). As the chain length of C_n alkenes increases, the selectivities towards C_{n+1} aldehydes (hydroformylation products) gave increasing trend.

Table 1
Effect of the carbon chain length of alkenes on the selectivity of C_{2n+2} aldol derivatives

Run	Alkenes	% Conversion	Product distribution (%)			
			C_{2n+2} Aldol derivatives	C_{n+1} Aldehydes (<i>n</i> to iso ratio)	Isomerization of alkenes	Hydrogenation of alkenes
1	Ethylene		87	13 (1.6)	0	0
2	Propylene	98	71	29 (1.5)	0	0
3	1-Butene	95	68	32 (1.4)	0	0
4	1-Pentene	90	64	36 (1.5)	0	0
5	1-Hexene	98	43	17 (1.2)	10	30
6	1-Heptene	95	38	30 (1.2)	9	23
7	1-Octene	96	34	25 (1.8)	12	29
8	1-Nonene	96	18	64 (1.4)	8	10
9	1-Decene	95	7	84 (1.5)	1	8

Reaction conditions: partial pressure of C_n -alkenes (where, $n = 2, 3$) = 10 bar, weight of C_n -alkenes (where, $n = 4-10$) = 2 g, partial pressure of CO = 5 bar, partial pressure of H_2 = 15 bar, weight of *n*-tridecane = 0.2 g, weight of [HF/HT] = 700 mg, HT/HF ratio = 7, $T_1 = 60^\circ\text{C}$, $t_1 = 3$ h, $T_2 = 150^\circ\text{C}$, $t_2 = 9$ h, total time (t) = 12 h at 1000 rpm.

Due to its huge commercial significance the synthesis of C_8 aldol derivatives from propylene in single pot using multi-functional catalyst system [HF/HT] was studied in detail. The main reaction pathway for the single pot synthesis of C_8 aldol derivatives involves hydroformylation of propylene then self-condensation of butyraldehyde to 2-ethyl-3-hydroxyhexenal, followed by dehydration to 2-ethylhexenal, which was then hydrogenated to 2-ethylhexanol and subsequently to 2-ethylhexanol.

The single pot synthesis of C_8 aldol derivatives from propylene was carried out using [HF/HT] catalysts under varied reaction parameters like changing the HT/HF weight ratio, Mg/Al molar ratio of HT, aldol condensation temperature (T_2) at a fixed hydroformylation temperature (T_1).

The ratio of HT to HF complex plays a significant role in the activity of the [HF/HT]. Therefore, the multi-functional catalyst system [HF/HT] was prepared with HT/HF ratio from 1 to 25 keeping same HT having chemical composition with Mg/Al = 3.5 for studying the synthesis of C_8 aldol derivatives from propylene. It is observed from the data given in Table 2 that C_8 aldol derivatives namely 2-ethylhexanal and 2-ethylhexenal are formed in a single pot reaction from propylene using multi-functional catalyst [HF/HT]. The selectivity of 2-ethylhexanal is observed to

increase from 7% to 48% by increasing the HT to HF ratio from 1 to 10. The product distribution profile (% selectivity) of each product with respect to time is given in Fig. 2.

The gradual decrease in the selectivity of the 2-ethylhexanal (31%) was observed on further increasing the HT/HF ratio upto 25. The selectivity of butanal followed decreasing trend with increasing the HT/HF ratio of the multi-functional catalyst system. The least selectivities for C_8 aldol derivatives were observed when the selectivities of butanol were highest (Run 1; Table 2, at the lower HT/HF ratio) indicating the diversion of the reaction path towards another competitive reaction (Step 6, Scheme 1) in place of desired step 2 (Scheme 1) due to enhanced concentration of HF complex and lack in sufficient amount of solid base HT in the multi-functional catalyst system. The observed trend is difficult to explain as in this reaction, the butanal are simultaneously consumed into the two separate reactions, one is the aldol condensation and another is the hydrogenation reaction. In view of higher selectivity of C_8 aldol derivatives observed in the range of HT/HF ratio 5–10, further investigations were performed using HT/HF ratio 7 in the multi-functional catalyst system.

The effect of the Mg/Al molar ratio of HT in the multi-functional catalyst system was studied at 150°C and 250°C aldol condensation temperature (T_2) using constant

Table 2
Effect of HT/HF ratio of [HF/HT] catalyst on the selectivity of C_8 aldehydes

Run	HT/HF ratio	% Conversion ^a of propylene	Product distribution (%)			
			2-Ethylhexanal	2-Ethylhexenal	Butanal (<i>n</i> to iso ratio)	Butanol (<i>n</i> to iso ratio)
1	1	100	7	0	43 (1.5)	50 (0.9)
2	3	98	24	8	50 (1.4)	18 (0.8)
3	4	98	27	17	17 (1.4)	39 (0.7)
4	5	97	43	6	45 (1.3)	6 (0.8)
5	6	98	43	22	14 (1.1)	21 (0.7)
6	7	98	45	9	40 (1.0)	6 (0.6)
7	10	96	48	13	39 (0.9)	0
8	15	95	37	21	31 (1.0)	11 (0.7)
9	25	90	31	12	39 (1.0)	18 (0.6)

Reaction conditions: partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial pressure of H_2 = 15 bar, weight of [HF/HT] = 700 mg, Mg/Al ratio = 3.5, $T_1 = 60^\circ\text{C}$, $t_1 = 3$ h, $T_2 = 150^\circ\text{C}$, $t_2 = 9$ h, total time (t) = 12 h at 1000 rpm.

^a Conversion of propylene was calculated using following formula $C_p = C_{p0}(1 - X_p)$; where X_p = conversion of propylene, C_{p0} = initial concentration of propylene and calculated as $C_{p0} = p_p/RT$; where p_p = partial pressure of propylene.

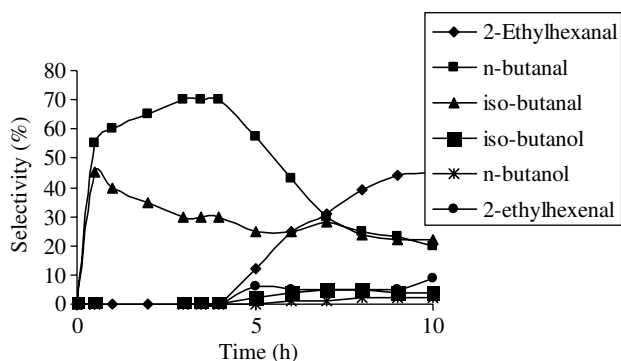


Fig. 2. Product distribution with time; Reaction conditions: partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial pressure of H₂ = 15 bar, weight of [HF/HT] = 700 mg, HT/HF ratio = 7, T₁ = 60 °C, t₁ = 3 h, T₂ = 150 °C t₂ = 9 h, total time (t) = 12 h at 1000 rpm.

HT/HF ratio of 7. The selectivity of C₈ aldol derivatives increases on increasing the Mg/Al molar ratio of HT from 1.5 to 3.5 (Run 1–5; Table 3) at 150 °C (T₂). The selectivity of 2-ethylhexanal was achieved upto 45% using Mg/Al ratio 3.5 under employed reaction conditions. The concentration of butanal also decreases in accordance to the increase of the concentration of C₈ aldol derivatives. One of the prominent changes in the product distribution was noticed during the course of experiments at aldol condensation temperature (T₂) 250 °C. A significant amount of 2-ethylhexanal was formed within 12 h at 250 °C temperature (T₂) via hydrogenation of C₈ aldehydes (Step 5, Scheme 1). The selectivity of 2-ethylhexanal increased from 11% to 21% on increasing the Mg/Al molar ratio of HT from 1.5–3.5 in the multi-functional catalyst system. The increment of Mg-contents in the HT increases the basic character of the hydrotalcites [16]. Hence, higher basicity of HT increases the yields of C₈ aldol derivatives. In case

of Mg/Al ratio of HT in the range 1.5–3.5, the higher selectivity of the aldol derivatives was observed at 150 °C as compared to 250 °C (T₂). The lower selectivities of C₄ and C₈ aldehydes at 250 °C (T₂) were observed due to continuous hydrogenation of aldehydes to the respective alcohols at employed reaction conditions, therefore, only butanols and 2-ethylhexanal were formed as major products at higher reaction temperature.

Table 3, clearly shows that the reaction is significantly influenced by the aldol condensation temperature (T₂). Therefore, in order to study the effect of T₂ on the selectivities of aldol derivatives, [HF/HT] multi-functional catalyst with HT/HF ratio 7 and Mg/Al ratio of HT at 3.5, the experiments for single pot synthesis of C₈ aldol derivatives from propylene was carried out at aldol temperature (T₂) ranging from 120 °C to 250 °C. The selectivity of 2-ethylhexanal was found to increase from 14% to 61% by increasing the temperature (T₂) from 120 to 200 °C (Run 6–7; Table 3) without any observation of 2-ethylhexanal. On further increasing the temperature T₂, selectivity of 2-ethylhexanal decreases from 61% to 4%. At aldol temperature T₂ of 250 °C, selectivity for 2-ethylhexanal was found to be 18% whereas no 2-ethylhexanal was observed upto 200 °C. The selectivity of butanal is found to decrease from 73% to 1% by increasing the T₂ from 120 °C to 250 °C. At 250 °C, the selectivity of the butanol sharply increases from 27% at 200 °C to 75%. The lower selectivity of the C_{2n+2} aldol derivatives of the propylene at 250 °C aldol temperature may be due to the deactivation of the HF complex at the higher temperature [17]. The rapid decreases in selectivity of butanal on increasing the T₂, indicates the consumption of butanal either for the aldol condensation or reduction to butanol. From the results, it was clearly observed that the higher temperature favors for the reduction of butanal and 2-ethylhexanal, which also catalyzed by the HF complex of the multi-functional catalyst system.

Table 3

Effect of the Mg/Al molar ratio of HT of [HF/HT] on the selectivity of C₈ aldehydes/alcohols at 150 and 250 °C aldol temperature (T₂)

Run	Mg/Al molar ratio	% Conversion	Product distribution (%)									
			Aldol condensation temperature (T ₂) = 150 °C					Aldol condensation temperature (T ₂) = 250 °C				
			2-Ethyl hexanol	2-Ethyl hexanal	2-Ethyl hexenal	Butanal (n to iso ratio)	Butanol (n to iso ratio)	2-Ethyl hexanol	2-Ethyl hexanal	2-Ethyl hexenal	Butanal (n to iso ratio)	Butanol (n to iso ratio)
1	1.5	97	–	30	14	51 (0.9)	4 (0.53)	11	5	–	28 (0.6)	56 (1.0)
	1.5 ^a	96	–	–	–	–	–	27	4	5	1 (iso)	63 (0.6)
2	2.0	98	–	35	18	35 (0.8)	12 (0.7)	12	2	–	1 (0.6)	85 (1.0)
3	2.5	99	–	40	10	37 (0.8)	14 (0.6)	11	2	2	2 (0.7)	83 (1.0)
4	3.0	98	–	39	15	36 (0.9)	10 (0.7)	21	3	2	1 (0.5)	73 (1.2)
5	3.5	98	–	45	9	40 (0.9)	6 (0.62)	18	4	2	1 (0.6)	75 (0.9)
6	3.5 ^b	96	–	14	2	73 (1.5)	11 (0.9)	–	–	–	–	–
7	3.5 ^c	98	–	61	3	9 (0.8)	27 (0.8)	–	–	–	–	–

Reaction conditions: partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial pressure of H₂ = 15 bar, weight of [HF/HT] = 700 mg, HT/HF ratio = 7, T₁ = 60 °C, t₁ = 3 h, t₂ = 9 h, Total time (t) = 12 h at 1000 rpm.

^a Total time = 24 h.

^b T₂ = 120 °C.

^c T₂ = 200 °C.

In conclusion, the multi-functional catalyst system [HF/HT] reported has shown the ability for single pot synthesis of C_{2n+2} aldol derivatives from C_n alkene under hydroformylation reaction conditions in an eco-friendly way.

Acknowledgements

Authors are thankful to Dr. P.K. Ghosh, Director, CSMCRI, Bhavnagar, India, for encouragement of this publication and CSIR Network Programme on Catalysis, CSIR, New Delhi, India, for the financial supports.

References

- [1] V.K. Srivastava, D.U. Parmar, R.V. Jasra, *Chem. Weekly* 8 (July) (2003) 173;
V.K. Srivastava, D.U. Parmar, R.V. Jasra, *Chem. Weekly* 15 (July) (2003) 181.
- [2] SRI International Chemical Economic Handbook, Oxo Chemicals Report, January 2003.
- [3] C.D. Frohning, C.W. Kohlpaintner, in: B. Cornils, W.A. Hermann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, vol. 1, Wiley-VCH, Weinheim, 2000, p. 29.
- [4] M. Tomoyuki, O. Yasukazu, F. Koichi, E. Hiroki, T. Akio, *JP* 11,269,118 (1999).
- [5] B.J. Arena, J.S. Holmgren, *US* 5,144,089 (1992).
- [6] G. Horn, C.D. Frohning, H. Liebern, W. Zgorzelski, *US* 5,475,161 (1995).
- [7] W. Bueschken, J. Hummel, *US* 5,756,856 (1998).
- [8] H.G. Lueken, U. Tanger, W. Droste, G. Ludwig, D. Gubisch, *US* 4,968,849 (1990).
- [9] K. Weisssermel, H.J. Arpe, *Industrial Organic Chemistry*, 3rd ed., Wiley, 1997.
- [10] K. Inui, S. Oshima, T. Kurabayashi, S. Kawamura, M. Yokota, *US-B2* 6,632,959 (2003).
- [11] J. Pedain, H. Mueller, D. Mager, M. Schoenfelder, *EP* 566,953.
- [12] J.J. Spivey, M.R. Gogate, Research Triangle Institute, USEPA Grant, *Pollution Prevention in Industrial Condensation Reactions*, 1996.
- [13] R.V. Jasra, V.K. Srivastava, R.S. Shukla, H.C. Bajaj, S.D. Bhatt, *US and PCT* patent filed (Application No. PCT/IN04/00443, Dec. 31, 2004).
- [14] F. Cavani, F. Trifiro, A. Vaccari, *Catal. Today* 11 (1991) 195.
- [15] S. Abello, F. Medina, D. Tichit, J.P. Ramirez, J.C. Groen, J.E. Sueiras, P. Salagre, Y. Cesteros, *Eur. J. Chem.* 11 (2005) 728.
- [16] F. Basile, G. Fornasari, V. Rosetti, F. Trifirò, A. Vaccari, *Catal. Today* 91–92 (2004) 293.
- [17] V.K. Srivastava, S.K. Sharma, R.S. Shukla, N. Subrahmanyam, R.V. Jasra, *Ind. Eng. Chem. Res.* 44 (2005) 1764.