One-pot synthesis of C_8 aldehydes/alcohols from propylene using eco-friendly hydrotalcite supported $HRhCO(PPh_3)_3$ catalyst†

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A multi-functional catalyst [HF/HT] containing a rhodium complex, $HRh(CO)(PPh_3)_3$ [HF] and a solid base, hydrotalcite $Mg_{1-x}Al_x(OH_2)^{x+}(CO_3{}^{2-})_{x/n}\cdot mH_2O$ [HT], synthesized by impregnation of [HF] onto the surface of [HT], was investigated for the one-pot synthesis of C_8 aldol derivatives (aldehydes or alcohols) from propylene. The catalyst was found to be efficient to carry out hydroformylation, aldol condensation and hydrogenation reactions in one pot. The catalytic activity of [HF/HT(X)] was studied in detail as functions of Mg/Al molar ratio (X) of [HT], amount of [HF] complex and [HT], and reaction temperature. The selectivity for 2-ethylhexanal was observed to increase upon increasing X and amount of [HT]. The highest selectivity for 2-ethylhexanol was observed for [HT] Mg/Al molar ratio of 3.5 at 250 °C. The kinetic profiles of the various products obtained were in agreement with the reaction pathway proposed to understand the role of the [HF/HT] catalyst on the formation of C_8 aldol derivatives. Thermal stability of the [HF/HT] catalyst system was also investigated.

Introduction

Industrially, oxo products such as aldehydes and alcohols are synthesized by hydroformylation of alkenes with synthesis gas in the presence of a catalyst. Nearly 86% of the total hydroformylation production capacity (8.8 million tons/year) is based on propylene hydroformylation to give butanals (*n*- and *iso*-) and butanols (*n*- and *iso*-) as major products.[1] *n*-Butanal is largely used for the production of C_8-aldol products such as 2-ethylhexanal and 2-ethylhexanol, which are valuable intermediates for the production of dioctylphthalate, other plasticizers, coatings, adhesives, lubricants, alkyd resins and fine chemicals.

Presently, the synthesis of C_8 aldol derivatives from propylene is a three-step process. In the first step, the hydroformylation of alkene is carried out to produce the aldehyde using Rh or Co based catalysts.[2] In the second step, the obtained aldehyde undergoes an aldol condensation in the presence of stoichiometric amount of a strong base, namely KOH or NaOH, to produce unsaturated aldol derivatives.[3,4] Hydrogenation of unsaturated aldol derivatives is carried out using Ni or Cu catalysts in the third step.[5–8] Thus, existing commercial strategies for the production of C_8 aldol derivatives involve multi-step processes using stoichiometric amounts of hazardous base solutions and require post synthesis work-up for the separation of spent KOH/NaOH from the products' mixtures. 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. In fact, 30% of the selling price of C_8 aldol derivatives is estimated to be contributed by product purification, recovery and waste treatment.[9]

Research efforts to develop catalytic processes alternative to environmentally and economically inefficient stoichiometric chemical processes are in progress. For example, the one-pot synthesis of methyl isobutyl ketone (MIBK) from acetone has been reported in the literature using Pd/Mg(Al)O catalyst.[10] The aldol condensation process during production of 2-ethylhexanol has also been modified by Mitsubishi Chemicals by converting *n*-butanal into 2-ethylhexenal in the second step in the presence of a basic ion-exchanger at 80–100 °C.[11] The third hydrogenation step is carried out under vapor phase conditions over either Ni or Cu catalysts. After a three-step distillation process, pure products are obtained. Shell and Exxon both have developed a single-step process, known as the 'Aldox' process, to produce ethylhexanol directly from propylene by adding co-catalysts such as compounds of Ti, Sn, Zn, Al, or Cu or KOH, to the original hydroformylation catalyst.[12] However, these processes still have disadvantages such as the use of strong base solutions for the aldol condensation of *n*-butanal, low selectivity for the C_8 aldol derivatives and relatively low liquid space velocity in the hydroformylation.

The present study reports a novel approach[13] for the one-pot synthesis of C_8 aldol derivatives (aldehydes or alcohols) from propylene (Scheme 1) employing a multi-functional

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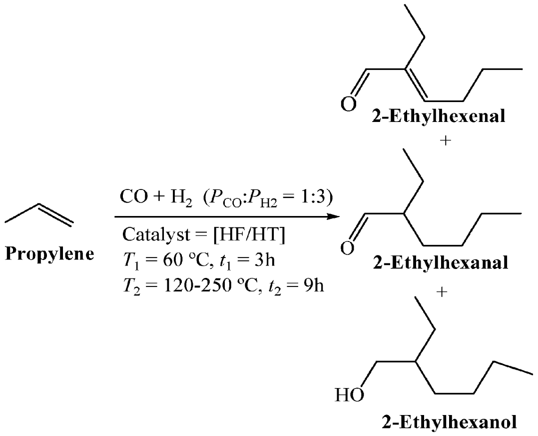
† Electronic supplementary information (ESI) available: Fig. S1: ^{31}P FT-NMR of [HF] complex in C_6D_6. Fig. S2: P-XRD patterns of [HF] complex, [HT(3.5)] and [HF/HT(X)]. Fig. S3: SEM images of [HT(3.5)] and [HF/HT(3.5)]. Fig. S4: TGA of [HT(3.5)], [HF] complex and [HF/HT(3.5)]. See DOI: 10.1039/b616977e



Scheme 1 One-pot synthesis of C_8 aldol derivatives from propylene using [HF/HT].

heterogeneous catalyst [HF/HT] prepared by impregnation of a rhodium complex, $HRh(CO)(PPh_3)_3$ [HF], on the surface of a solid base, hydrotalcite $Mg_{1-x}Al_x(OH_2)^{x+}(CO_3{}^{2-})_{x/n} \cdot mH_2O$ [HT].

Experimental

Materials

Propylene (99.6%), carbon monoxide (CO, 99.8%) and hydrogen (H_2, 99.98%) were procured from Alchemie Gases and Chemicals Private Limited, India. The rhodium metal precursors $RhCl_3 \cdot 3H_2O$, triphenylphosphine (PPh_3), sodium borohydride ($NaBH_4$, 99.98%) and formaldehyde (HCHO, 34%) were purchased from Sigma-Aldrich, USA for the synthesis of $HRh(CO)(PPh_3)_3$ [HF] complex. Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$, 99.99%), aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$, 99.99%), sodium carbonate (Na_2CO_3, 99.99%) and sodium hydroxide (NaOH, 99.99%) 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]. Organic solvents required for the synthesis of [HF] complex were purchased from Rankem, India and were purified by reported methods.[14] Double-distilled milli-pore de-ionized water was used throughout the present study.

Catalyst synthesis

Synthesis of $HRh(CO)(PPh_3)_3$ [HF]. The complex [HF] was synthesized as per reported method.[15] A solution of $RhCl_3 \cdot 3H_2O$ (7.6 mmol) in ethanol (70 ml) was added into a refluxing solution of triphenylphosphine (46.0 mmol) in ethanol (300 ml). After 2 min aqueous formaldehyde solution (10 ml) was added dropwise and the resulted solution was observed to turn yellow with the formation of *trans*-$RhCl(CO)(PPh_3)_2$. Addition of the ethanolic solution of sodium borohydride (2.0 g) into this hot mixture yielded the yellow crystals of $HRh(CO)(PPh_3)_3$. The yellow crystals were washed with ethanol to remove unreacted rhodium metal.

Synthesis of hydrotalcites [HT]. Co-precipitation method at constant pH was employed to synthesize the hydrotalcite [HT] samples with Mg/Al molar ratios varying from 1.5 to 3.5.[16] Typically, an aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ (0.22 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.088 mol) in 200 ml double-distilled deionized water was prepared. A second solution (200 ml) containing NaOH (0.72 mol) and Na_2CO_3 (0.21 mol) was prepared and was slowly added to the first solution over around 2 h in a 1 L round bottom flask under vigorous stirring at room temperature. The content was aged at 65 °C for 16 h. The precipitate formed was filtered off and washed with hot distilled water until pH of the filtrate was neutral. The precipitate was dried in an oven at 80 °C for 12 h to give a hydrotalcite sample with Mg/Al molar ratio = 2.5.

Synthesis of multi-functional catalyst [HF/HT(*X*)]. Typically, a 10 ml toluene solution of [HF] complex $HRh(CO)(PPh_3)_3$ (500 mg) and triphenylphosphine (1050 mg) was poured into a flask containing 3.5 g [HT(*X*)] (where X = Mg/Al ratio). The slurry was stirred for 32 h at room temperature under inert atmosphere (N_2). After 32 h, toluene was removed under vacuum. The final product obtained was a free-flowing light yellow powder and was stored under inert atmosphere at room temperature.

Characterization of the catalyst

The FT-NMR characterization of the [HF] complex was carried out by Bruker Avance DPX 200 MHz FT-NMR system. The C, H and N elemental analysis of the [HF] complex was done by Perkin Elmer CHNS/O 2400 analyzer. The FT-IR spectra of the [HF] complex, [HT(*X*)] and [HF/HT(*X*)] of different Mg/Al ratio (*X*) were recorded with a Perkin–Elmer Spectrum GX Fourier transform infrared spectrophotometer (FT-IR) system in the region of 400 to 4000 cm^{-1} using KBr pellets. The powder X-ray diffraction patterns of [HT(*X*)] and [HF/HT(*X*)] were recorded with Phillips X'Pert MPD system equipped with XRK 900 reaction chamber, using Cu-Kα radiation (λ = 1.5405 Å). Scanning electron microscopy images of [HT(*X*)] and [HF/HT(*X*)] were measured on a microscope (Leo Series VP1430, Germany) having silicon detector equipped with EDX facility (Oxford instruments). The samples were coated with gold using sputter coating to avoid charging. Analyses were carried out at an accelerating voltage of 18 kV and probe current of 102 pA. Thermogravimetric analysis (TGA) of [HF] complex, [HT(*X*)] and [HF/HT(*X*)] was carried out using a Mettler TGA/SDTA 851e equipment in flowing N_2 (flow rate = 50 ml min^{-1}), at a heating rate of 10 °C min^{-1} and data were processed using Star^e software.

One-pot synthesis of C_8 aldol derivatives

Reactions for the one-pot synthesis of C_8 aldol derivatives were carried out in 100 ml EZE-Seal Stirred Reactor supplied by Autoclave Engineers, USA, equipped with a controlling unit.[17,18] The requisite amount of [HF/HT(*X*)] was added into the autoclave reactor having 50 ml toluene as a solvent. The autoclave was flushed twice with N_2 gas prior to introducing desired amount of propylene (10 atm). The reactor was then brought to 60 °C temperature (T_1) for hydroformylation reaction. The CO and H_2 (1 : 3) gases were introduced in the reactor. The reaction was then initiated by starting the magnetic stirrer at 1000 rpm. The reaction was kept at 60 °C temperature for 3 h (t_1) following which, the reaction temperature was raised to T_2 °C to initiate aldol condensation reaction. The reaction temperature was kept for 9 h (t_2) at T_2 °C. The reaction was continued at constant pressure by supplying H_2 from the reservoir vessel. After 12 h total reaction time (t), the reactor was cooled to room temperature under flowing water. The product mixture was then analyzed using Gas Chromatography (GC). For kinetic studies liquid samples were withdrawn for GC analysis by a sampling valve at different time intervals during the experiments.[17]

Analysis of the product mixture was carried out by GC-MS (Shimadzu, GCMS-QP2010) and GC (Shimadzu 17A, Japan) 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^{-1}. N_2 was used as the carrier gas. The temperature of injection port and FID was kept constant at 200 °C. The retention times of different compounds were determined by injecting pure compounds under the identical conditions. The conversions were determined in terms of consumption of propylene and were found in the range of 95–99%. The consumption of propylene was calculated by reported method,[19,20] using formula: $C_p = C_{po}(1 - X_p)$; where X_p = conversion of propylene, C_{po} = initial concentration of propylene and calculated as $C_{po} = p_p/RT$; where p_p is the partial pressure of propylene. The percentage selectivity for each product was calculated by the method reported earlier.[20] To ensure the reproducibility of the reaction, experiments were repeated under the identical reaction conditions. The conversions and selectivities were reproducible in the range of 5% variation.

In a catalyst thermal stability experiment, a known amount of [HF/HT(3.5)] catalyst and solvent toluene (50 ml) were charged into the reactor and the reactor was flushed with N_2 before introducing CO and H_2 at desired pressure. The CO and H_2 (1 : 3) were fed into the reactor at 20 atm. The reactor was then brought to set temperature. After 12 h reaction time, the reaction mixture was cooled to room temperature and the catalyst was filtered off. The obtained solid material was dried under vacuum at room temperature. The dry solid material was characterized by the powder X-ray diffraction (P-XRD) and FT-IR analysis.

Results and discussion

Characterisation of the complexes

The appearance of the doublet at 56.34 and 58.31 ppm [J(Rh–P) = 160 Hz] in ^{31}P NMR spectra of [HF] complex showed that all the three phosphorus atoms possess the same environment and are in the equatorial position. The hydride (H^-) and CO axial positions showed trigonal bipyramidal structure in the complex. The %C and %H for the [HF] complex are: calculated (found): %C = 71.9 (71.6); %H = 5.0 (5.1).

P-XRD patterns of [HT(X)], [HF] complex and [HF/HT(X)] are shown in Fig. 1. The P-XRD patterns of [HT(X)] showed sharp, intense and symmetric peaks at lower diffraction angles (2θ = 10–25) and broad asymmetric reflections at higher diffraction angles (2θ = 30–50), which are characteristics of hydrotalcite.[21] The sharp peaks at 2θ = 8.5 and 20 were observed in the P-XRD pattern of the [HF] complex and were also present in the P-XRD patterns of the [HF/HT(X)] catalyst. The P-XRD patterns of the [HF/HT] catalyst showed that the characteristic planes of the [HT] are retained after impregnation of [HF] complex. The intensity of the 00l planes of the [HF/HT] catalyst, which is related to the crystallinity of [HT], decreased on the impregnation of the [HF] complex. With increase in Mg/Al ratio of [HT] from 1.5 to 3.5, a slight shift towards lower 2θ values for the peaks corresponding to (003) and (006) planes was observed due to concurrent decrease of the positive charge of the layers of [HT]. These small shifts in the peaks of the (003) and (006) planes were also observed in the P-XRD patterns of the [HF/HT(X)] catalyst systems. However, lack of broadening of the 00l plane peak of [HF/HT] compared to P-XRD patterns of the starting [HT] sample, showed the absence of intercalation of [HF] complex into the [HT] interlayer space.

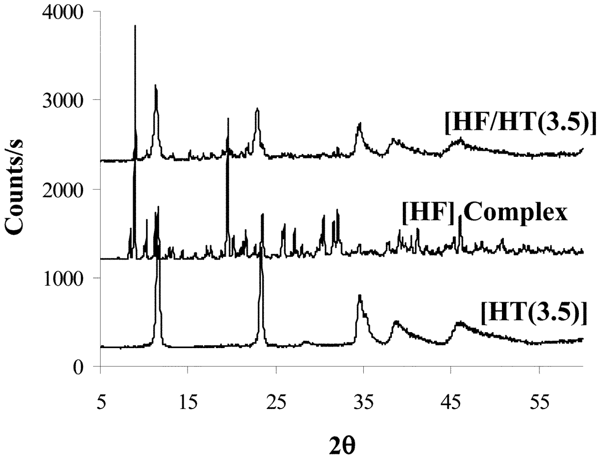


Fig. 1 P-XRD patterns of [HF] complex, [HT(3.5)] and [HF/HT(3.5)] system.

The appearance of a band at 2036 cm^{-1} for ν(Rh–H) and at 1965 cm^{-1} for ν(C=O) in the FT-IR spectrum of the [HF] complex (Fig. 2), confirmed the formation of the [HF] complex. The FT-IR spectra of [HF/HT(X)] prepared using different Mg/Al molar ratios of HT(X) were quite similar, though, some difference was observed in the intensity and the broadness of the bands. The absorption at 3500–3600 cm^{-1}, present in [HT(X)] is attributed to the H-bonding stretching vibrations of the OH group in the brucite-like layer. The maximum of this band is shifted depending upon the Mg/Al molar ratio of [HT].[21] The hydrogen stretching and bending frequencies in [HT] were increased with increase in the Mg/Al ratio from 2.0 to 3.5. In the FT-IR spectra of [HT(X)], the appearance of the shoulders at 1647 and 1435 cm^{-1}, characteristic bands of H_2O and CO_3^{2-}, confirmed the formation of Mg–Al hydrotalcites. The shoulder present at 3000 cm^{-1} is attributed to the hydrogen bonding between water molecules and the interlayer CO_3^{2-} anions. The vibration of carbonates (asymmetric stretching, ν_3) appeared at 1350–1380 cm^{-1} and

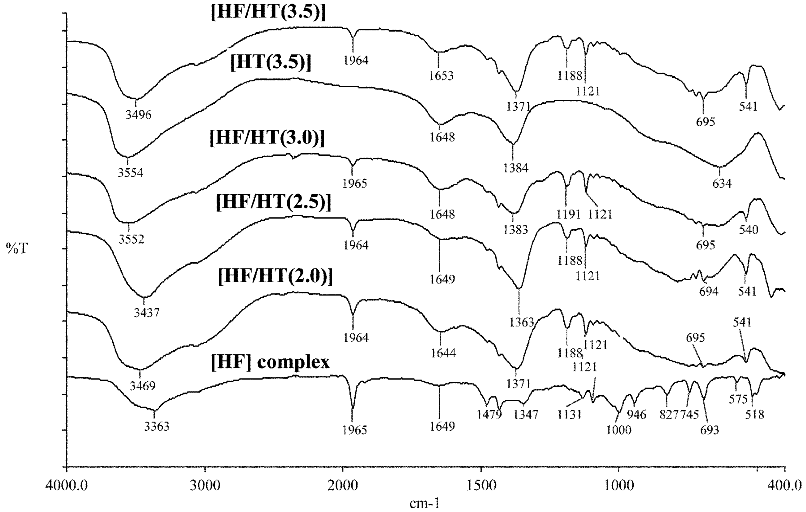


Fig. 2 FT-IR spectra of [HF] complex, [HT(3.5)] and [HF/HT(*X*)] systems.

could be assigned to interlayer carbonates (chelating or bridging bidentate). The lower wavenumber region showed a band at about 541 cm^{-1}, corresponding to the translation modes of hydroxyl groups, influenced by Al^{3+} cations. The peak at the 664 cm^{-1} (ν_4) is assigned to the in-plane carbonate bending.[22] The SEM images were recorded to observe the effect of the impregnation of [HF] complex on the morphology of the [HT]. The micrographs of the [HT(3.5)] and [HF/HT(3.5)] catalysts showed a well developed layered structure and possessed platelet structures. However, due to overlapping of such platelets spongy type structure was observed.

The TGA of [HT(3.5)] showed two stages of weight loss accompanied by an endothermic transformation (Fig. 3). The first weight change (15%) was observed in the range 200–220 °C due to the loss of interlayer water molecules, without collapse of the structure and this step is reversible.[21] The second weight loss (29%) was observed in the range 250–450 °C and is attributed to the removal of condensed water molecules (hydroxyl group) and carbon dioxide from the carbonate anion present in the brucite layer. The second weight loss usually appeared broad because of the simultaneous loss of water and carbon dioxide.[21] The weight loss in the TGA for the [HF] complex at 150 °C is observed to be less than 4%. The 62% weight loss of the [HF] complex is observed in the range 170–450 °C due to thermal decomposition of the complex. The weight loss observed for [HF/HT(3.5)] occurred in three steps. In the first step, only 5% weight loss was observed in temperature range 160–200 °C that increased up to 33% on increasing the temperature from 220 to 400 °C in the second step. However, on further increase in the temperature from 400 to 650 °C, a weight loss of 5% was observed. The weight losses for [HF/HT(3.5)] in the second and third steps are attributed to the removal of condensed water molecules (hydroxyl group) and carbon dioxide from the carbonate anion present in the brucite layer of [HT] and the thermal decomposition of the [HF] complex.

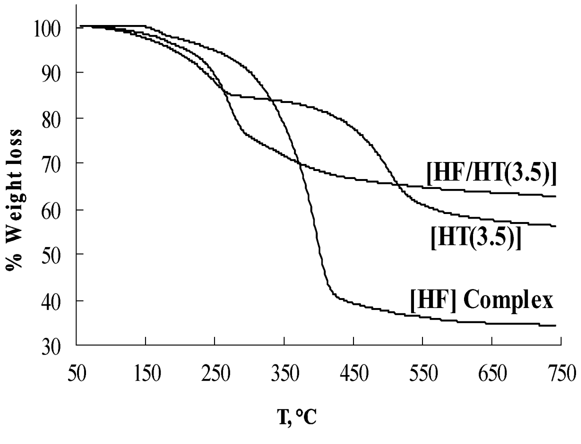
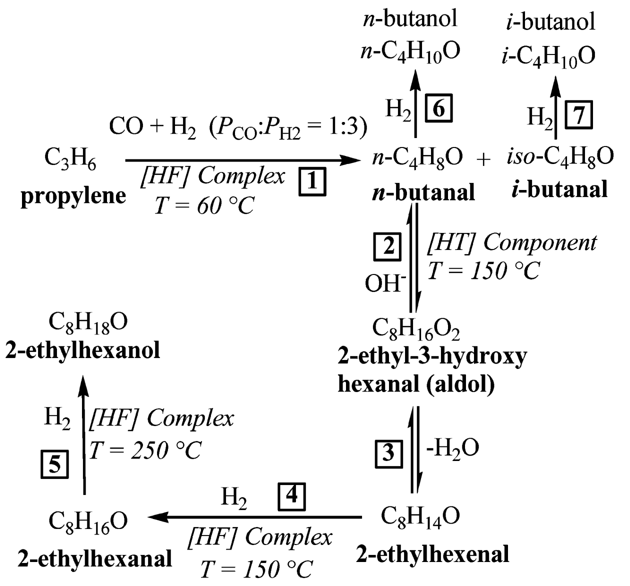


Fig. 3 TGA of [HT(3.5)], [HF] complex and [HF/HT(3.5)] system.

Mechanistic considerations

To understand the function of each component of the multifunctional catalysts [HF/HT] during the synthesis of C_8 aldol derivatives from propylene, the proposed reaction pathway is shown in Scheme 2. The reaction gets initiated by formation of *n*-butanal *via* hydroformylation of propylene (step **1**) by [HF] complex of the catalyst. This is followed by condensation step wherein two molecules of *n*-butanal undergo condensation reaction in the presence of solid base [HT] to give 2-ethyl-3-hydroxyhexanal (β-hydroxyaldehyde) and subsequently 2-ethylhexenal after removal of one molecule of water. The condensation of *n*-butanal is a base catalyzed reaction and dehydration of β-hydroxyaldehyde is catalyzed by the Lewis basic sites of the catalyst.[22,23] The [HT] component of the [HF/HT] catalyst facilitates the steps **2** and **3**. The step **4** is a hydrogenation step, which includes hydrogenation of 2-ethylhexenal to 2-ethylhexanal. As per the stoichiometry, this step requires a second hydrogen molecule. The [HF] complex under the employed reaction conditions assists this hydrogenation step. The final step **5** is again a hydrogenation step, that involves reduction of 2-ethylhexanal to 2-ethylhexanol catalyzed by the [HF] complex. Stoichiometrically, the third



Scheme 2 Mechanistic pathways for the formation of 2-ethylhexanol from propylene in one step.

hydrogen molecule is utilized in the step **5**. Thus, the [HF] complex of the [HF/HT] catalyst plays role in three reactions, once in the hydroformylation and twice in the hydrogenation reactions during the one-step preparation of 2-ethylhexanol from propylene.

However, the possibilities of side reactions involved in a one-step preparation of 2-ethylhexanol from propylene under the hydroformylation conditions cannot be ignored. The most probable possibility is the reduction of butanals (*n*- and *iso*-) to their corresponding butanols (step **6** and **7**) under the studied reaction conditions.

The [HF] complex can catalyze the reduction of butanals in the presence of hydrogen and this was confirmed by carrying out hydrogenation of *n*-butanal in a separate experiment by taking 2 g *n*-butanal, 20 mg [HF] complex in 50 ml solvent (toluene) at 30 atm (hydrogen) and 150 °C. Therefore, to avoid this competitive reaction, the amount of solid base [HT] in the [HF/HT] catalyst and the reaction conditions, *i.e.*, aldol reaction temperature (T_2), are to be optimized to divert the reaction to step **2** rather than steps **6** and **7**. The other side reactions, cross aldol condensation of *n*- and *iso*-butanal were not observed in the present study.

The [HF/HT] catalyst was investigated in detail for the one-pot synthesis of C_8 aldol derivatives from propylene under varied reaction parameters namely changing the amount of [HT] and [HF] complex, Mg/Al molar ratio (X) of [HT], aldol condensation temperature (T_2) and partial pressure of CO and H_2 at a fixed hydroformylation temperature (T_1).

Effect of Mg/Al molar ratio (X) of [HT] in the [HF/HT(X)] catalysts

The effect of Mg/Al molar ratio (X) from 1.5 to 3.5 of [HT] in the [HF/HT(X)] catalyst was studied at 150 and 250 °C (Fig. 4 and 5) aldol condensation temperatures (T_2) while keeping the hydroformylation temperature (T_1) constant at 60 °C. At 150 °C aldol condensation temperature, the selectivity for 2-ethylhexanal was observed to increase linearly up to 45% on increasing the Mg/Al molar ratio up to 3.5 with decrease in the selectivity for butanals.

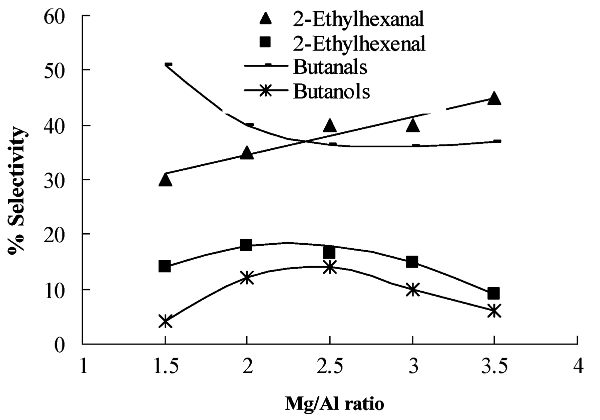


Fig. 4 Effect of Mg/Al ratio of [HT] in [HF/HT] at 150 °C aldol temperature at partial pressure of propylene = 10 atm, partial pressure of CO = 5 atm, partial pressure of H_2 = 15 atm, [HF/HT] = 700 mg, HT/HF ratio = 7, T_1 = 60 °C, t_1 = 3 h, T_2 = 150 °C, t_2 = 9 h, total time (t) = 12 h.

Conducting the experiments at higher aldol condensation temperature (T_2) 250 °C showed (Fig. 5) formation of significant amount of 2-ethylhexanol within 12 h by hydrogenation of 2-ethylhexanal (step **5**, Scheme 2). The selectivity for 2-ethylhexanol increased from 11 to 21% on increasing the Mg/Al molar ratio of [HT] from 1.5 to 3.5. On increasing the total reaction time to 24 h, the selectivity for 2-ethylhexanol was observed to increase up to 27% at the Mg/Al molar ratio of 1.5 of [HT] (entry 6, Table 3). The higher selectivity for C_4 and C_8 aldehydes was observed at 150 °C as compared to 250 °C (T_2). The lower selectivity for C_4 and C_8 aldehydes at 250 °C (T_2) was observed due to continuous hydrogenation of aldehydes to the respective alcohols at employed reaction conditions, thereby, butanols and 2-ethylhexanol were formed as major products at higher T_2.

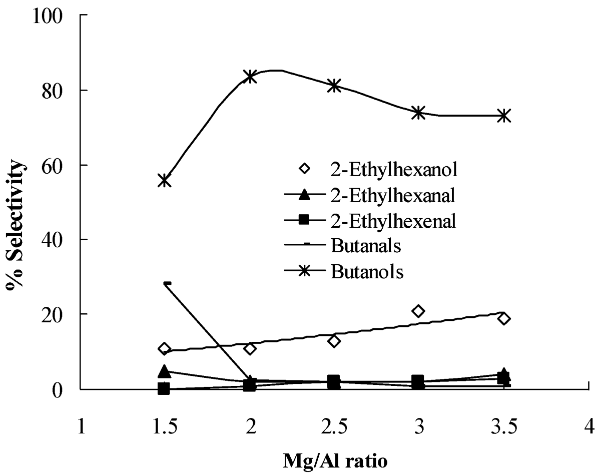


Fig. 5 Effect of Mg/Al ratio of [HT] in [HF/HT] at 250 °C aldol temperature at partial pressure of propylene = 10 atm, partial pressure of CO = 5 atm, partial pressure of H_2 = 15 atm, [HF/HT] = 700 mg, HT/HF ratio = 7, T_1 = 60 °C, t_1 = 3 h, T_2 = 250 °C, t_2 = 9 h, total time (t) = 12 h.

Table 1 Effect of [HT(3.5)] in [HF/HT(3.5)] on the selectivity for C_8 aldol derivatives

		Selectivity (%)			
Entry	[HT(3.5)] (mg)	2-Ethylhexanal	2-Ethylhexanel	Butanals	Butanols
1	100	7	0	43	50
2	300	24	8	50	18
3	500	43	6	45	6
4	700	45	9	40	6
5	1000	48	13	39	0

Reaction conditions: Partial pressure of propylene = 10 atm, partial pressure of CO = 5 atm, partial pressure of 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 2 Effect of [HF] complex in [HF/HT(3.5)] on selectivity for C_8 aldol derivatives

		Selectivity (%)			
Entry	[HF] complex (mg)	2-Ethylhexanal	2-Ethylhexenal	Butanals	Butanols
1	15	24	10	51	15
2	30	29	12	41	18
3	50	37	20	31	12
4	100	45	9	40	6
5	125	43	22	14	21
6	160	27	16	17	40

Reaction conditions: Partial pressure of propylene = 10 atm, partial pressure of CO = 5 atm, partial pressure of H_2 = 15 atm, [HT(3.5)] = 700 mg, T_1 = 60 °C, t_1 = 3 h, T_2 = 150 °C, t_2 = 9 h, total time (t) = 12 h.

Table 3 Effect of aldol reaction temperature (T_2) on the selectivity for C_8 aldol derivatives using [HF/HT(3.5)]

		Selectivity (%)				
Entry	T_2/°C	2-Ethylhexanol	2-Ethylhexanal	2-Ethylhexenal	Butanals	Butanols
1	120	—	14	2	73	11
2	150	—	45	9	40	6
3	200	—	61	3	9	27
4	250	18	4	2	1	75
5[a]	150	—	54	8	21	17
6[b]	250	27	4	5	1	63

Reaction conditions: Partial pressure of propylene = 10 atm, partial pressure of CO = 5 atm, partial pressure of H_2 = 15 atm, [HF/HT(3.5)] = 700 mg, HT/HF = 7, T_1 = 60 °C, t_1 = 3 h, t_2 = 9 h, total time (t) = 12 h. [a] Single reaction temperature (T) = 150 °C for 12 h. [b] Total time (t) = 24 h, Mg/Al molar ratio of [HT] = 1.5.

The increase in the selectivity for C_8 aldol derivatives with increasing Mg-content in [HT] is explained in terms of enhanced basicity of [HT] which aids condensation reaction. It is known that the basic strength of a hydrotalcite increases with increasing the Mg/Al molar ratio.[24–27] The basicity of the hydrotalcite resulting from surface hydroxyl groups and two types of basic sites are identified for hydrotalcite, one weaker Brønsted OH^- and second, stronger Lewis O^{2-} sites.[23] The Brønsted OH^- sites are responsible for the aldol condensation of *n*-butanal to β-hydroxyaldehyde and Lewis O^{2-} sites are responsible for dehydration of β-hydroxyaldehyde.[22,23] 2-Ethylhexenal is produced by the dehydration of aldol condensation dimer by Lewis O^{2-} sites present on the hydrotalcite surface of [HF/HT] catalysts.

Effect of ratio of [HT(3.5)] and [HF] complex

The effect of the variation of the amount of [HT(3.5)] in the [HF/HT(3.5)] catalyst on the selectivity was studied with varying the amount of [HT(3.5)] from 100 mg to 1000 mg. The selectivity for 2-ethylhexanal increased from 7 to 48% (Table 1). The selectivity for 2-ethylhexenal was observed to increase on increasing the amount of the [HT(3.5)]. Decrease in selectivity for butanals and butanols shows that condensation reactions become predominant with increasing amount of [HT] in the [HF/HT(3.5)] catalyst.

The amount of [HF] complex was varied from 15 to 160 mg in the [HF/HT(3.5)] catalyst by keeping the amount of the [HT(3.5)] constant. On increasing the amount of [HF] complex from 15 to 100 mg, the selectivity for 2-ethylhexanal increased (entries 1–4, Table 2) and was found to be 45% at the 100 mg weight of [HF] complex (entry 4, Table 2). On further increasing the amount of [HF] complex, the selectivity for 2-ethylhexanal was observed to decrease at the expense of increase in the selectivity for butanols (entries 5 and 6, Table 2).

Higher selectivity for butanols observed at lower amount of [HT(3.5)] (entries 1 and 2, Table 1), could be due to the insufficient amount of solid base in the [HF/HT(3.5)] catalyst to affect aldol condensation reaction. The active catalyst for the aldol condensation of *n*-butanal possesses basic sites on their surface which are responsible for the condensation reaction.[28] At lower HT/HF ratios, a higher amount of the hydroformylation complex is on the surface of [HT]. The impregnated [HF] complex on the surface could be blocking the basic sites of [HT], and thereby, suppressing the condensation reaction. Therefore, at higher amount of [HF] complex, the hydrogenation of aldehydes is observed to be more pronounced than the aldol condensation of *n*-butanal. The maximum selectivities for C_8 aldol derivatives (entries 1–5, Table 1) were observed at higher amount of [HT] due to the availability of more basic sites for the condensation reaction on the surface of the catalyst.

Effect of the aldol temperature (T_2)

The results given in Fig. 4 and 5 show that the reaction is significantly influenced by the aldol condensation temperature (T_2). The effect of T_2 on the selectivity for C_8 aldol derivatives was studied at different T_2 (120 to 250 °C) using the [HF/HT(3.5)] catalyst (Table 3). The selectivity for 2-ethylhexanal was found to increase from 14 to 61% on increasing T_2 from 120 to 200 °C (entries 1–3, Table 3) and formation of 2-ethylhexanol was not observed. On further increasing the temperature T_2 from 200 to 250 °C, the selectivity for 2-ethylhexanal decreased from 61 to 4% and the selectivity for 2-ethylhexanol was observed to be 18%. At 250 °C, the selectivity for the butanols sharply increased from 27% (at 200 °C) to 75%. The selectivity for butanals was found to decrease from 73 to 1% on increasing the T_2 from 120 °C to 250 °C. The rapid decrease in selectivity for butanals on increasing T_2 shows the consumption of butanals either for the aldol condensation or reduction to butanols.

It is observed from the results (Table 3), that the higher temperature favoured butanals reduction that is catalyzed by the [HF] complex present in the [HF/HT(3.5)] catalyst. It is clear from the TGA data that the [HF] present in the [HF/HT] catalyst was stable up to 150 °C, and after that decomposition was observed. The decomposition of the [HF] complex may result into a rhodium species which could be more active for the hydrogenation of aldehydes. To confirm this assumption, one separate experiment was carried out by taking *n*-butanal (2 g) as reactant in 50 ml of toluene as solvent at 250 °C and at 30 atm of H_2 with 700 mg [HF/HT(3.5)] for 12 h reaction time. After 12 h, 72% selectivity for butanols was observed which are in accordance with the results observed in the case of propylene as a reactant (entry 4, Table 3).

An important observation that was made regarding the selectivity for 2-ethylhexanal increased from 45 to 54% on carrying out the experiment at a single temperature (T = 150 °C) rather than in two stages with temperatures at 60 and 150 °C (entries 2 and 5, Table 3). One of the possible reasons for higher selectivity on carrying the reaction at a single temperature (150 °C) could be the increased activity of solid base component [HT(3.5)] for condensation reaction at the beginning of the reaction.

Effect of the partial pressures of CO and H_2

The effect of partial pressures of CO and H_2 (1 : 3), from 12.5 to 80 atm on product distribution of C_8 aldol derivatives was studied using the [HF/HT(3.5)] catalyst (Table 4). The partial pressure of CO and H_2 was varied with the CO : H_2 ratio kept at 1 : 3. For example, on increasing the partial pressure of CO and H_2 from 12.5 to 40 atm, the selectivity for 2-ethylhexanal increased from 38 to 47% (entries 1–3, Table 4). After that, the selectivity decreased from 47 to 40% on increasing the partial pressure of CO and H_2 from 40 to 60 atm (entries 3 and 4, Table 4). However, the selectivity for 2-ethylhexanal was found to increase from 40 to 47% on increasing the partial pressure of CO and H_2 from 60 to 80 atm (entries 4 and 5, Table 4). The formation of butanols was observed with butanols selectivity being more at higher partial pressure of CO and H_2.

Kinetic profiles for one-pot synthesis of C_8 aldol derivatives

In order to calculate the rate constants for hydroformylation of propylene, aldol condensation of *n*-butanal and hydrogenation of 2-ethylhexenal, separate experiments were conducted by taking propylene, *n*-butanal and 2-ethylhexenal as a reactant under the reaction conditions identical to those used for one-step synthesis of 2-ethylhexanal from propylene. The rate constants for the hydroformylation of the propylene, aldol condensation of the *n*-butanal and hydrogenation of 2-ethylhexenal were found to be 0.50, 0.07 and 0.20 h^{-1}, respectively. These rate constant values showed that the hydroformylation of propylene for synthesis of butanals is the fastest reaction. Aldol condensation of *n*-butanal for the production of the 2-ethylhexenal is the slowest reaction among the three subsequent reactions. The rate of the formation of the 2-ethylhexenal is dependent on the rate of aldol condensation which is catalyzed by [HT] of the [HF/HT] catalyst. The rate of hydrogenation of 2-ethylhexenal is also slower compared to hydroformylation of propylene. After the hydroformylation of propylene, butanals can either undergo aldol condensation or hydrogenation depending on the reaction conditions. The rate

Table 4 Effect of the partial pressures of CO and H_2 on the selectivity of for C_8 aldol derivatives using [HF/HT(3.5)]

	Pressure/atm		Selectivity (%)			
Entry	CO	H_2	2-Ethylhexanal	2-Ethylhexenal	Butanals	Butanols
1	2.5	10	38	12	42	8
2	5	15	45	9	40	6
3	10	30	47	7	38	8
4	15	45	40	7	39	14
5	20	60	47	9	31	13

Reaction conditions: Partial pressure of propylene = 10 atm, [HF/HT(3.5)] = 700 mg, HT/HF = 7, T_1 = 60 °C, t_1 = 3 h, T_2 = 150 °C, t_2 = 9 h, total time (t) = 12 h.

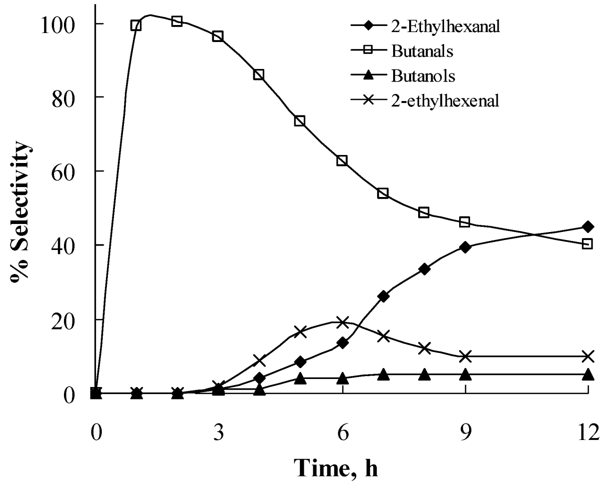


Fig. 6 Kinetics profiles for synthesis of C_8 aldol derivatives from propylene in one step using [HF/HT(3.5)] catalytic system at partial pressure of propylene = 10 atm, partial pressure of CO = 5 atm, partial pressure of H_2 = 15 atm, [HF/HT(3.5)] = 700 mg, HT/HF ratio = 7, T_1 = 60 °C, t_1 = 3 h, T_2 = 150 °C, t_2 = 9 h, t = 12 h.

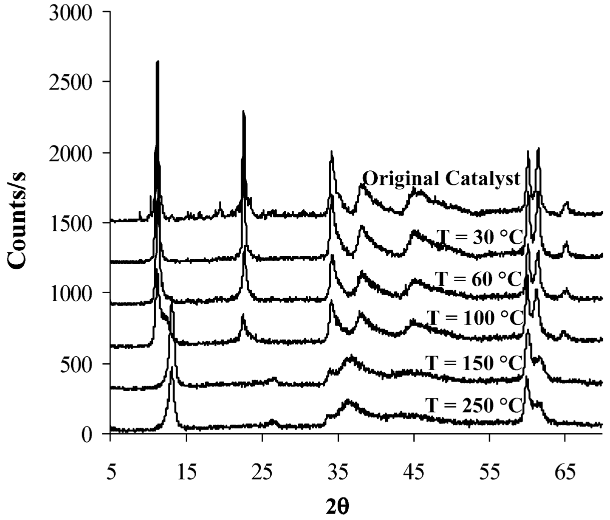


Fig. 7 P-XRD Patterns for study of thermal stability of the [HF/HT(3.5)] system.

constant for hydrogenation of *n*-butanal was found to be 0.40 h^{-1} at higher amount of [HF] complex (HT/HF ratio = 2), T_2 = 250 °C, and 0.37 h^{-1} at HT/HF ratio = 1, T_2 = 150 °C, which are comparable with the calculated rate constant for hydroformylation reaction. The kinetic profiles of the products formed during the one-pot synthesis of C_8 aldol derivatives give important information for different stages of formation of various products with time to arrive at the actual reaction pathway. The kinetic profile for the formation of 2-ethylhexanal from propylene in one step is shown in Fig. 6. The formation of butanals *via* propylene hydroformylation at 60 °C catalyzed by the [HF] complex was observed up to 3 h. As the T_1 increased to T_2, the formation of 2-ethylhexenal was seen after 3.25 h *via* aldol condensation of *n*-butanal, which is subsequently consumed into 2-ethylhexanal in the presence of the hydrogen. As the reaction time increased, the selectivity for 2-ethylhexanal was found to increase up to 9 h, with decrease in the selectivity for the 2-ethylhexenal, due to the simultaneous consumption of the 2-ethylhexenal into 2-ethylhexanal. No significant change in the selectivity for 2-ethylhexanal and 2-ethylhexenal were observed after 9 h reaction time. The decrease in the selectivity for butanals after 3 h indicated it's regular consumption in the formation of C_8 aldol derivatives and butanols. It was interesting to see that the formation of butanols also started after 4 h, the time after which formation of C_8 aldol derivatives were observed.

Thermal stability of multi-functional [HF/HT] catalysts

The experiments were conducted at different temperatures to study the thermal stability of the [HF/HT(3.5)] catalyst at partial pressure of CO and H_2 at 20 atm; 700 mg of [HF/HT(3.5)]; 50 ml toluene and 12 h reaction time. The thermal treatment temperature was varied in the range 30–250 °C by keeping the other reaction parameters constant. The P-XRD patterns of the original [HF/HT(3.5)] catalyst and thermally treated catalyst are shown in Fig. 7.

The P-XRD patterns of the thermally treated catalyst are divided into two categories. In the first category (T = 30–100 °C), sharp and intense peaks at low diffraction angles (2θ = 10–27°) and broad reflections at high angles (2θ = 30–67°) were observed, the spectra being identical to the original [HF/HT(3.5)] catalyst. In the second category, (T = 150–250 °C), significant changes in the P-XRD patterns were observed. For example, the peaks corresponding to the 003 and 006 planes were shifted to higher angles, 13.2 and 26.6°, respectively, when compared to the original catalyst (11.3 and 22.7°, respectively). Furthermore, as the treatment temperature was raised up to 250 °C, the intensity of all peaks decreased. The maximum decrease in peak intensity was observed in the 2θ range 20–50°. In contrast, the region around 2θ = 60° was less affected by the rise in temperature. The temperature at which these changes appear (transition temperature) in the P-XRD patterns was found to depend on the Mg/Al molar ratio of [HT]. The transition temperature was found to decrease with increasing the Mg/Al molar ratio of [HT]. The observed changes are due to the reaction between interlayer carbonates and interlayer water molecules, producing hydroxyl anions at the interlayer gallery of this phase. The TGA of the [HF] complex confirmed the stability of complex up to 150 °C, where decomposition of [HF] resulting in the observed shifting of the peaks of the 003 and 006 planes of [HF/HT]. The layered structure of [HF/HT(3.5)] was still maintained above this temperature, but it contained hydroxyl anions in the interlayer, which are less bulky than the carbonate anions found in the interlayer of the original catalyst. The observed P-XRD patterns of [HF/HT] are more comparable to that of [HT] than to that of [HF]. Similar observations have been reported in the literature for hydrotalcite at different temperatures characterized by high temperature *in situ* powder XRD (HTXRD).[29,30]

All the peaks of the original [HF/HT(3.5)] catalyst were found in the FT-IR spectra of the thermally treated catalysts (Fig. 8).

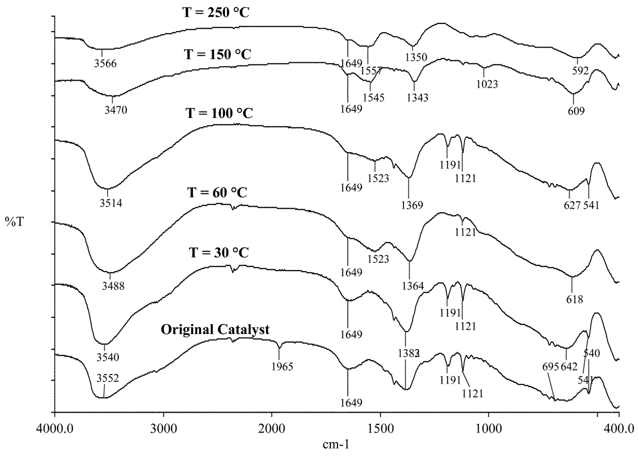


Fig. 8 FT-IR spectra for study of the thermal stability of the [HF/HT(3.5)] system.

Table 5 Effect of the high temperature treatment on the activity of the catalyst

	Selectivity (%)		
	C_4 aldehydes	C_4 alcohols	C_8 aldehydes/alcohols
Fresh catalyst	40	6	54
Second run	28	71	<1
Third run	23	76	<1
Fourth run	22	77	<1

Reaction conditions: Partial pressure of propylene = 10 atm, partial pressure of CO = 5 atm, partial pressure of H_2 = 15 atm, [HF/HT (3.5)] = 700 mg, HT/HF = 7, T_1 = 60 °C, t_1 = 3 h, T_2 = 150 °C, t_2 = 9 h, total time (t) = 12 h.

High-temperature treatment in hydrogen may cluster the [HF] complex into Rh(0) supported aggregates, which is an efficient catalyst for hydrogenation, but quite unreactive in the hydroformylation of propylene. Keeping this point in view, we have checked the catalytic activity of [HF/HT(3.5)] after four successive runs, using the same catalyst under identical reaction conditions. The results are shown in Table 5.

As seen from the data in Table 5, no change of activity of the [HF] complex was observed in the hydroformylation and hydrogenation reaction after high temperature treatment in the presence of excess hydrogen atmosphere (Table 5). Therefore, it can be safely said that under the conditions employed in our reaction, the formation of Rh(0) is less likely. However, the activity of [HT] on the aldol condensation of the aldehyde was influenced significantly with a loss of selectivity for C_8 aldehydes/alcohols. This can be attributed to the structural changes of hydrotalcite as evidenced by X-ray diffraction (Fig. 7). This clearly shows that the [HF/HT] catalyst is thermally stable up to 150 °C and slow decomposition follows up to 200 °C. This is consistent with our experimental data, which showed that excellent selectivity with respect to C_8 aldol derivatives was observed in the temperature range 150–200 °C.

Conclusions

Rhodium complex; $HRh(CO)(PPh_3)_3$ [HF] and hydrotalcite $(Mg_{1-x}Al_x(OH_2))^{x+}(CO_3{}^{2-})_{x/n}\cdot mH_2O)$ [HT] based catalyst [HF/HT] has been developed and their multi-functional potential evaluated for the one-pot selective synthesis of C_8 aldol derivatives (aldehydes/alcohols) from propylene. The [HF/HT] catalyst showed catalytic activity for hydroformylation, aldol condensation and hydrogenation in one pot. The Mg/Al ratio of [HT], amount of [HF] complex and [HT], and reaction temperature showed pronounced effect on the selectivity for C_8 aldol derivatives. Aldol condensation temperature T_2 played a significant role in the formation of 2-ethylhexanol in one pot. As the Mg/Al molar ratio and amount of [HT] was increased, the selectivity for 2-ethylhexanal also increased due to the enhancement in the basicity of the catalyst. The amount of [HF] complex in the catalyst significantly influenced the selectivity of 2-ethylhexanal. From the kinetic experiments, it was observed that the rate of formation of 2-ethylhexanal is dependent on the rate of aldol condensation which is catalyzed by hydrotalcite in the catalyst. The reaction pathways and role of each component of multi-functional catalysts [HF/HT] for the synthesis of 2-ethylhexanol is discussed with the help of the kinetic profiles of the reaction with time.

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