



The multi-step reactions for the synthesis of C₈ aldehydes and alcohol from propene in a single pot using an eco-friendly multi-functional catalyst system: Kinetic performance for parametric optimization

Sumeet K. Sharma^{a,b}, Ram S. Shukla^{a,*}, Parimal A. Parikh^b, Raksh V. Jasra^{a,1}

^a Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (Council of Scientific and Industrial Research, CSIR), G.B. Marg, Bhavnagar – 364 021, Gujarat, India

^b Department of Chemical Engineering, S.V. National Institute of Technology, Surat – 395 007, Gujarat, India

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ABSTRACT

Kinetics of multi-step reactions including hydroformylation, aldol condensation and hydrogenation was carried out in a single pot for optimization of the reaction parameters for the synthesis of C₈ aldehydes and alcohol from propene using an eco-friendly multi-functional heterogeneous catalyst system [HF/HT] where [HF] = rhodium complex, HRh(CO)(PPh₃)₃ and [HT] = hydrotalcite, Mg_{1-x}Al_x(OH)₂^{x+}(CO₃²⁻)_{x/n}·mH₂O. The catalyst [HF/HT] was synthesized by impregnation of [HF] onto the surface of [HT]. In the typical catalytic experiments conducted in a 100 mL high pressure reactor under the employed reaction conditions: propene = 10 atm, CO = 5 atm, H₂ = 15 atm, [HF/HT] = 700 mg, HT/HF ratio = 7, Mg/Al molar ratio of [HT] = 3.5, aldol temperature = 250 °C, reaction time = 12 h, agitation speed = 1000 rpm, and in 50 mL toluene as a solvent, 68.4 × 10⁻³ M of 2-ethylhexanol with 18% selectivity was achieved. The rates of reactions were determined by analyzing the amounts of products formed at different time using gas chromatography. Kinetics of the various reactions were performed in detail by investigating the effect of reaction parameters such as Mg/Al molar ratio of [HT] at aldol temperature 150 and 250 °C, amount of [HT] and [HF] complex, aldol temperature, partial pressure of CO and H₂ on the rates of formation of products namely, 2-ethylhexanol, 2-ethylhexanal, 2-ethylhexenal, butanals and butanols. The rates of reactions were found to be influenced by all these studied parameters. On increasing these parameters, the rates of formation of the products and their further conversions in single pot were favored.

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1. Introduction

Synthesis of C₈ aldehydes and alcohol from propene is an important reaction for production of these chemicals at commercial scale. C₈ aldehydes and alcohol (aldol products) like 2-ethylhexanal and 2-ethylhexanol are valuable intermediates for the production of dioctylphthalate, other plasticizers, coatings, adhesives, lubricants, alkylid resins, fine and specialty chemicals [1]. Commercially, synthesis of C₈ aldol derivatives from propene is a three steps process in which first step is the hydroformylation of propene to butanals using rhodium-based catalyst [1]. The second step is the aldol condensation of the obtained *n*-butanal in the presence of strong liquid base KOH or NaOH, used in stoichiometric amounts for the produc-

tion of 2-ethylhexenal [2–3]. The hydrogenation of 2-ethylhexenal is carried out in third step using palladium or copper based catalyst using fixed bed reactor [4–7]. The existing commercial processes for the synthesis of C₈ aldol derivatives are multi-steps processes using hazardous liquid base KOH/NaOH in stoichiometric amounts. These processes involve the problems like handling of strong liquid NaOH or KOH, separation and disposal of spent KOH or NaOH which require post-synthesis work-up and corrosion of reaction vessel. These processes are not eco-friendly also. A huge amount of spent liquid base gets generated during the formation of the product from aldol condensation in homogeneous conditions. It is estimated that approximately, 1.0–1.5 tons of spent base solutions are generated for every 10 tons of product formed in homogeneous aldol condensation [8]. To overcome the drawbacks of the commercially employed processes, a novel approach has been reported previously to combine all the steps into a single pot by using multi-functional heterogeneous catalyst system [HF/HT] prepared by impregnation of HRh(CO)(PPh₃)₃ [HF] complex on the surface of a solid base hydrotalcite; (Mg_{1-x}Al_x(OH)₂)^{x+}(CO₃²⁻)_{x/n}·mH₂O [HT] [9–12]. This multi-functional heterogeneous catalyst system [HF/HT] has shown

* Corresponding authors. Tel.: +91 278 2567760; fax: +91 278 2566970.

E-mail addresses: rshukla@csmcri.org (R.S. Shukla), rakshvir.jasra@ril.com (R.V. Jasra).

¹ Present address: R&D Centre, VMD, Reliance Industries Limited, Vadodara 391 346, Gujarat, India.

a good selectivity for the formation of 2-ethylhexanal at 150 °C and on further increasing the temperature to 250 °C, the formation of 2-ethylhexanol was achieved. The reaction parameters were optimized by studying the effect of, HT/HF weight ratio, Mg/Al molar ratio of [HT], aldol condensation temperature (T_2) at a fixed hydroformylation temperature (T_1) for single pot synthesis of C_8 aldol derivatives from propene using [HF/HT] catalyst. The selectivity of 2-ethylhexanal was observed to increase from 7 to 48% by increasing the [HT] (Mg/Al = 3.5) to [HF] complex ratio from 1 to 10.

The literature available is scanty for such a complicated reactions involving three different reactions catalyzed by two different components of the multi-functional catalyst in a single pot. Investigations on the kinetic aspects of such complicated reactions are fundamentally important for understanding the stages of formation of various products with time. The rates of formation and consumption of various products dictate the potential of products for their efficient utilization in further conversions in the same reactor under employed reaction conditions. In the catalytic processes, reactivity of the catalyst significantly depends on the kinetic factors. These kinetic factors play significant role to monitor and control the reactions at stages of the formation of desired products and optimization of the reaction parameters. Studies on the kinetics are also instructive for improvement of the catalytic system and provide basic information for design and scale-up of appropriate reactors. In our investigations [11] on the development of multi-functional heterogeneous catalyst system for the synthesis of 2-ethylhexanal and 2-ethylhexanol from propene in a single pot, it was observed that the selectivity of the formation of various products is influenced on varying Mg/Al molar ratio of the hydroxalite, ratio of [HT(3.5)] in [HF/HT(3.5)], amount of [HF] complex in [HF/HT(3.5)], partial pressures of CO and H_2 and aldol temperature. Hence, a pressing need was realized to perform detail kinetic investigations to understand the stages of formation and consumption of the products, which, in turn, become important to control reaction for the required product and to optimize the reaction parameters.

In the present manuscript, kinetic investigations have been substantiated for the formation of various reaction products during the synthesis of 2-ethylhexanal and 2-ethylhexanol from propene in a single pot. The detail kinetic investigations have been carried out by observing the effect of various reaction parameters for their optimization on the rates of different reactions such as hydroformylation, aldol condensation and hydrogenation occurring in a single pot. The kinetic profiles and reaction rates with the commercially employed catalyst using [HF] complex for hydroformylation and hydrogenation and KOH for aldol condensation, were also compared under identical reaction conditions of [HF/HT(3.5)].

2. Experimental

2.1. Materials

Propene (99.6%) and syn-gas (99.8%) were purchased from Alchemie Gases and Chemicals Private Limited, India. The rhodium metal precursors $RhCl_3 \cdot 3H_2O$, triphenylphosphine (PPh_3), sodium borohydride ($NaBH_4$) and formaldehyde (HCHO) were purchased from Sigma–Aldrich, USA for the synthesis of $HRh(CO)(PPh_3)_3$ [HF] complex. Magnesium ($Mg(NO_3)_2 \cdot 6H_2O$), aluminum ($Al(NO_3)_3 \cdot 9H_2O$), sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) were purchased from s.d. Fine Chemicals, India for synthesizing $(Mg_{1-x}Al_x(OH_2))^{x+}(CO_3^{2-})_{x/n} \cdot mH_2O$ [HT] component of the multi-functional catalyst system. Organic solvents required for the [HF] complex synthesis were purchased from Rankem, India and were purified by reported methods [13]. The double distilled milli-pore deionized water was always used.

2.2. Catalyst synthesis

The synthesis and characterization procedure of multi-functional catalyst [HF/HT] system was reported in details in our earlier publications [10,11]. For example for the synthesis of the catalyst, in a typical synthesis procedure, 10 mL of toluene solution containing 500 mg $HRh(CO)(PPh_3)_3$ [HF complex] with 1050 mg triphenylphosphine was poured into a flask having 3.5 g hydroxalite [HT]. The slurry was stirred for 32 h at room temperature in the inert atmosphere. After 32 h, toluene was removed under vacuum and final product was obtained in the form of a free-flowing light yellow powder.

2.2.1. Kinetics measurements and reaction products analysis

A series of kinetic experiments for determining the rates of the formation of various products in a single pot were carried out in 100 mL EZE–Seal Stirred Reactor supplied by Autoclave Engineers, USA, equipped with a controlling unit [14]. The desired amount of [HF/HT] catalyst was added into the autoclave reactor having 50 mL toluene as a solvent. The autoclave was flushed twice with nitrogen prior to introducing propene at 10 atm. The reactor was then brought to 60 °C temperature (T_1) for the hydroformylation reaction. The CO and H_2 (1:3) gases were introduced in the reactor up to the desired pressure. The reaction was then initiated by starting the stirrer at 1000 rpm. The reaction was kept at 60 °C for 3 h (t_1) for the hydroformylation of propene following which, the reaction temperature was raised to T_2 °C to initiate aldol condensation reaction and hydrogenation of the condensation product. The reaction was kept for 9 h (t_2) at T_2 °C. The reaction was continued at constant pressure by supplying CO and H_2 from the reservoirs. For kinetic studies, liquid samples were withdrawn using a sampling valve provided in the reactor at desired time intervals during the course of experiments. These carefully withdrawn samples were gas chromatographically analyzed to estimate the concentration of products formed with time. The gas chromatograph (GC) (Shimadzu 17A, Japan) was equipped with 5% diphenyl and 95% dimethyl siloxane universal capillary column (60 m length and 0.25 mm diameter) and a flame ionization detector (FID). The GC oven temperature was programmed from 40 to 200 °C at the rate of 10 °C/min. Nitrogen gas was used as the carrier gas. The temperatures of injection port and FID were kept constant at 200 °C. The retention time of different products were determined by injecting pure compounds under identical reaction conditions. The consumptions of propene were calculated by reported method [10–12] using formula: $C_p = C_{p0}(1 - X_p)$; where X_p = conversion of propene, C_{p0} = initial concentration of propene and calculated as $C_{p0} = p_p/RT$; where p_p is the partial pressure of propene. The various rates in the form of concentration of the products formed with time were computed from the slopes of the plots of products' concentration versus time. The values of the rates were reproducible in the range of 12% variation. While varying one reaction parameter to observe its effect on the rates of various products formation, the other physical and chemical parameters were kept constant in order to maintain an identical reaction conditions during all the kinetic runs.

3. Results and discussion

3.1. Products of single pot synthesis of C_8 aldehydes and alcohol from propene

In the typical catalytic experiments conducted in a 100 mL high pressure reactor with 700 mg of [HF/HT] catalyst, HT/HF ratio = 7, Mg/Al molar ratio of [HT] = 3.5, 250 °C aldol temperature, 1000 rpm agitation speed, 50 mL solvent toluene, at 10, 5 and 15 atm partial pressures of propene, carbon monoxide and hydrogen gases, respectively, 68.4×10^{-3} M of 2-ethylhexanol was achieved in 12 h

along with the other products, 2-ethylhexanal (15.20×10^{-3} M), 2-ethylhexenal (7.60×10^{-3} M), butanals (3.80×10^{-3} M) and butanols (285.0×10^{-3} M).

3.2. Kinetics of single pot synthesis of C_8 aldol derivatives

The reaction in a single pot is initiated by hydroformylation of propene catalyzed by metal complex sites of the [HF/HT] catalyst system at 60°C . Then the formed aldehyde undergoes aldol condensation, consecutively catalyzed by the basic sites of hydroxalcite of [HF/HT] catalyst system at 150°C . The hydrogenation of 2-ethylhexenal (product of aldol condensation of butanal) is carried out again by the metal complex sites of [HF/HT] catalyst at 150°C . Finally, hydrogenation of 2-ethylhexenal to 2-ethylhexanol took place at 250°C on the metal complex sites of [HF/HT] catalyst. The side reaction, hydrogenation of butanals to butanols also occurred at metal complex sites under the reaction conditions identical to the synthesis of C_8 aldehyde from propene. Initially, kinetic experiments were carried out by varying the agitation speed from 100 to 1200 rpm. The rate of reaction was observed to be independent on agitation speed after 600 rpm, which indicated negligible diffusional (mass transfer) resistance.

The effect of various reaction parameters on the formation of products such as butanals, butanols, 2-ethylhexenal, 2-ethylhexenal and 2-ethylhexanol from the hydroformylation of propene, condensation of *n*-butanal and hydrogenation of 2-ethylhexenal in a single pot were investigated. The rates of the various reactions were determined from the kinetic profiles made for the formation of the various products and their consumption with time. The representative kinetic profiles for the formation of various products at each stages and consumption of products for further conversions with time are given in Fig. 1 to understand the progress of a consecutive reaction in a single pot with the multifunctional catalyst [HF/HT] during kinetic studies (Scheme 1).

The calculation of the rates for the formation (v) of the products were done by considering the early linear portions of the increasing concentration with time of such (Fig. 1) plots. A very fast hydroformylation (Fig. 1) reaction was observed to occur in the beginning of the reaction with the formation of butanals in first 1 h time and concentration of butanals remained almost constant up to ~ 3 h, and after that, the concentration of butanals started decreasing with

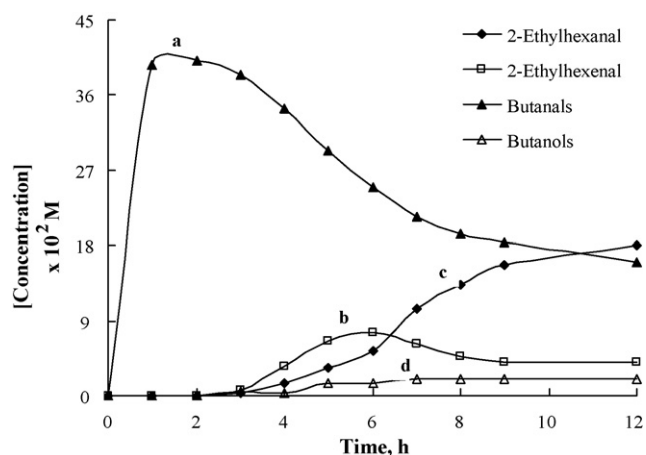


Fig. 1. Kinetic profile for the formation of reaction products with respect to time at propene = 10 atm, CO = 5 atm, H_2 = 15 atm, [HF/HT(3.5)] = 700 mg, HT/HF ratio = 7, $T_1 = 60^\circ\text{C}$, $T_2 = 150^\circ\text{C}$, $t_1 = 3$ h, $t_2 = 9$ h, total time (t) = 12 h at 1000 rpm.

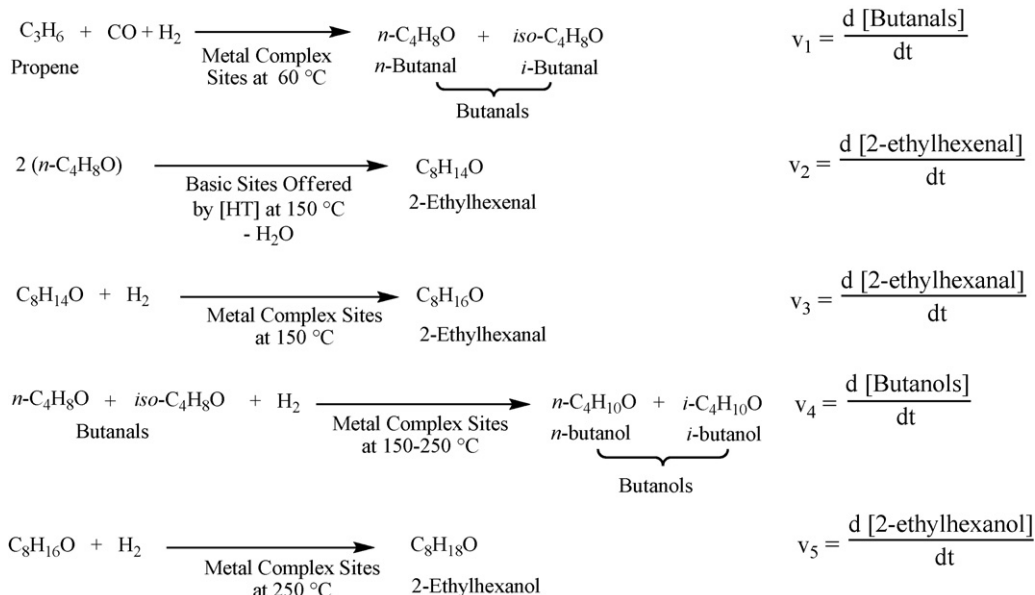
time. The rate of the formation of butanals (v_1) given in Eq. (1) was calculated from the slope of the linear portion of the plot of the increasing concentration of butanals versus time (Fig. 1) and was found to be $20 \times 10^{-2} \text{ M h}^{-1}$:

$$v_1 = \frac{d[\text{butanals}]}{dt} \quad (1)$$

Significant decrease in the concentration of butanals was observed after 3 h time indicating their consumption for further conversions. The rate of consumption of butanals (v'_1) given in Eq. (2) was calculated from the slope of the linear portion of the plot of the decreasing concentration of butanals versus time (Fig. 1(a)) and was found to be $2.6 \times 10^{-2} \text{ M h}^{-1}$:

$$v'_1 = \frac{-d[\text{butanals}]}{dt} \quad (2)$$

After 3 h, as the temperature T_1 increased to T_2 (150°C), the formation of 2-ethylhexenal was observed at ~ 3.25 h onwards via aldol condensation of *n*-butanal. The concentration of 2-ethylhexenal was linearly increased from ~ 3.25 to 6 h. The rate of formation of 2-ethylhexenal (v_2 , Eq. (3)) was calculated from the



Scheme 1. The reaction steps during synthesis of C_8 aldehydes and alcohol from propene in a single pot.

slope of the linear portion of the increasing concentration of 2-ethylhexenal during the time ~3.25–6 h (Fig. 1(b)) and was found to be $2.28 \times 10^{-2} \text{ M h}^{-1}$. After 6 h, concentration of 2-ethylhexenal got decreased and the rate calculated for its consumption (v'_2 , Eq. (4)), from the slope of the linear portion of decreasing concentration (Fig. 1(b)) was $0.9 \times 10^{-2} \text{ M h}^{-1}$:

$$v_2 = \frac{d[2\text{-ethylhexenal}]}{dt} \quad (3)$$

$$v'_2 = \frac{-d[2\text{-ethylhexenal}]}{dt} \quad (4)$$

The decrease in the concentration of 2-ethylhexenal indicates its consumption for the formation of 2-ethylhexenal in the presence of hydrogen. Similar to the formation of 2-ethylhexenal, the formation of its hydrogenated product 2-ethylhexanal was observed after 3.25 h reaction time. As the reaction time increased, the formation of 2-ethylhexanal was found to be increased up to 9 h, with decrease in the concentration of 2-ethylhexenal, due to the simultaneous consumption of the 2-ethylhexenal into the formation of 2-ethylhexanal. The rate of formation of 2-ethylhexanal determined from the slope of the increasing concentration (Fig. 1(c)) was (v_3 , Eq. (5)) $2.13 \times 10^{-2} \text{ M h}^{-1}$:

$$v_3 = \frac{d[2\text{-ethylhexanal}]}{dt} \quad (5)$$

After 9 h, no significant change in the concentration of 2-ethylhexenal and 2-ethylhexenal were observed. A little formation of butanols started almost at the same time when formation of C_8 aldol derivatives were observed. The rate of butanols formation (v_4 , Eq. (6)) determined from the slope of the increasing concentration (Fig. 1(d)) was very slow, $0.20 \times 10^{-2} \text{ M h}^{-1}$:

$$v_4 = \frac{d[\text{butanols}]}{dt} \quad (6)$$

Concentration of the formed butanals was found to contribute majority for the formation of 2-ethylhexenal with a little formation of butanols since a nice balance in the rate of formation of products and consumption of butanals ($v'_1 \approx (v_2 + v_4)$) was observed under the employed reaction conditions. Summation of the rates v_2 and v_4 ($v_2 + v_4 = 2.48 \times 10^{-2} \text{ M h}^{-1}$) was found to be almost identical with the rate v'_1 ($2.60 \times 10^{-2} \text{ M h}^{-1}$).

It is of interest to have an insight into the comparison of the rates for the formation of products determined [12] individually with [HF] for hydroformylation of propene (v_1), [HT(3.5)] for aldolization of butanal (v_2) and [HF] for hydrogenation of 2-ethylhexenal (v_3), under conditions identical with those employed for [HF/HT] catalyst system. The rates v_1 , v_2 and v_3 were found to be $20 \times 10^{-2} \text{ M h}^{-1}$, $2.8 \times 10^{-2} \text{ M h}^{-1}$ and $8 \times 10^{-2} \text{ M h}^{-1}$ respectively. These results indicated that the trend of these rates were in the order of $v_1 > v_3 > v_2$. For comparative studies, reaction rates were also determined with the commercially employed catalyst, [HF+KOH] under identical reaction conditions of [HF/HT(3.5)]. The determined rates v_1 , v_2 and v_3 with the [HF+KOH] system were $8 \times 10^{-2} \text{ M h}^{-1}$, $0.8 \times 10^{-2} \text{ M h}^{-1}$ and $2.50 \times 10^{-2} \text{ M h}^{-1}$ respectively. Under identical conditions the values of the rates

v_1 , v_2 and v_3 with [HF/HT(3.5)] catalyst system were found to be $20.0 \times 10^{-2} \text{ M h}^{-1}$, $2.28 \times 10^{-2} \text{ M h}^{-1}$ and $2.13 \times 10^{-2} \text{ M h}^{-1}$ respectively. The rates of hydroformylation ($8.00 \times 10^{-2} \text{ M h}^{-1}$) and aldol condensation ($0.80 \times 10^{-2} \text{ M h}^{-1}$) associated with [HF+KOH] system were observed to be lower than those associated with [HF/HT(3.5)] under the employed reaction conditions. In terms of the rates of the reactions, the performance of the impregnated [HF/HT] catalyst is similar to the individual [HF] and more than the commercial [HF+KOH] catalyst for the hydroformylation step. The order of the rate performance of these catalysts for aldolization step was: [HT] > [HF/HT] > [HF+KOH]. For the step of the hydrogenation of 2-ethylhexenal to 2-ethylhexanal the rate with the [HF/HT] catalyst was lower than the individual catalyst [HF] and closer to [HF+KOH].

The detail kinetics including the rates of formation of butanal, butanol, 2-ethylhexenal, and 2-ethylhexanal was investigated as a function of aldol condensation temperature (T_2), amount of [HT] and [HF] complex, and Mg/Al molar ratio of [HT] in the [HF/HT] system at a fixed hydroformylation temperature (T_1) using [HF/HT] catalyst system for synthesis of C_8 aldol derivatives from propene in a single pot. The rates of the formation (v_1 , v_2 , v_3 and v_4) of the various products were determined by above described methods.

3.3. Effect of Mg/Al molar ratio of [HT] on the rates of products formation at 150 and 250 °C aldol temperature (T_2)

Effect of Mg/Al molar ratio of [HT] on the rates of formation of products was studied at 150 and 250 °C aldol temperature (T_2) by varying the Mg/Al molar ratio of [HT] from 1.5 to 3.5 in the [HF/HT] catalyst system (Table 1). At 150 °C, the rate of formation of 2-ethylhexenal was observed to increase on increasing the Mg/Al molar ratio of [HT]. At Mg/Al molar ratio of 1.5, the rate of formation of 2-ethylhexenal determined to be $1.41 \times 10^{-2} \text{ M h}^{-1}$ was increased to $2.13 \times 10^{-2} \text{ M h}^{-1}$ on increasing the Mg/Al molar ratio of [HT] up to 3.5. Similar to the rate of formation of 2-ethylhexenal, the rate of formation of 2-ethylhexenal was also observed to increase on increasing the Mg/Al molar ratio of [HT]. At all the studied Mg/Al molar ratios, the rate of formation of 2-ethylhexenal was observed to be higher than the rate of formation of 2-ethylhexenal. The rate of the formation of butanals was decreased regularly from $27.5 \times 10^{-2} \text{ M h}^{-1}$ at Mg/Al molar ratio 1.5 to $20 \times 10^{-2} \text{ M h}^{-1}$ at Mg/Al molar ratio of [HT] 3.5. The rates of the formation of butanols were extremely slow. At 150 °C aldol temperature, the formation of the 2-ethylhexanol was not observed in the entire studied reaction conditions for the single pot synthesis of C_8 aldol derivatives from propene.

On conducting the experiments at 250 °C aldol condensation temperature (T_2), the formation of 2-ethylhexanol was observed by the further hydrogenation of 2-ethylhexenal (Table 2). The rate of formation of 2-ethylhexanol (v_5 , Eq. (7)) was determined from the slope of the linear portion of its increasing concentration with time:

$$v_5 = \frac{d[2\text{-ethylhexanol}]}{dt} \quad (7)$$

Table 1
Effect of the Mg/Al molar ratio of [HT] on the rates of products formation at 150 °C aldol temperature (T_2).

Entry	Mg/Al molar ratio	$v_3 \times 10^2 \text{ M h}^{-1}$	$v_2 \times 10^2 \text{ M h}^{-1}$	$v_1 \times 10^2 \text{ M h}^{-1}$	$v_4 \times 10^2 \text{ M h}^{-1}$
1	1.5	1.41	1.52	27.5	0.12
2	2.0	1.62	1.67	24.2	0.36
3	2.5	1.83	1.90	23.1	0.44
4	3.0	1.90	1.97	22.4	0.32
5	3.5	2.13	2.28	20.0	0.19

Reaction conditions: propene = 10 atm, CO = 5 atm, H_2 = 15 atm, [HF/HT] = 700 mg, HT/HF ratio = 7, $T_1 = 60^\circ\text{C}$, $T_2 = 150^\circ\text{C}$, $t_1 = 3 \text{ h}$, $t_2 = 9 \text{ h}$, total time (t) = 12 h at 1000 rpm. v_1 = rate of formation of butanals, v_2 = rate of formation of 2-ethylhexenal, v_3 = rate of formation of 2-ethylhexenal, and v_4 = rate of formation of butanols.

Table 2Effect of the Mg/Al molar ratio of [HT] on the rate of products formation at 250 °C aldol temperature (T_2).

Entry	Mg/Al molar ratio	$\nu_5 \times 10^2 \text{ M h}^{-1}$	$\nu_3 \times 10^2 \text{ M h}^{-1}$	$\nu_2 \times 10^2 \text{ M h}^{-1}$	$\nu_1 \times 10^2 \text{ M h}^{-1}$	$\nu_4 \times 10^2 \text{ M h}^{-1}$
1	1.5	0.59	0.23	–	14	1.76
2	2.0	0.61	0.1	–	0.5	2.68
3	2.5	0.65	0.11	0.26	0.5	2.62
4	3.0	1.13	0.14	0.26	0.5	2.30
5	3.5	1.21	0.19	0.26	0.5	2.37

Reaction conditions: propene = 10 atm, CO = 5 atm, H_2 = 15 atm, [HF/HT] = 700 mg, HT/HF ratio = 7, T_1 = 60 °C, T_2 = 250 °C, t_1 = 3 h, t_2 = 9 h, total time (t) = 12 h at 1000 rpm, ν_5 = rate of formation of 2-ethylhexanol.

Similar to the results observed at 150 °C aldol temperature, the rate of formation of 2-ethylhexanol was observed to increase on increasing the Mg/Al molar ratio of [HT]. At the Mg/Al molar ratio of [HT] 1.5, the rate of formation of 2-ethylhexanol was $0.59 \times 10^{-2} \text{ M h}^{-1}$ and got increased to $1.21 \times 10^{-2} \text{ M h}^{-1}$ on increasing the ratio to 3.5. The rates for the formation of 2-ethylhexanal and 2-ethylhexenal were observed to be lower at 250 °C than those of at 150 °C (Table 1). The lower rates (ν_3) for the formation of 2-ethylhexenal is attributed due to efficient consumption of 2-ethylhexanal for the formation of 2-ethylhexanol at 250 °C. The lower rates for the formation of 2-ethylhexenal at 250 °C as compared to the rate observed at 150 °C is attributed for the consumption of butanals for the formation of butanols via hydrogenation reaction catalyzed by [HF] component of multi-functional catalyst. This is in line of the results of the rates for the formation of the butanols, which are significantly higher at 250 °C (Table 2) than those at 150 °C (Table 1). The rates of the formation of butanals at 250 °C being quite lower than those at 150 °C, indicated a fast consumption of butanals for the formation of butanols, 2-ethylhexenal and finally for 2-ethylhexanol. Significantly, higher rate of formation of butanols was observed at 250 °C as compared to the rate observed at 150 °C.

Increase in the rates of the formation of 2-ethylhexenal, 2-ethylhexanal at 150 °C and 2-ethylhexanol at 250 °C, on increasing the Mg/Al molar ratio of [HT] is attributed due to the enhancement in the basicity of the [HF/HT] catalyst system, which increases the rate of the condensation reaction. The basicity of the [HT] component of [HF/HT] system is due to the presence of surface hydroxyl groups and is controlled by either changing the Mg/Al molar ratio or selection of suitable anions in the interlayer. It is known that the basicity of [HT] increases with increasing the Mg/Al molar ratio due to increase in the Mg content in the hydrotalcite [15–18]. Therefore, the observed increase in the rates of products formation on increasing Mg/Al molar ratio of [HT] in the present study is explainable in terms of the increase in basic character of the hydrotalcite.

3.4. Effect of the amount of [HT(3.5)] and [HF] complex in [HF/HT(3.5)] system on the rates of product formation

The rates of the formation of C_8 aldehydes, butanals and butanols were determined by varying the amount of [HT] in the range of 100–1000 mg, at constant amount of [HF] complex to understand the effect of [HT] amount on the kinetics of reaction (Table 3). The rate (ν_3) of formation of 2-ethylhexanal was observed to increase

on increasing the amount of [HT]. On varying the amount of [HT] from 100 to 1000 mg, the rate ν_3 was continuously increased from $0.33 \times 10^{-2} \text{ M h}^{-1}$ to $2.28 \times 10^{-2} \text{ M h}^{-1}$. A similar trend of increasing the rate of formation of 2-ethylhexenal (ν_2) was also observed on increasing the amount of [HT]. The rate ν_2 was regularly increased from $0.13 \times 10^{-2} \text{ M h}^{-1}$ to $2.4 \times 10^{-2} \text{ M h}^{-1}$ on varying [HT] in the range of 100–1000 mg. The rates of formation of butanals and butanols both were observed to decrease on increasing the amount of the [HT]. In the studied range of the amount of the [HT], the rate ν_1 was decreased from $32.5 \times 10^{-2} \text{ M h}^{-1}$ to $19.5 \times 10^{-2} \text{ M h}^{-1}$. The rate of formation of butanols was decreased from $1.56 \times 10^{-2} \text{ M h}^{-1}$ to $0.19 \times 10^{-2} \text{ M h}^{-1}$ and no butanols formation was observed with 1000 mg [HT].

Lower rates of the formation of the 2-ethylhexanal and 2-ethylhexenal observed at lower amount of [HT] could be due to the insufficient amount of solid base in [HF/HT] to carry out aldol condensation reaction. The active catalyst for the aldol condensation of *n*-butanal possesses basic active sites on their surface and these active sites are responsible for the condensation reaction [19]. At the lower [HT] amount, amount of [HF] complex is more on the surface of [HF/HT] catalyst system, which results into higher rates of the formation of butanals and butanols. As the amount of [HT] increases, the more active sites available for the condensation reaction on the surface of catalyst also increased which aids to the faster condensation reaction and consequently to the higher rates of formation of 2-ethylhexanal and 2-ethylhexenal were achieved.

Table 4 shows the effect of the variation in [HF] complex amount on the rates of formation of the 2-ethylhexanal, 2-ethylhexenal, butanals and butanols for the synthesis of C_8 aldehydes from propene in a single pot. The rates of formation of 2-ethylhexenal and 2-ethylhexenal were observed to give a mixed trend on increasing the amount of [HF] complex. The rates were increased up to certain amount of [HF] complex and afterwards on further increasing the amount, the rates were decreased significantly. The rate ν_3 was increased from $1.14 \times 10^{-2} \text{ M h}^{-1}$ (at 15 mg) to $2.13 \times 10^{-2} \text{ M h}^{-1}$ (at 100 mg). On further increase in the amount of the [HF] complex to 160 mg, the rate of formation of 2-ethylhexenal was decreased to $1.28 \times 10^{-2} \text{ M h}^{-1}$. The rate of formation of 2-ethylhexenal was also observed to increase up to 100 mg of [HF] complex ($2.58 \times 10^{-2} \text{ M h}^{-1}$) and decreased to $1.67 \times 10^{-2} \text{ M h}^{-1}$ at 160 mg. An increasing trend on the rates of the formation of butanals and butanols were observed on increasing the amount of [HF] complex. Hence, on increasing the amount of [HF] complex, all the rates corresponding to ν_1 , ν_2 , ν_3 and ν_4 were increased. How-

Table 3

Effect of [HT(3.5)] amount in [HF/HT(3.5)] on the rate of products formation.

Entry	[HT(3.5)] (mg)	$\nu_3 \times 10^2 \text{ M h}^{-1}$	$\nu_2 \times 10^2 \text{ M h}^{-1}$	$\nu_1 \times 10^2 \text{ M h}^{-1}$	$\nu_4 \times 10^2 \text{ M h}^{-1}$
1	100	0.33	0.13	32.5	1.56
2	300	1.14	1.04	28.2	0.56
3	500	2.04	1.78	25.1	0.19
4	700	2.13	2.28	20.0	0.19
5	1000	2.28	2.4	19.5	0

Reaction conditions: propene = 10 atm, CO = 5 atm, H_2 = 15 atm, [HF] complex = 100 mg, T_1 = 60 °C, t_1 = 3 h, T_2 = 150 °C, t_2 = 9 h, total time (t) = 12 h.

Table 4
Effect of [HF] complex amount in [HF/HT(3.5)] on the rate of products formation.

Entry	[HF] complex (mg)	$\nu_3 \times 10^2 \text{ M h}^{-1}$	$\nu_2 \times 10^2 \text{ M h}^{-1}$	$\nu_1 \times 10^2 \text{ M h}^{-1}$	$\nu_4 \times 10^2 \text{ M h}^{-1}$
1	15	1.14	1.3	12.5	0.47
2	30	1.38	1.56	15.5	0.50
3	50	1.76	2.06	18.2	0.55
4	100	2.13	2.58	20.0	0.59
5	125	1.98	2.08	27.7	0.66
6	160	1.28	1.67	29.8	1.26

Reaction conditions: propene = 10 atm, CO = 5 atm, H₂ = 15 atm, [HF/HT(3.5)] = 700 mg, T₁ = 60 °C, t₁ = 3 h, T₂ = 150 °C, t₂ = 9 h, total time (t) = 12 h.

Table 5
Effect of aldol reaction temperature (T₂) on the rate of products formation.

Entry	T ₂ °C	$\nu_5 \times 10^2 \text{ M h}^{-1}$	$\nu_3 \times 10^2 \text{ M h}^{-1}$	$\nu_2 \times 10^2 \text{ M h}^{-1}$	$\nu_1 \times 10^2 \text{ M h}^{-1}$	$\nu_4 \times 10^2 \text{ M h}^{-1}$
1	120	–	0.66	2.25	36.5	0.34
2	150	–	2.13	2.28	20	0.19
3	200	–	2.87	1.39	4.5	0.85
4	250	1.20	0.20	0.25	0.5	2.37

Reaction conditions: propene = 10 atm, CO = 5 atm, H₂ = 15 atm, [HF/HT(3.5)] = 700 mg, HT/HF = 7, T₁ = 60 °C, t₁ = 3 h, t₂ = 9 h, total time (t) = 12 h.

ever after 100 mg of [HF], the rates ν_2 and ν_3 were decreased. Both rates ν_2 and ν_3 found to be lower at, below as well as above 100 mg of [HF] complex, indicated that the amount of [HF] complex plays an significant role. There was not much significant difference in the rates of the formation of 2-ethylhexanal at 15 and 160 mg of [HF] complex (Table 4, Entries 1 and 6). This may be due to the less availability of [HF] complex towards lower amount (below 100 mg) of the complex [HF]. The lower amount of [HF] complex causes lower rate for the hydrogenation of 2-ethylhexenal to 2-ethylhexanal. On the other hand, the higher amount of [HF] complex favors the faster hydroformylation of propene and hydrogenation of the butanals. The decrease in the rates ν_2 and ν_3 above 100 mg of [HF] is assignable due the blockages of active site present on the surface of the HF/HT catalyst. Impregnation of [HF] complex on the surface could be blocking active sites of the solid base, which are responsible for aldol condensation of *n*-butanal and due to blockage of the active sites; condensation reaction is suppressed significantly. This indicated that at higher amount of [HF] complex, formation of butanols via hydrogenation of aldehydes is faster than the aldol condensation of butanal.

3.5. Effect of the aldol temperature (T₂) using [HF/HT(3.5)]

The effect of aldol condensation temperature (T₂) on the rates of formation of the products is given in Table 5. The formation of 2-ethylhexanol was observed at 250 °C only. Up to 200 °C, only 2-ethylhexanal and 2-ethylhexenal was formed as C₈ aldol derivatives. The rate of formation of 2-ethylhexanal was observed to increase on increasing the reaction temperature up to 200 °C, after that this rate decreased significantly due to consumption of 2-ethylhexanal in the formation of the 2-ethylhexanol via hydrogenation. The rate of formation of 2-ethylhexanal determined to be $0.66 \times 10^{-2} \text{ M h}^{-1}$ at 120 °C was increased up to $2.87 \times 10^{-2} \text{ M h}^{-1}$ at 200 °C. The rate of formation of 2-ethylhexenal was decreased from $2.25 \times 10^{-2} \text{ M h}^{-1}$ to $0.25 \times 10^{-2} \text{ M h}^{-1}$ on

Table 6
Effect of partial pressures of CO and H₂ on the rate of products formation.

Entry	CO (atm)	H ₂ (atm)	$\nu_3 \times 10^2 \text{ M h}^{-1}$	$\nu_2 \times 10^2 \text{ M h}^{-1}$	$\nu_1 \times 10^2 \text{ M h}^{-1}$	$\nu_4 \times 10^2 \text{ M h}^{-1}$
1	2.5	10	1.01	2.56	24	0.11
2	5	15	2.13	2.28	20	0.19
3	10	30	2.43	0.91	19	0.25
4	15	45	2.61	0.81	17.5	0.44
5	20	60	2.68	0.78	15	0.41

Reaction conditions: propene = 10 atm, [HF/HT(3.5)] = 700 mg, HT/HF = 7, T₁ = 60 °C, t₁ = 3 h, T₂ = 150 °C, t₂ = 9 h, total time (t) = 12 h.

increasing the temperature from 120–200 °C. The rate of formation of butanals decreased drastically from $36.5 \times 10^{-2} \text{ M h}^{-1}$ (at 120 °C) to $0.5 \times 10^{-2} \text{ M h}^{-1}$ (at 250 °C). This may be due to the faster consumption of butanals for further consecutive reactions such as aldol condensation and hydrogenation at higher temperature in a single pot. The rate of formation of butanols via hydrogenation of butanals increased significantly on increasing the aldol temperature. At lower aldol temperature (120 °C), lower rate of formation ($0.34 \times 10^{-2} \text{ M h}^{-1}$) of butanol was obtained, which increased to $2.37 \times 10^{-2} \text{ M h}^{-1}$ at 250 °C.

From the results shown in Table 5, higher rates of hydrogenated products were observed at higher aldol temperature. The higher temperature favored the hydrogenation reaction, which is catalyzed by [HF] complex of [HF/HT]. In our earlier publication [11] on the multi-functional catalyst, we have demonstrated that the [HF] component of the [HF/HT] is stable up to 150 °C, after which decomposition of [HF] complex is started. The decomposition of [HF] complex of [HF/HT] may result into a rhodium species, which is more active for the hydrogenation of aldehydes. This reason is assigned for favoring the hydrogenation reactions at higher temperature and formation of 2-ethylhexenol at 250 °C.

3.6. Effect of the partial pressures of CO and H₂ using [HF/HT(3.5)]

The effect of partial pressure of CO and H₂ at constant CO to H₂ ratio (1:3) on the rates of formation of products is given in Table 6. At lower partial pressure of CO and H₂, lower rate of formation of 2-ethylhexanal was observed, which were enhanced on increasing the partial pressures. The rates of formation of 2-ethylhexenal and butanals were found to decrease on increasing the partial pressure of CO and H₂. These observations indicate that the consumption of 2-ethylhexenal and butanals for the formation of 2-ethylhexanal and butanols, respectively become predominant at higher partial pressure of CO and H₂. The rates of formation of butanols were also increased on increasing the partial pressure of CO and H₂. Hence,

increase in partial pressure of CO and H₂ increases the consumption of 2-ethylhexenal and butanals, which in turn enhances the rates of their hydrogenated products, 2-ethylhexanal and butanols, respectively.

4. Conclusions

In present work, kinetic performance of an eco-friendly multi-functional heterogeneous catalyst, comprising a rhodium complex, HRh(CO)(PPh₃)₃ impregnated on the surface of a hydrotalcite, Mg_{1-x}Al_x(OH)₂^{x+}(CO₃²⁻)_{x/n}·mH₂O, has been investigated for multi-step reactions for the synthesis of C₈ aldehydes and alcohol from propene in a single pot, to explore the optimization of the reaction parameters. Kinetics investigated as the function of amount of [HF] complex, amount of [HT], Mg/Al molar ratio of [HT], aldol temperature, and partial pressures of CO and H₂ indicated that on increasing these parameters, the rates of reactions tended to be enhanced significantly. Higher aldol temperature (250 °C) and Mg/Al molar ratio (3.5) of [HT] have markedly contributed towards the rate of formation of 2-ethylhexanol (C₈ alcohol) and rates were almost linearly increased on increasing the Mg/Al ratio due to increase in basicity, which effectively enhances the rate of aldol condensation. The present catalyst system has shown better kinetic performance in terms of the rates of hydroformylation and aldol condensation and almost parallel performance in terms of the rate of hydrogenation of 2-ethylhexenal, with those associated with commercially employed catalyst [HF+KOH]. The rates of hydroformylation and aldol condensation with [HF/HT(3.5)] were observed to be 2.5 and ~3 times respectively, higher than those associated with [HF+KOH] under the employed reaction conditions. The impregnated catalyst [HF/HT] may be realizable to have a future to replace the hazardous liquid base KOH with solid base hydrotalcite.

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References

- [1] 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.
- [2] A.D. Godwin, R.H. Schlosberg, F. Hershkowitz, M.G. Matturro, G. Kiss, K.C. Nadler, P.L. Buess, R.C. Miller, P.W. Allen, H.W. Deckman, R. Caers, E.J. Mozeleski, J. Edmund, R.P. Reynolds, US Patent 6,307,093 (2001), to ExxonMobil Chemical Patents Inc.
- [3] B.J. Arena, J.S. Holmgren, US Patent 5,144,089 (1992), to UOP.
- [4] G. Horn, C.D. Frohning, H. Liebern, W. Zgorzelski, US Patent 5,475,161 (1995), to Hoechst Aktiengesellschaft.
- [5] W. Bueschken, J. Hummel, US Patent 5,756,856 (1998), to Huels Aktiengesellschaft.
- [6] H.G. Lueken, U. Tanger, W. Droste, G. Ludwig, D. Gubisch, US Patent 4,968,849 (1990), to Huels Aktiengesellschaft.
- [7] T. Mori, K. Fujita, H. Hinoishi, US Patent 5,550,302 (1996), to Mitsubishi Chemical Corporation.
- [8] J.J. Spivey, M.R. Gogate, Research Triangle Institute, USEPA Grant, *Pollution Prevention in Industrial Condensation Reactions*, 1996.
- [9] R.V. Jasra, V.K. Srivastava, R.S. Shukla, H.C. Bajaj, S.D. Bhatt, US and PCT pat. US Appl. No. 20060149101 (2006).
- [10] V.K. Srivastava, S.K. Sharma, R.S. Shukla, R.V. Jasra, *Catal. Commun.* 7 (2006) 879–884.
- [11] S.K. Sharma, V.K. Srivastava, R.S. Shukla, P.A. Parikh, R.V. Jasra, *New J. Chem.* 31 (2007) 277–286.
- [12] V.K. Srivastava, S.K. Sharma, R.S. Shukla, R.V. Jasra, *Ind. Eng. Chem. Res.* 47 (2008) 3795–3803.
- [13] D.D. Perrin, W.L.F. Armarego, D.D. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon Press, Oxford, 1980.
- [14] V.K. Srivastava, S.K. Sharma, R.S. Shukla, N. Subrahmanyam, R.V. Jasra, *Ind. Eng. Chem. Res.* 44 (2005) 1764.
- [15] F. Basile, G. Fornasari, V. Rosetti, F. Trifirò, A. Vaccari, *Catal. Today* 91–92 (2004) 293.
- [16] J.M. Herman, P.J. Van Den Berg, J.J.F. Scholten, *Chem. Eng. J.* 35 (1987) 25.
- [17] S.K. Sharma, P.A. Parikh, R.V. Jasra, *J. Mol. Catal. A: Chem.* 278 (2007) 135–144.
- [18] S.K. Sharma, P.A. Parikh, R.V. Jasra, *J. Mol. Catal. A: Chem.* 286 (2008) 55–62.
- [19] H. Tsugi, F. Yagi, H. Hattori, H. Kita, *J. Catal.* 148 (1994) 759.