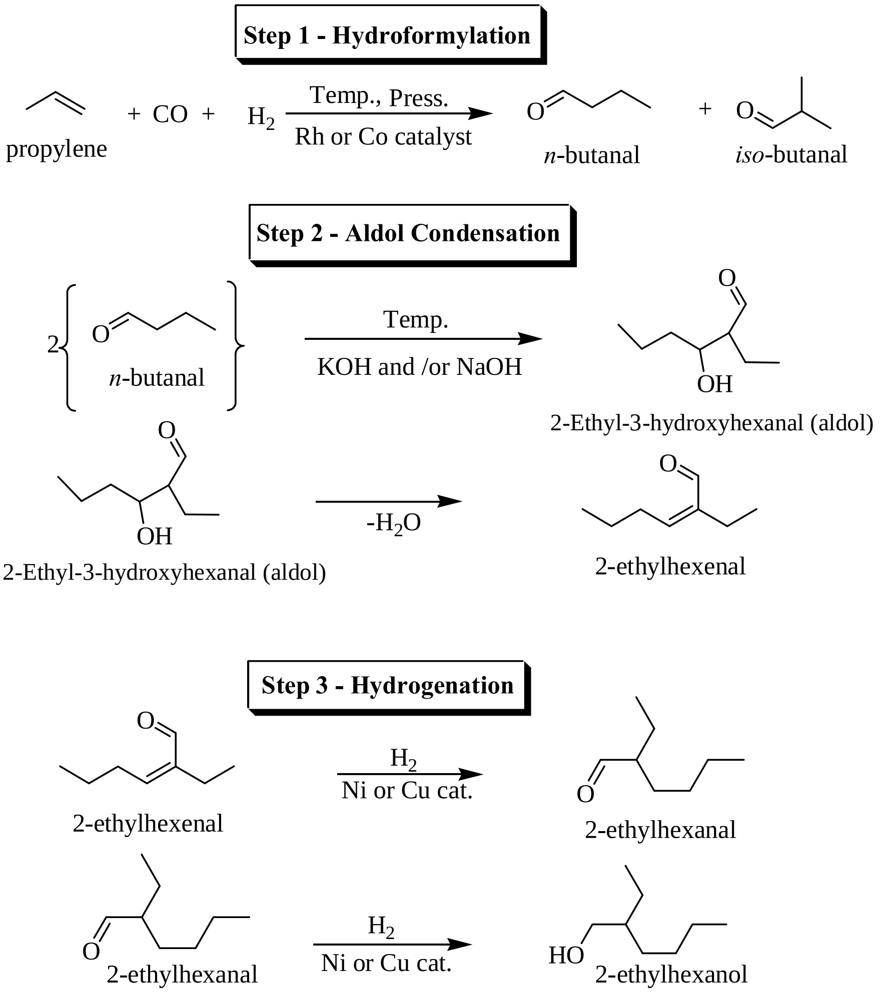
desired chemical compounds, it is often necessary to pass through a sequence of different reaction steps because side reactions can occur, making the composition of the medium more and more complex and, thus, opening additional undesired reaction pathways. The presence of a large numbers of by-products decreases the concentrations of the desired intermediate by dilution processes, leading to lower reaction rates of the necessary reactions. In most of these cases, the consequence is an extremely low yield of the final product in question. Therefore, it is always preferred to synthesize the desired product directly in a single step. This in many cases necessitates the use of multi-functional catalysts that is not always possible.

Of total hydroformylation production capacity (8.8 million tons/year) approximately 86% is based on propylene hydroformylation or C_4-products i.e. butyraldehyde and butanol. The reason for high production and demand for C_4-aldehydes, butanals and butanol via propylene hydroformylation reaction is due to its use in the production of 2-ethylhexanol (2-EH). The reason for high production and demand of C4-aldehyded is due to its use in the production of 2-EH. It is estimated 60% of world consumption of *n*-butyraldehyde (C_4 product) is converted to 2-ethylhexanol (2-EH) [1]. 2-Ethylhexanol is a valuable intermediate product for the chemical industry. It finds application in a variety of plasticizers and is also used in the synthesis of specialty chemicals. 2-Ethyhexanol is used in the production of dioctylphthalate, other plasticizers, coatings, adhesives and specialty chemicals. In these end use areas, it also contributes significantly to many high performance characteristics such as flexibility, good adhesion, lower emissions and fuel performance improvement. Additionally, 2-Ethylhexanol is oxidized to 2-ethylhexanoic acid. This acid can also be manufactured by oxidation of 2-ethylhexanal produced by selective hydrogenation of 2-ethylhexenal. 2-Ethylhexanoic acid is also used for modifying alkyd resins while 2-ethylhexanal can also be used as a raw material for perfumes. The detailed use of 2-ethylhexanol for the production of versatile chemical has already been described in Chapter 1, section 1.3.2.

The synthesis of 2-EH from propylene via *n*-butanal (from hydroformylation reaction) is a three steps process as shown in Scheme 5.1. In the first step, the hydroformylation of propylene is being carried out to produce *n*-butanal with the use of Rh or Co based ond step, *n*-butanal thus obtained undergoes to aldol iquid base like KOH or NaOH for production of 2-ethylhexenal. In the third step, 2-ethylhexenal is hydrogenated 2-ethylhexanal and subsequently to 2-ethylhexanol with use of appropriate catalytic system of Ni or Cu.



Scheme 5.1. Synthetic step for the preparation of 2-ethylhexanol from propylene.

It is estimated for 2-EH that approximately 25-30% of its selling price is product purification, recovery and waste treatment [2] during its production. The high capital expenses are also connected with the handling of strong liquid bases like KOH and/or NaOH during aldol condensation reaction. In addition to that, it was estimated that, presently, about 1-1.5 tons of spent catalyst is being generated for every 10 tones of product formed in the homogeneous catalysis [2] including production of 2-EH. Hence, the industrial manufacture of 2-EH involves very high capital cost since the synthetic

EH (mentioned above) has many drawbacks as written

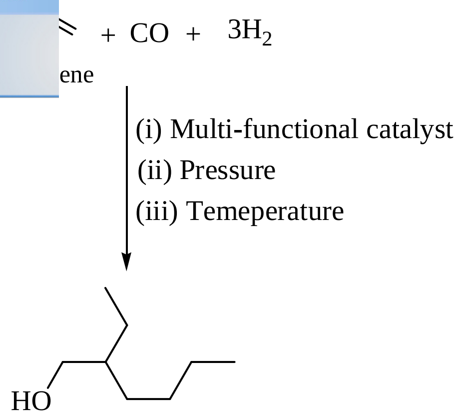
(i) it is a three steps process which is not economical from industrial and energy perspective.

(ii) the use of hazardous reagents liquid KOH or NaOH in large amount for aldol condensation in the second step and the effluent problem in disposal of hazardous KOH/NaOH is not an eco-friendly step.

(iii) the handelling of liquid base KOH/NaOH and post synthesis work-up in separation of spent KOH/NaOH from reactants/products increases the capital as well production cost of 2-EH.

As 2-EH synthesis is a commercially highly significant process with hundreds of millions of dollars business [1], research efforts are directed to overcome these drawbacks. The aldol condensation process during production of 2-EH has been modified by Mitsubishi Chemical [3] in which in the second step, *n*-butanal is converted into 2-ethylhexenal in the presence of a basic ion-exchanger at 80ï 100^{0}C. The third hydrogenation step can be carried out in the vapor phase conditions over either Ni or Cu catalysts. After a three-step distillation process pure products is obtained. However, the process of Mitsubishi Chemical is still a multi-step process. On the other hand, Shell [4] and Exxon both developed a single-step process for producing 2-EH directly from propylene by adding co-catalysts such as compounds of Ti, Sn, Zn, Al, or Cu or KOH, to the original hydroformylation catalyst which is known as óAldoxô process. This process again have several disadvantages over the three-step process outlined above with a relatively low liquid space velocity in the hydroformylation, a low selectivity to the C$_8$-product and use of hazardous KOH.

It is, therefore, highly desirable, to develop a multifunctional catalyst system, which is environmentally accepted and can produce 2-ethylhexanol from propylene, in a single step (Scheme 5.2.). This will certainly have high impact on both industrial and academic level, as it would be highly atom economical, cost economical, energy economical and environmentally acceptable.



2-ethylhexanol

Scheme 5.2. Hypothetical single-step synthesis of 2-ethylhexanol from propylene

For that purpose, we closely looked into the catalysts used in each three steps involved in production of 2-EH from propylene. Generally, the Rh/PPh_3 system is one of the best-known and industrially established catalysts for the hydroformylation reaction to produce *n*-butanal from propylene [1]. Additionally, it is also well known that Rh/PPh_3 catalytic system has a great potential for hydrogenation reactions [5]. Hence, by the choice of an appropriate Rh/PPh_3 catalyst and varied process conditions the first hydroformylation step (for converting propylene to *n*-butanal) and the third hydrogenation step (for converting 2-ethylhexenal to 2-ethylhaxanal and subsequently 2-ethylhexanol) involved in production of 2-EH (Scheme 5.1.) can be accomplished.

The second step (aldol condensation), requires a base catalyst, which should be environmentally permissible. The solid base catalysts seem to be an attractive alternative of conventional homogenous or liquid base like KOH, NaOH [6]. The main advantages of solid base catalysts over conventional liquid base are theses do not corrode reaction vessels or reactors, easier separation from the products and repeated use is possible. Less waste produced than from stoichiometric reagents, lower operation and maintenance costs and no base containing waste streams will be there. The Mg-Al-hydrotalcites are potential alternative to the hazardous liquid base. The Mg-Al-hydrotalcites are anionic clay with the ideal unit cell formula of $Mg_6Al_2(OH)_{16}(CO_3).4H_2O$, and closely related analogs with variable magnesium/aluminum ratios and are known as ósynthetic hydrotalcitesô. The extensive work was reported on the use of "synthetic hydrotalcite" in various base-catalyzed reactions [7] and it is reported that the aldol condensations in a alyzed by "synthetic hydrotalcite" compositions having

oreover, the study of activation of Mg-Al- hydrotalcites as a catalyst for aldol condensation reactions by Figueras et al. [8], showed that a good yield of aldol can be obtained, provided the solid base is suitably activated and the reaction is performed at a low temperature and the aldolization is catalyzed by OH^-, as assumed in the classical organic mechanism. Therefore, due to the potential of hydrotalcite materials for the aldol condensation reaction, we have studied Mg-Al-hydrotalcite as a catalyst in place of the liquid base (KOH and/or NaOH).

In view of above we have attempted to study $HRh(CO)(PPh_3)_3$ metal complex as a catalyst for the first hydroformylation and third hydrogenation step under varied conditions and hydrotalcites as a solid base catalyst for second *n*-butanal condensation step. Two following approaches were adapted;

1. Mechanical mixing of $HRh(CO)(PPh_3)_3$ + Mg-Al hydrotalcites of varied Mg/Al ratio
2. Impregnation of the metal complex $HRh(CO)(PPh_3)_3$ onto the surface of Mg-Al hydrotalcites of Mg/Al ratio 2.0 and 3.5.

The present chapter is focused on the preparation of $C_{2(n+1)}$-aldol derivatives from C_n-alkenes (n = 2-10) in a single-step via oxo-aldol reaction using the above catalyst system and approaches.

5.2. Experimental

5.2.1. Materials

Ethylene (99.5%) propylene (99.6%) and syn-gas (99.8%) were procured from Alchemie Gases & Chemicals Pvt. Ltd., India respectively. 1-Butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene and 1-decene (all of 99.9%) were procured from Sigma-Aldrich U.S.A. The metal precursors $RhCl_3.3H_2O$, ligand PPh_3, $NaBH_4$ and HCHO solutions were purchased from Sigma-Aldrich U.S.A. for synthesizing $HRh(CO)(PPh_3)_3$ metal complex. $Mg(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, Na_2CO_3, and NaOH were purchased from s.d. Fine Chemicals, India for synthesizing Mg-Al-hydrotalcites. Organic solvents required for complex synthesis were purchased from Rankem, India and purified by reported methods [9]. The double distilled milli-pore de-ionized water was always used wherever necessary.

CO)(PPh$_3$)$_3$ complex

The metal complex HRh(CO)(PPh$_3$)$_3$ has been prepared by reported method [10]. A solution of metal salt, RhCl$_3$.3H$_2$O (2.0 g, 7.6 mmol) in ethanol (70 ml) was added to a refluxing solution of triphenylphosphine, PPh$_3$ (12 g, 46.0 mmol) in ethanol (300 ml). After 2 minute aqueous formaldehyde, HCHO (10 ml) was added drop wise and the solution turned yellow with formation of *trans*-RhCl(CO)(PPh$_3$)$_2$. Addition of sodiumborohydride, NaBH$_4$ (2.0 g) in ethanol to this hot mixture yielded the yellow crystals of HRh(CO)(PPh$_3$)$_3$. The yellow crystal was washed with ethanol to remove un-reacted rhodium metal.

5.2.2.2. Synthesis of Mg-Al hydrotalcite

The synthesis of Mg-Al hydrotalcites was done as per reported method [11]. An aqueous solution (0.22 L) containing Mg(NO$_3$)$_2$.6H$_2$O (0.223 mol) and Al(NO$_3$)$_3$.9H$_2$O (0.088 mol) for a ratio of Mg/Al = 2.5, was added slowly to a second solution (0.221 L) containing NaOH (0.716 mol) and Na$_2$CO$_3$ (0.208 mol) in 1.0 L round bottom flask under vigorous stirring. The addition took nearly 3 h. Then the suspension was heated at 65^{0}C for 16 h. The precipitate formed was filtered and washed with hot distilled water until pH of the filtrate was 7. The precipitate was dried in the oven at 80^{0}C for 15 h. The Powder-XRD patterns shows the presence of pure Mg-Al mixed oxide, with lattice parameter corresponding to those reported in the literature. The Mg-Al hydrotalcites of different Mg/Al ratio have been synthesized according to above written procedure having appropriate moles of Mg(NO$_3$)$_2$.6H$_2$O and Al(NO$_3$)$_3$.9H$_2$O.

5.2.2.3. Mechanical mixing of the complex HRh(CO)(PPh$_3$)$_3$ with Mg-Al hydrotalcites

The complex HRh(CO)(PPh$_3$)$_3$ (18.4 mg, 0.02 mmol) was mixed with desired amount of Mg-Al-hydrotalcites of different Mg/Al ratio. The resulting mixture was blended at room temperature by mechanical stirrer to obtain the free-flowing yellow material and stored in vacuum at room temperature.

complex $HRh(CO)(PPh_3)_3$ onto the surface of Mg-Al

A 10 ml toluene solution of $HRh(CO)(PPh_3)_3$ (450 mg, 0.489 mmol) and PPh_3 (1050 mg, 4.00 mmol) was poured into a flask containing 3.2 g Mg-Al-hydrotalcites of Mg/Al ratio = 2.0. The slurry was stirred for 32 h at room temperature under inert atmosphere of N_2 or Ar-gas. After 32 h, the toluene was removed under vacuum at room temperature. The final product was a dry free-flowing light yellow powder, which was stored under inert atmosphere at room temperature. The same procedure was followed for the Mg/Al ratio 3.5.

5.2.3. Characterization of the catalysts

5.2.3.1. ^{31}P-FT-NMR spectra

The FT-NMR characterization of the metal complex $HRh(CO)(PPh_3)_3$, was done by using Bruker Avance DPX 200MHz FT-NMR system. The ^{31}P-FT-NMR spectra of the metal complex are shown below in Figure 5.1. The appearance of the doublet at 46.34 and 48.31 ppm [*J (Rh-P)* = 160 Hz] in ^{31}P-NMR spectra of $HRh(CO)(PPh_3)_3$ (Figure 5.1), indicates that the all the three phosphorous atoms present in the same environment and are in the equatorial position. The hydride (H) and CO finds axial positions making the complex into trigonal bipyramidal structure.

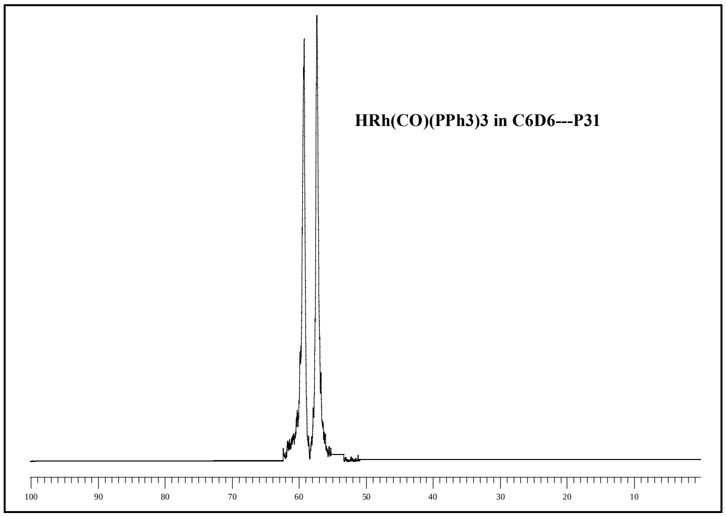


Figure 5.1. ^{31}P-FT-NMR of the metal complex $HRh(CO)(PPh_3)_3$ in C_6D_6

of the complex and Mg-Al-hydrotalcites were done by using Perkin Elmer Spectrum GX FT-IR system. In the FT-IR spectra of the complex, appearance of bands at 2036 cm^{-1} for з (Rh-H) and 1936 cm^{-1} for з (C=O) confirmed the formation of rhodium complex $HRh(CO)(PPh_3)_3$.

In the FT-IR spectra of Mg-Al-hydrotalcites for each Mg/Al ratio, the appearance of the shoulders at 1637 cm^{-1} and 1489 cm^{-1} that are the characteristic bands of CO_3^{2-} and H_2O confirmed the formation of Mg-Al hydrotalcites.

5.2.3.4. Elemental analysis

The C, H and N elemental analysis of the complexes was done by using Perkin Elmer CHNS/O 2400 analyzer. For the complex $HRh(CO)(PPh_3)_3$ cal. (found): %C; 71.9 (71.6); %H; 5.0 (5.1).

5.2.3.5. Powder X-Ray diffraction analysis

Powder X-ray diffraction patterns of pure Mg-Al hydrotalcites and impregnated catalysts were recorded with Phillips XôPert MPD system equipped with XRK 900 reaction chamber, using Cu-KŬ radiation (ә =1.54050A^0). The P-XRD pattern of Mg-Al mixed oxides for each Mg/Al ratio showed sharp and symmetric peaks at lower 2ɗ values, which were characteristics of hydrotalcites-like-compounds and the materials consisted of one phase only as shown in Figures 5.2. and 5.4. The P-XRD spectra clearly show that the characteristic original planes of the Mg-Al-hydrotalcites are retained after impregnation of metal complex $HRh(CO)(PPh_3)_3$ (Figure 5.3. and 5.4.).

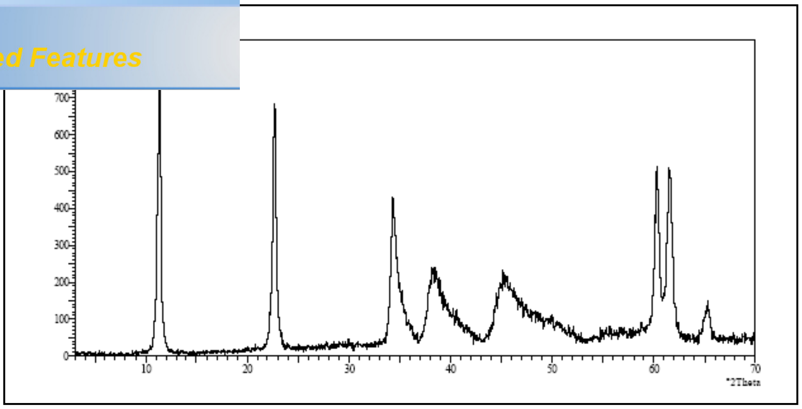


Figure 5.2. P-XRD pattern of Mg-Al-hydrotalcite (Mg/Al ratio = 2.0)

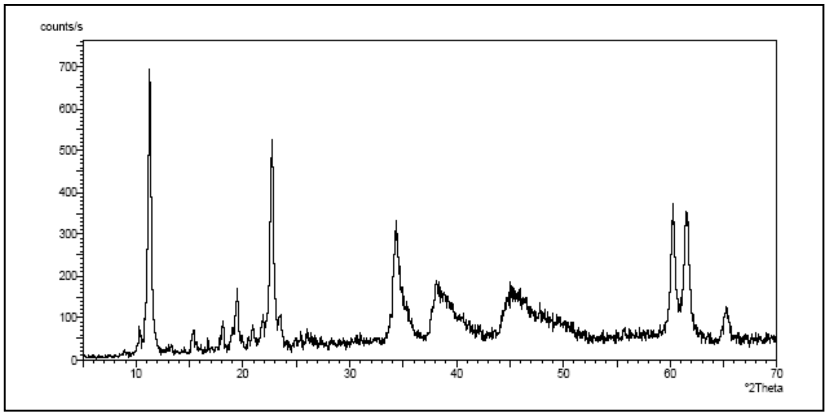


Figure 5.3. P-XRD pattern of impregnated $HRh(CO)(PPh_3)_3$/HT(2.0)

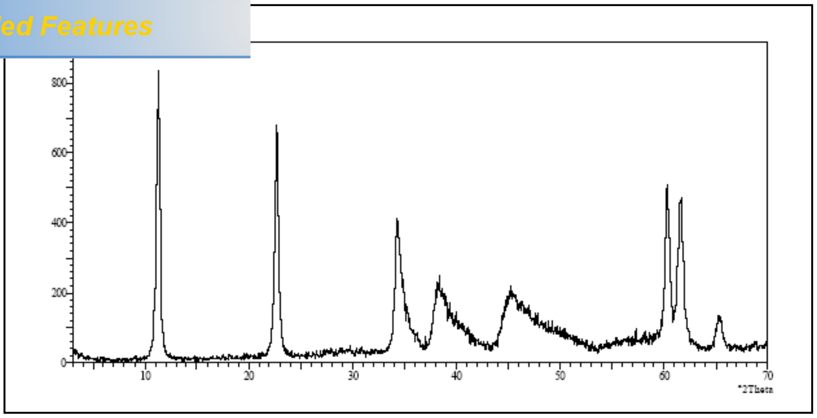


Figure 5.4. P-XRD pattern of Mg-Al-hydrotalcites (Mg/Al ratio = 3.5)

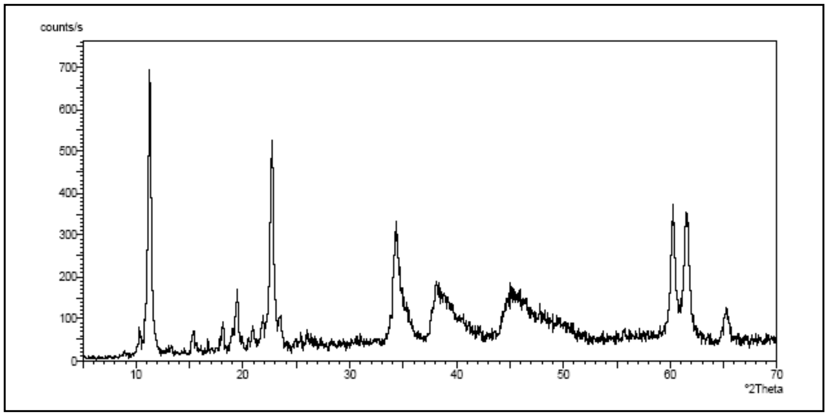


Figure 5.5. P-XRD pattern of impregnated $HRh(CO)(PPh_3)_3$/HT(3.5)

5.2.4. Hydroformylation reactions

5.2.4.1. The autoclave reactor

All the hydroformylation reactions were carried out in 100 ml stainless steel autoclave reactor (Autoclave Engineers, U.S.A.) equipped with a controlling unit. The detail experimental, operational and safety procedures for conducting hydroformylation reactions in autoclave reactor has already been described in Chapter 2, Section 2.2.7.1.

ction of gaseous olefins

the multi-functional catalyst system was poured in the autoclave reactor having 50 ml toluene as solvent. The autoclave was flushed twice with nitrogen prior to introducing desired pressure of gaseous C_n-alkene (n = 2-4). The reactor was then brought to the desired reaction temperature (T_1) for hydroformylation reaction. Then CO and H_2 (1:3) gases were introduced to the reactor upto desired pressures respectively. The reaction was then initiated by starting the magnetic stirrer at desired rotation per minute (rpm). The reaction temperature kept for desired time (t_1) at T_1 temperature. After time (t_1) of T_1 temperature, the reaction temperature was raised to desired reaction temperature (T_2) from T_1 to initiate aldolization (aldol condensation) reaction. The reaction temperature kept for desired time (t_2) at T_2 temperature. Hence, the total reaction time (t) was (t_1+t_2). Meanwhile, the reaction was continued at constant pressure, by supplying CO and H_2 (1:3) from the reservoir vessel. After the total reaction time (t), the reaction was quenched by disconnecting the gas-supply to the autoclave reactor. The autoclave was then brought to room temperature with the help of a cooling system and the pressure drops were noted. The orange-red solution of the product mixture is then subjected to GC analysis.

5.2.4.3. Hydroformylation reaction of liquid olefins

The desired amount of the multi-functional catalyst system and the liquid C_n-alkene (n = 5-10) were pored into the autoclave reactor having 50 ml toluene. The reactor was then brought to the desired reaction temperature (T_1) for hydroformylation reaction. The autoclave was flushed twice with nitrogen prior to successively introducing desired pressure of CO and H_2 (1:3) gases respectively. The reaction was then initiated by starting the magnetic stirrer at desired rotation per minute (rpm). The reaction temperature kept for desired time (t_1) at T_1 temperature. After time (t_1) of T_1 temperature, the reaction temperature was raised to desired reaction temperature (T_2) from T_1 to initiate aldolization (aldol condensation) reaction. The reaction temperature kept for desired time (t_2) at T_2 temperature. Hence, the total reaction time (t) was (t_1+t_2). Meanwhile, the reaction was continued at constant pressure, by supplying CO and H_2 (1:3) from the reservoir vessel. After reaction time (t), the reaction was quenched by disconnecting the gas-supply to the autoclave reactor. The autoclave was then brought to of a cooling system and the pressure drops were noted. roduct mixture is then subjected to GC analysis.

5.2.4.4. Reaction product analysis

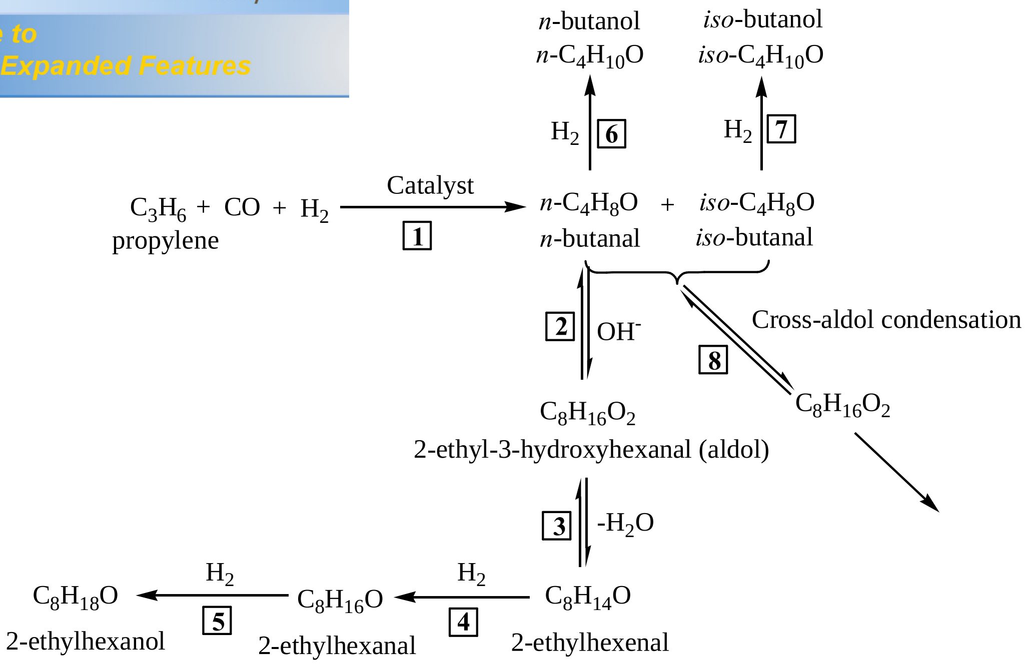
The reaction product analysis was carried out using gas chromatography (GC) (Shimadzu 17A, Japan); the instrument has a 5% diphenyl and 95% dimethyl siloxane universal capillary column (60m length and 0.32mm diameter) and a flame ionization detector (FID). The initial column temperature was increased from 40 to 200^{0}C at the rate of 10^{0}C/min. Nitrogen gas was used as the carrier gas. The temperatures of the injection port and FID were kept constant at 200^{0}C during product analysis. The retention times for different compounds were determined by injecting pure compounds under identical gas chromatography conditions.

5.3. Results and discussions

Two different types of catalytic systems were used for the present study; the first one is the obtained by mechanical mixing of the metal complex $HRh(CO)(PPh_3)_3$ and Mg-Al-hydrotalcites with different Mg/Al ratio, would be termed as HF+HT(X), where X is the numerals of Mg/Al ratio. The second one is the catalytic system obtained by impregnation of the metal complex $HRh(CO)(PPh_3)_3$ onto the surface of Mg-Al-hydrotalcites with different Mg-Al ratio would be termed as HF/HT(X). Each catalytic system would be discussed here in separate sections.

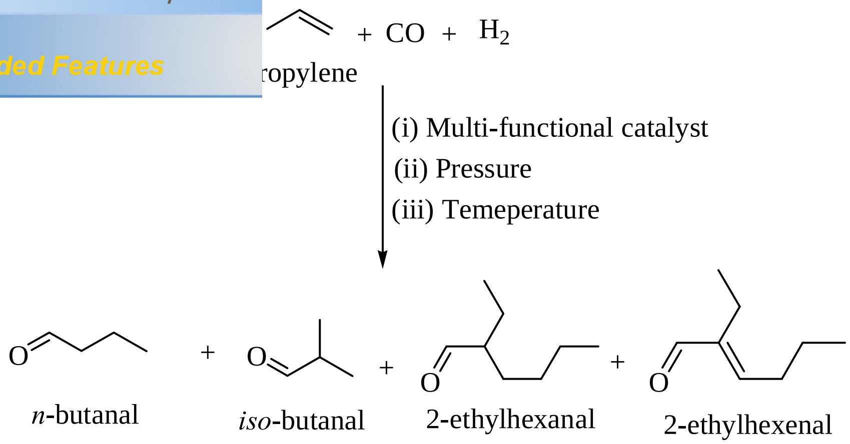
It would be worthy to look closely over the each steps involved in the preparation of 2-ethylhexanol from propylene in order to understand of the role-played by the multi-functional catalytic system for each steps. As seen from the Scheme 5.3., the reaction will be initiated by formation of *n*-butanal via hydroformylation reaction (step **1**). The rhodium-component of the multifunctional catalytic system would catalyze the step **1**. The next step is condensation step; two molecules of *n*-butanal undergo condensation reaction to give 2-ethyl-3-hydroxyhexanal (aldol products) and subsequently 2-ethylhexenal after removal of one molecule of water. The Mg-Al hydrotalcite-component of the multi-functional catalytic system will facilitate this step **2** and **3**. The step **4** is a hydrogenation step which includes hydrogenation of 2-ethylhexenal to 2-ethylhexanal. This step stoichiometrically requires second hydrogen molecules. The rhodium component of the multi-functional catalytic system and the employed reaction conditions step. The last and final step **5** is again hydrogenation step -ethylhexanal to 2-ethylhexanol. Stoichiometrically, the third hydrogen molecule would be utilized in the step **5**. Another time, the Rh-component of the multi-functional catalytic system and the employed reaction conditions would facilitate the hydrogenation step **5**. Therefore, the Rh-component of the multifunctional catalytic system has to catalyze three reactions; one hydroformylation and another two are hydrogenation reactions during the single step preparation of 2-ethylhexanol from propylene.

However, the possibilities of side reactions involved in a single step preparation of 2-ethylhexanol from propylene under the hydroformylation conditions cannot be overlooked. The first and most probable possibility is the reduction of butanals (*n*- and *iso*- both) to their corresponding butanols (step **6** and **7**). The hydrogen molecules are required, for these two steps **6** and **7**, which would be present stoichiometrically three-times more than carbon monoxide molecules under employed reaction conditions. Moreover, the rhodium-component of the multi-functional catalytic systems is present to catalyze these two steps **6** and **7**. Hence, in order to avoid this competitive reaction, the solid base (Mg-Al-hydrotalcite)-component of the multi-functional catalytic system and the reaction conditions, i.e., aldol reaction temperature (T_2), must be sufficient-enough to divert the reaction to step **2** not to step **6** and **7** after step **1**. Another possible side reaction is cross-aldol reaction of *n*-butanal and *iso*-butanal (step **8**). However, in our investigations, the products of cross-aldol reaction were not observed, during all our catalytic studies under employed reaction conditions.



Scheme 5.3. The formation 2-ethylhexanol from propylene in single step

It is worth mentioning here that although our target was to prepare 2-ethylhexanol from propylene in a single step under hydroformylation reaction conditions using catalyst system but during the course of experiments mixture of products were observed (Scheme 5.4.) under employed reaction conditions. Among the products obtained, 2-ethylhexanal, which is the second last product of Scheme 5.3., was the end-product during all catalytic studies. Therefore the studied multi-functional catalytic system and/or the employed reaction conditions were not sufficient-enough to carry out the last and final step, i.e., reduction of 2-ethylhexanal to 2-ethylhexanol. However, the formation of final desired products 2-ethylhexanol was also observed during some catalytic studies but the values were too low to report.



Scheme 5.4. The products obtained with the multi-functional catalytic systems

5.3.1. The catalytic activity of HF+HT(X) systems

In order carry out studies for the single step preparation of 2-ethylhexanal and 2-ethylhexenal from using HF+HT(X) catalyst system, various reaction-influencing parameters were varied and are discussed below;

5.3.1.1. Effect of different Mg/Al ratio of hydrotalcites in HF+HT(X) catalytic system

In order to see the effects of variation of the Mg/Al ratio in the HF+HT(X) catalytic system for the selectivities $C_{2(n+1)}$-aldol-derivatives, the experiments were conducted by varying the Mg/Al ratio from 1.5 to 3.5. As the Mg/Al ratio of HF+HT(X) catalytic system increases the selectivity of 2-ethylhexanal increases except for Mg/Al = 2.0 and 2.5 (Table 5.1.). The increment of Mg/Al ratio is directly proportional to the Mg-contents in the hydrotalcites and it is well-known that the increment of Mg-contents in the hydrotalcites increases the basic character of the hydrotalcites [12]. Hence, higher the basic nature of the hydrotalcites, yields of the $C_{2(n+1)}$-aldol derivatives will be higher. The selectivity of 2-ethylhexanal has been achieved upto 58% with Mg/Al ratio 3.5 under the employed reaction conditions. The concentration of butanals also decreases in accordance to the increase of the concentration of $C_{2(n+1)}$-aldol derivatives. Additionally, the formation of butanols was observed in only some cases. This indicates that the employed reaction conditions were sufficient-enough to carry out the desired reaction pathways (Scheme 5.3.).

h HF + HT(X) system of different Mg/Al ratio

		Product distribution (%)			
		2-ethylhexanal	2-ethylhexenal	Butanal	Butanol
1	1.5	46	20	34	0
2	2.0	43	28	24	5
3	2.5	38	8	51	3
4	3.5	58	13	29	0

Reaction conditions: Partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial Pressure of H_2 = 15 bar, total pressure of the reaction (P) = 30 bar, weight of HF + HT(X) = 700 mg, $T_1 = 50^0$C, t_1 = 3h, $T_2 = 150^0$C, t_2 = 9h, total reaction time (T) = 12h, RPM = 1000, and solvent (volume) = toluene (50 ml).

5.3.1.2. Effect of variation of the amount of HF+HT(1.5) catalytic system

To observe the effect of amount of hydrotalcites (Mg/Al = 1.5) for the selectivities of $C_{2(n+1)}$-aldol derivatives from propylene, the experiments were carried out by varying the amount of HT(1.5) in the catalytic system HF+HT(1.5) from 100 mg to 1400 mg keeping the amount of the metal complex $HRh(CO)(PPh_3)_3$ constant. The results obtained (Table 5.2.) were quite interesting that there was an regular increase for the selectivities of 2-ethylhexanal on increasing the amount of HT(1.5) in the HF+HT(1.5) catalytic system upto 700 mg. After that the selectivity of 2-ethylhexenal decreased even the amount of HT(1.5) hydrotalcites was double (Run 4 and 6, Table 5.2.). On the other hand the selectivity of 2-ethylhexenal increases uniformly on increasing the amount of HT(1.5) hydrotalcites, however, the magnitude of increase was low. The selectivity of butanal also decreases significantly on increasing the amount of HT(1.5) hydrotalcites indicating continuous consumption of butanal to subsequent reactions (Scheme 5.3). It was also interesting to note that when the amount of HT(1.5) in the HF+HT(1.5) catalytic system was less, the selectivities of butanols were high (Run 1 and 2, Table 5.2.). The formation of butanols are the consequences of competitive side reaction of hydroformylation product, butanals (Scheme 5.3.) which occurs in absence of adequate amount of solid base HT(1.5) in the HF+HT(1.5) catalytic system.

In order to find the possible reasons the decrease in the selectivity of 2-ethylhexanal on increasing the amount of HT(1.5) after 700 mg, one has to look closely the new material HF+HT(1.5), which was obtained by blending the metal complex

The ratio of the metal complex $HRh(CO)(PPh_3)_3$ to

role in the activity of HF+HT(1.5) catalytic system. As it can be seen from Table 5.2. (Run 4, 5 and 6) that the selectivities of butanal were slightly decreasing without any significant increase in the concentration of $C_{2(n+1)}$-aldol derivative and the concentration of butanols (products of the side reaction). Since the formation $C_{2(n+1)}$-aldol derivative and butanols are the products of two subsequent reaction in which the starting reactants are butanals (Scheme 5.3.) which indicates that the hydroformylation activity, which is first step (Scheme 5.3.), was suppressed upto some extent on increasing the amount of HT(1.5) in the HF+HT(1.5) catalytic system.

Table 5.2. Product distribution with the variation of the amount of HF+HT(1.5) catalytic system

Run	HT (1.5) (mg)	Product distribution (%)			
		2-ethylhexanal	2-ethylhexenal	butanal	butanol
1	100	8	6	65	21
2	300	18	10	52	20
3	500	30	18	46	6
4	700	46	20	34	0
5	1050	41	22	32	5
6	1400	39	23	34	4

Reaction conditions: Partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial Pressure of H_2 = 15 bar, total pressure of the reaction (P) = 30 bar, $T_1 = 50^0C$, t_1 = 3 h, $T_2 = 150^0C$, t_2 = 9 h, total reaction time (T) = 12 h, RPM = 1000 and solvent (volume) = toluene (50 ml).

ol temperature (T_2) with HF+HT(1.5) catalytic system

h occurs after hydroformylation reaction (Scheme 5.3.), is highly influenced by the (aldol) temperature (T_2). Therefore, in order to study the effect of the aldol temperature (T_2) with the present multi-functional catalytic system, experiments have been conducted by varying T_2 from 80^0 to 250^0C (Table 5.3.). It was observed that on increasing the temperature T_2, the selectivity of 2-ethylhexanal increases upto 150^0C. After that there was a rapid decline in the selectivity of 2-ethylhexanal from 46% to 12% (Run 4, 5, 6; Table 5.3.). On the other hand, there was a linear increase in the selectivity of 2-ethylhexenal on increasing the aldol-temperature (T_2). The selectivity of butanals decreases gradually which indicates a uniform consumption of butanals either to aldol-condensation reactions or to hydrogenation reaction to form butanols (when the aldol-temperature T_2 was low).

The gradual increase in the selectivities of 2-ethyhexenal, which is an aldol products of butanal (Scheme 5.3.), on increasing the aldol-temperature (T_2) indicates that the rate of aldol condensation is directly proportional to T_2. However, a sharp decline in the selectivities of 2-ethylhexanal, which is obtained by subsequent hydrogenation of 2-ethyhexenal (Scheme 5.3.), after a regular increase may be due to the deactivation of rhodium-component of the multi-functional catalytic system above 150^0C which is supposed to catalyzed this hydrogenation reaction (Step 4; Scheme 5.3.). The deactivation of the rhodium-component of the multi-functional catalyst system was also evidenced by suppressed formation of butanols at the temperature 150^0C and above since this competitive side reaction also requires Rh-component to be catalyzed.

h the variation of the aldol temperature (T_2) with HF+HT(1.5)

Run	T_2 (^{0}C)	Product distribution (%)			
		2-ethylhexanal	2-ethylhexenal	butanal	Butanol
1	80	12	0	70	18
2	100	23	2	53	20
3	125	32	8	47	13
4	150	46	20	34	0
5	175	42	30	29	0
6	200	12	62	26	0

Reaction conditions: Partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial Pressure of H_2 = 15 bar, total pressure of the reaction (P) = 30 bar, T_1 = 50^{0}C, t_1 = 3 h, t_2 = 9 h, total reaction time (T) = 12 h, RPM = 1000 and solvent (volume) = toluene (50 ml).

5.3.1.4. Effect of variation of alkenes with HF+HT(3.5) catalytic system

The HF+HT(3.5) multi-functional catalytic was also used for the various C_n-alkene where n ranges from 2 to 10 to observe the trend of formation of $C_{2(n+1)}$-aldol derivatives (Table 5.4.). There was a gradual decrease in the selectivities of $C_{2(n+1)}$-aldol derivatives on increasing the chain length of C_n-alkenes (n = 2 to 10). As the chain length of C_n-alkenes increases the selectivities of $C_{(n+1)}$-aldehydes (hydroformylation product) increases except for some alkene (Run 5, 6 and 7; Table 5.4.). However, it was also observable that the selectivities of $C_{(n+1)}$-aldehydes decreases at the expense of large amount of side reaction of alkene, i.e., isomerization and hydrogenation (Run 5, 6 and 7; Table 5.4.). It means that the large amount C_n-alkene (for n = 6 to 8) undergo to side reaction like isomerization and hydrogenation under employed reaction conditions. The decrease in the selectivities of $C_{2(n+1)}$-aldol derivatives on increasing the chain length of C_n-alkenes (n = 2 to 10) can be explained in terms of basicity of Mg-Al hydrotalcites that for higher liquid alkenes rather stronger solid base is required as compare to the lower alkenes.

h various alkenes

		Product distribution (%)			
		$C_{2(n+1)}$-aldol derivatives	$C_{(n+1)}$-aldehyde	Isomerization of C_n-alkene	hydrogenation of C_n-alkenes
1	Ethylene	87	13	0	0
2	Propylene	72	29	0	0
3	1-Butene	68	32	0	0
4	1-Pentene	64	36	0	0
5	1-Hexene	44	17	10	30
6	1-Heptene	38	30	9	23
7	1-Octene	34	25	12	29
8	1-Nonene	18	64	8	10
9	1-Decene	7	84	1	8

Reaction conditions: Partial pressure of C_n-alkenes (where, n = 2-4) = 10 bar, weight of C_n-alkenes (where, n =5-10) = 2.0 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(3.5) = 700.0 mg, $T_1 = 50^0$C, t_1 = 3 h, $T_2 = 150^0$C, t_2 = 9 h, total reaction time = 12 h, RPM = 1000 and solvent (volume) = toluene (50 ml).

5.3.2. The catalytic activity of HF/HT(X) systems

The catalytic activity of HF/HT(X) multi-functional catalyst systems have been checked for the preparation of 2-ethylhexanal and 2-ethylhexenal from propylene in a single step reaction, under various reaction-influencing parameters and are described below;

5.3.2.1. Effect of variation of the amount of HF/HT(2.0) catalytic system

The results obtained with HF/HT(X) are rather different from those obtained for HF+HT(X) catalytic system. In the case of HF/HT(2.0) multi-functional catalytic system the selectivity of 2-ethylhexanal uniformly increases from 10% to 47% by increasing the amount of the HF/HT(2.0) catalyst system from 100 to 1000 mg (Table 5.5.). The selectivity of 2-ethylhexenal also increases on increasing the amount of the catalyst system except in some cases (Run 3-4; Table 5.5.). A gradual decrease in the selectivity of butanal was observed on increasing the amount of HF/HT(2.0) catalyst system, which indicates a consistent consumption of butanal for the subsequent reactions. The gh when the amount of catalyst was low (Table 5.5.) due of solid base to carry out aldol reactions.

On increasing the amount of impregnated HF/HT(2.0) catalyst system the ratio of Rh-complex to the Mg-Al hydrotalcite within the catalyst system is constant. Hence, on increasing the amount of HF/HT(2.0) catalyst system the concentration of both the Rh-component and basic Mg-Al hydrotalcite increases, therefore, selectivity of $C_{2(n+1)}$-aldol derivatives increases.

One important observation was that the selectivity of 2-ethylhexanal increases 43% to 52% on putting the experiment at single temperature ($T = 150^0C$) throughout the reaction i.e. without putting experiment on two separate temperatures ($T_1 = 50^0$ and $T_2 = 150^0C$) (Run 4 and 6; Table 5.5.) with same amount of catalyst system. One of the possible reasons of getting higher selectivity on putting the reaction at single temperature, 150^0C, may be because of the solid base (Mg-Al hydrotalcites) component of HF/HT(2.0) catalyst system becomes activated in the beginning of the experiment. The solid base (Mg-Al hydrotalcites)-component of HF/HT(2.0) catalyst system does not present in its active form when the two separate temperature were used (50^0 and 150^0C) since aldol reaction is not possible at T_1 temperature (50^0C). During that period some side reactions like formation butanols can occur (Scheme 5.3.) which causes a decrease in the selectivity of $C_{2(n+1)}$-aldol derivatives.

the variation of the amount of HF/HT(2.0) catalytic system

		Product distribution (%)			
		2-ethylhexanal	2-ethylhexenal	butanal	Butanol
1	100	10	6	60	24
2	300	21	9	53	17
3	500	41	5	45	9
4	700	43	7	41	9
5	1000	47	13	40	0
6	700*	52	9	39	0

Reaction Conditions: Partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial pressure of H_2 = 15 bar, total pressure of the reaction (P) = 30 bar, $T_1 = 50^0$C, t_1 = 3 h, $T_2 = 150^0$C, t_2 = 9 h, RPM = 1000, total reaction time (t) = 12 h, solvent (volume) = Toluene (50 ml), *reaction temperature (T) = 150^0C *total reaction time (t) = 12 h.

5.3.2.2. Effect of variation of total reaction temperature (T) with HF/HT(2.0) catalytic system

As it was observed in the previous experiment (Run 6; Table 5.5.) that the selectivity of 2-ethylhexanal was enhanced by keeping the reaction at single temperature, therefore, experiments have been carried out by varying the single temperature (T) from 75^0C to 300^0C using HF/HT(2.0) catalytic system. The selectivity of 2-ethylhexanal increased from 15% to 70% by increasing the reaction temperature (T) from 75^0 to 225^0C (Run 1-3; Table 5.6.). After that, the selectivity of 2-ethylhexanal decreases 70% to 60% on increasing the reaction temperature (T) 225^0 to 300^0C (Run 5-6; Table 5.6.). It was interesting to see that the selectivities of 2-ethylhexenal were zero at 75^0, 225^0 and 300^0C which indicates the complete consumption of the 2-ethylhexenal to 2-ethylhexanal at these temperatures (Scheme 5.3). The selectivity of butanal falls from 80% to 45% by increasing the temperature (T) from 75^0 to 150^0C. After that, the selectivity of butanal goes to zero at 225^0 and 300^0C (Run 3-4; Table 5.6.).

The observed enhanced selectivities of both 2-ethylhexanal and butanol at 225^0 and 300^0C (Run 3 and 4; Table 5.6.) showed a contradicting results. The formation of 2-ethylhexanal (desired reaction) and butanols (competitive side reaction) both required same conditions in order to be facilitated, i.e., both the reaction require the Rhytic system and the sufficient concentration of hydrogen n the selectivity of 2-ethylhexanal on increasing the temperature 225^0 to 300^0C, at the expense of increased selectivity of butanol, shows that the rate of the competitive side reaction is rather faster than desired reaction at 300^0C.

Table 5.6. Product distribution with the variation of the total reaction temperature (T) with HF/HT(2.0) as a catalytic system

Run	T (^{0}C)	Product distribution (%)			
		2-ethylhexanal	2-ethylhexenal	butanal	butanol
1	75	15	0	80	5
2	150	41	5	45	9
3	225	70	0	0	30
4	300	60	0	0	40

Reaction conditions: Partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial pressure of H_2 = 15 bar, total pressure of the reaction = 30 bar, HF/HT(2.0) = 500 mg, total reaction time (t) = 12 h, RPM = 1000, solvent (volume) = Toluene (50 ml).

5.3.2.3. Effect of variation of amount of HF/HT(3.5) catalytic system

The effects of variation of amounts of HF/HT(3.5) catalytic system on the product distributions have also been carried out similar to previous study with HF/HT(2.0) (section 5.3.2.1.). It was interesting to see that the trends of selectivity of $C_{2(n+1)}$-aldol derivatives, butanals and butanols using HF/HT(3.5) catalytic system (Table 5.7.) were quite similar to that observed for HF/HT(2.0) catalytic system (Table 5.5.). Moreover, 45% selectivity of 2-ethylhexanal at two separate temperatures (50 and 150^0C) was again increased upto 54% at single temperature (T = 150^0C) with the same amount of catalyst system (Run 4 and 6; Table 5.7.), similar results have also been observed HF/HT(2.0) catalytic system (section 5.3.2.1.). The possible reasons have already been discussed in the section 5.3.2.1. The only remarkable difference was the magnitude of selectivity of $C_{2(n+1)}$-aldol derivatives which was higher for HF/HT(3.5) than HF/HT(2.0) catalytic system. This observation is further supports the observations of section 5.3.1.1. in which it was concluded that the selectivity of $C_{2(n+1)}$-aldol derivatives increases on increasing the Mg/Al ratio of hydrotalcite.

variation of the amount of HF/HT (3.5) catalytic system

		Product distribution (%)			
		2-ethylhexanal	2-ethylhexenal	butanal	butanol
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
6	700*	54	6	40	0

Reaction conditions: Partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial pressure of H_2 = 15 bar, total pressure of the reaction (P) = 30 bar, T_1 = 50^0C, t_1 = 3 h, T_2 = 150^0C, t_2 = 9 h, RPM = 1000, total reaction time (t) = 12 h, solvent (volume) = Toluene (50 ml), *reaction temperature (T) = 150^0C *total reaction time (t) = 12 h.

5.3.2.4. Effect of variation of CO and H_2 partial pressures with HF/HT(3.5) catalytic system

The study of the effects of variation of syn-gas pressure (1:3), from 12.5 to 80 bar, on the product distributions of $C_{2(n+1)}$-aldol derivatives have also been carried out using HF/HT(3.5) catalytic system (Table 5.8.). It was surprising to see that there was not any pronounced effect on varying the syn-gas pressure. For example, on increasing the syn-gas (1:3) pressure from 12.5 to 40 bar, the selectivity of 2-ethylhexanal increases from 38% to 47% (Run 1-3; Table 5.8.). After that, the selectivity fell down to 47% to 40% on increasing the syn-gas pressure 40 to 60 bar (Run 4-5; Table 5.8.) and again the selectivity of 2-ethylhexanal increases from 40% to 47% by increasing the syn-gas pressure from 60 to 80 bars (Run 5-6; Table 5.8.). Similar irregular results were also observed for the selectivities of 2-ethylhexenal. The selectivities of butanals were also not in uniform sequence. The formation of butanols was observed during all the studies and the selectivities were more at elevated syn-gas pressures. From these observations it can be concluded that the factors that influence the preparation of $C_{2(n+1)}$-aldol derivatives from C_n-alkenes (n = 3) are the reaction temperatures and the amount of catalytic system and syn-gas pressures have marginal influence.

ith the variation of the partial pressures of CO and H_2 using

Run	Pressure (bar)		Product distribution (%)			
	CO	H_2	2-ethylhexanal	2-ethylhexenal	butanal	butanol
1	2.5	10	38	12	42	8
2	5	15	43	6	45	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 bar, HF/HT(3.5) = 500 mg, $T_1 = 50^0$C, t_1 = 3 h, $T_2 = 150^0$C, t_2 = 9 h, RPM = 1000, total reaction time (t) = 12 h, solvent (volume) = Toluene (50 ml),

5.3.3. Kinetic studies

To understand the mechanistic trend of formation of various products during the course of the experiment and then optimize the process conditions, the kinetic studies with catalytic systems have also been carried out.

5.3.3.1. Kinetic studies with HF+HT(3.5) catalytic system

The results obtained with HF+HT(3.5) catalytic system at single temperature (T = 150^0C) is shown in Figure 5.6. It is interesting to see that under employed reaction conditions, 47% selectivity of 2-ethylhexanal can be achieved in 1.5 h and during that period the selectivity of 2-ethylhexenal was zero (Figure 5.6.). After that, the selectivity of 2-ethylhexanal decreases and the selectivity of 2-ethylhexenal increases with time. At 7.0 h the selectivity of 2-ethylhexanal was highest (50%) and again it started decreasing. The selectivity of butanal decreases uniformly indicating a constant consumption of butanal to subsequent aldol-reaction upto 9 h. It was remarkable to see that selectivity of butanal was least at 7.0 h at which the highest selectivity (50%) of 2-ethylhexanal was obtained (Figure 5.6.). The formation of butanols started after 9h reaction time was 20% at 12 h.

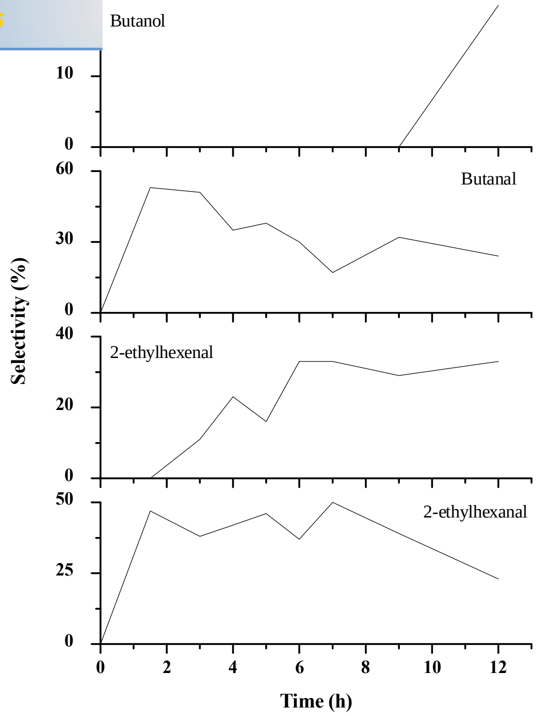


Figure 5.6. Kinetic studies of single step preparation of $C_{2(n+1)}$-aldol derivatives from propylene using HF+HT(3.5) catalytic system.

Reaction conditions: Partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial pressure of H_2 = 15 bar, total pressure of the reaction (P) = 30 bar, HF+HT(3.5) = 700 mg, T = 150^0C, t = 12 h, RPM = 1000 and solvent (volume) = Toluene (50 ml).

5.3.3.3. Kinetic studies with HF/HT(2.0) and HF/HT(3.5) catalytic systems

The kinetic experiments have been done with HF/HT(2.0) (Figure 5.9.) and HF/HT(3.5) (Figure 5.10.) catalytic systems in order see the effects Mg/Al ratio under identical experimental conditions. The selectivities of $C_{2(n+1)}$-aldol derivatives was zero upto 4 h reaction time with both the catalytic systems. After 13 h reaction time, the selectivities of both 2-ethylhexanal and 2-ethylhexenal were slightly higher with HF/HT(3.5) catalytic system (Figure 5.10.) than HF/HT(2.0) catalytic system (Figure 5.9.). This observation supports the conclusion drawn in previous section (5.3.1.1.) that selectivity of $C_{2(n+1)}$-aldol derivative increases on increasing the Mg/Al ratio of the hydrotalcites. The uniform decrease in the selectivity of butanal after 4 h reaction indicates its constant consumption in the formation of $C_{2(n+1)}$-aldol derivatives and e that the formation of butanols was also started after 4 h ch formation of $C_{2(n+1)}$-aldol derivatives were observed.

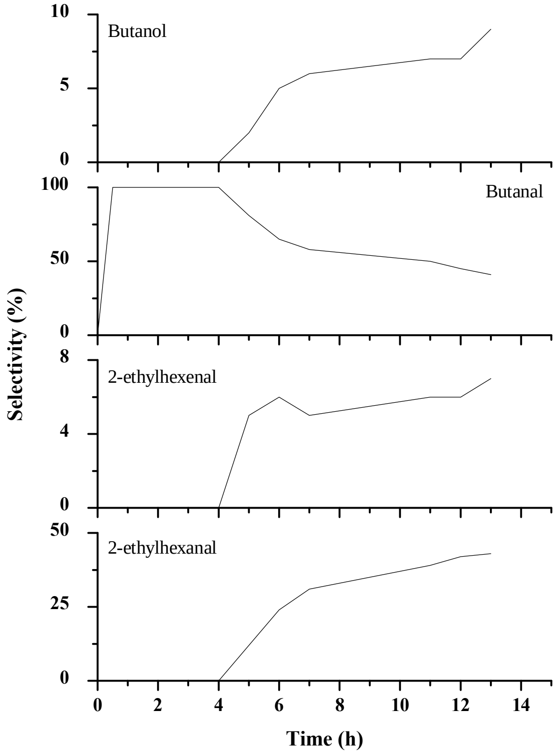


Figure 5.9. Kinetic studies of single step preparation of $C_{2(n+1)}$-aldol derivatives from propylene using HF/HT(2.0) catalytic system.

Reaction conditions: Partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial pressure of H_2 = 15 bar, total pressure of the reaction (P) = 30 bar, HF/HT(2.0) = 700 mg, T = 150^0C, t = 12 h, RPM = 1000 and solvent (volume) = Toluene (50 ml).

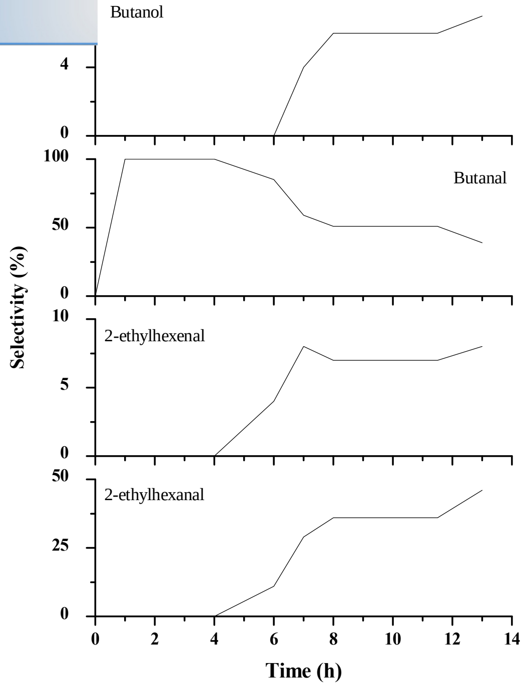


Figure 5.10. Kinetic studies of single step preparation of $C_{2(n+1)}$-aldol derivatives from propylene using HF/HT(3.5) catalytic system.

Reaction conditions: Partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial pressure of H_2 = 15 bar, total pressure of the reaction (P) = 30 bar, HF/HT(3.5) = 700 mg, T = 150^0C, t = 12 h, RPM = 1000 and solvent (volume) = Toluene (50 ml).

5.3.3.3. Kinetic studies with $HRh(CO)(PPh_3)_3$+KOH catalytic system

The experiments were also done with the use of KOH, which is known to be stronger base, in place Mg-Al hydrotalcites. The product distributions obtained were similar that was obtained with Mg-Al hydrotalcites.

The selectivity of $C_{2(n+1)}$-aldol derivatives were zero upto 5.0 h reaction time (Figure 5.7.). At 6.0 h reaction time, the obtained selectivity of 2-ethylhexanal was 37% which was equal to the selectivity of 2-ethylhexanal when HF+HT(3.5) catalytic system was used in previous experimental section (Figure 5.6.). At 6.0 h, the selectivity of 2-ethylhexenal was zero with KOH base. The highest selectivity of 2-ethylhexanal achieved with KOH base was 38% after 12 h (Figure 5.7.) reaction time which was lower than the values obtained with HF+HT(3.5) catalytic system under similar reaction conditions (Figure 5.6.). A notable difference was that the formations of the alcohols were not observed during the entire period of the reaction time with KOH as a base.

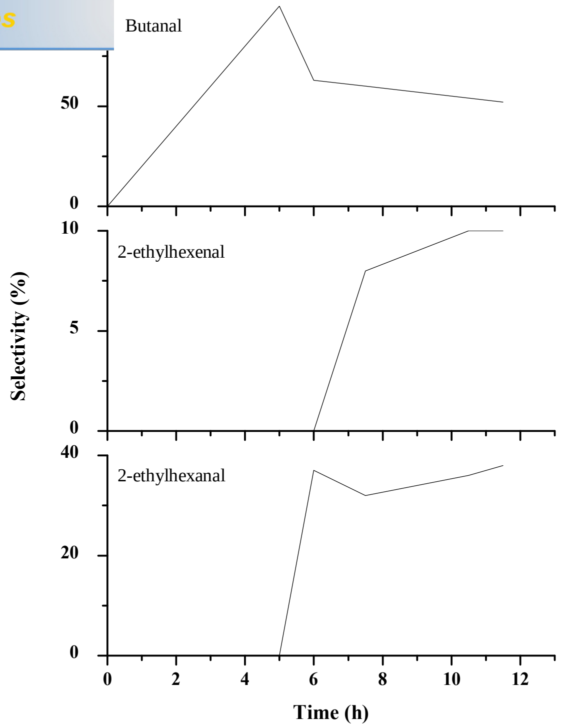


Figure 5.7. Kinetic studies of preparation of $C_{2(n+1)}$-aldol derivatives from propylene using KOH base.

Reaction conditions: Partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial pressure of H_2 = 15 bar, total pressure of the reaction (P) = 30 bar, $HRh(CO)(PPh_3)_3$ = 22.0 mg, KOH = 700 mg, T = 150^0C, t = 12 h, RPM = 1000 and solvent (volume) = Toluene (50 ml).

Another experiment has also been done using KOH as a base in place of Mg-Al-hydrotalcites with double concentration of the metal complex $HRh(CO)(PPh_3)_3$ than previous experiment (Figure 5.7.) The reaction temperature in the present experiment was 50^0C since it is not required to activate the KOH base like Mg-Al-hydrotalcites which generally requires 150^0C in order to get an optimum yields of $C_{2(n+1)}$-aldol derivatives. The results obtained are shown in Figure 5.8. The selectivity of 2-ethylhexanal was 67% at 3.5 h which further increases to 73% at 6.5h. After that the selectivity of 2-ethylhexanal decreases to 64% (12h). The selectivity of 2-ethylhexenal was only 13% after 12h. The least selectivity of butanal (17%) was obtained at 6.5 h, the time at which highest selectivity of 2-ethylhexanal (73%) was achieved. Once again, during the entire reaction periods, the formation of butanols was suppressed.

It was interesting to see that by increasing (doubling) the concentration of the $HRh(CO)(PPh_3)_3$ complex and keeping the concentration of KOH constant, the was almost double under similar reaction time and re 5.8.). This observation supports that the Rh-component of the catalytic system plays significant role in the conversion of 2-ethyhexenal to 2-ethylhexanal (Scheme 5.3.). Moreover, one more possible appealing reason for getting higher selectivities for 2-ethylhexanal in the present case may be that the reaction temperature was 50^{0}C which, reduces the possibility of deactivation of $HRh(CO)(PPh_3)_3$ complex at higher temperature like 150^{0}C in the case of Mg-Al-hydrotalcites.

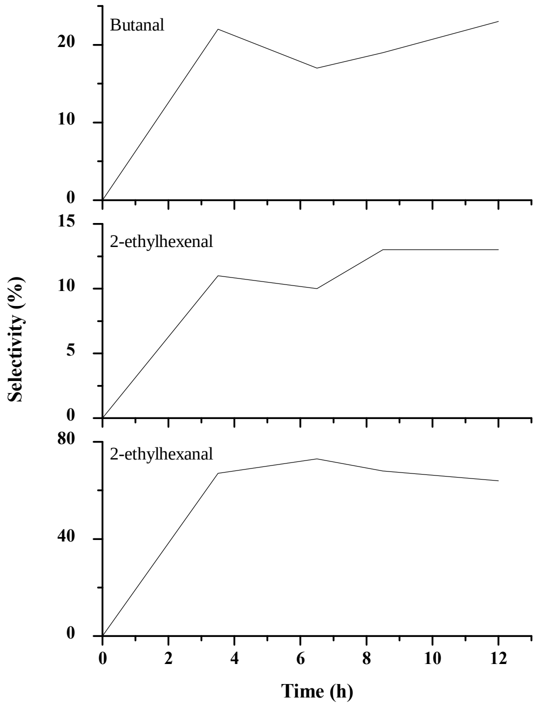


Figure 5.8. Kinetic studies of preparation of $C_{2(n+1)}$-aldol derivatives from propylene using KOH base.

Reaction conditions: Partial pressure of propylene = 10 bar, partial pressure of CO = 5 bar, partial pressure of H_2 = 15 bar, total pressure of the reaction (P) = 30 bar, $HRh(CO)(PPh_3)_3$ = 44.0 mg, KOH = 700 mg, T = 50^{0}C, t = 12 h, RPM = 1000 and solvent (volume) = Toluene (50 ml).

5.3.3.4. Kinetic studies with HF+HT(3.5) catalytic systems for ethylene as a substrate

As it was concluded in earlier section 5.3.1.4. that the selectivity of $C_{2(n+1)}$-aldol derivatives is inversely proportional to the chain length of the C_n-alkene i.e. highest yield of $C_{2(n+1)}$-aldol derivatives can be achieved with the lowest C_n-alkene (ethylene), the kinetic experiment has been carried out with the lowest alkene ethylene using

It was interesting to see that the selectivity of 2-

86% (in 5 h) to 91% (in 6 h) and during that period the selectivity of propanal (a hydroformylation product) was zero. The selectivity of 2-methylpentenal also decreases sharply during that period. After that the selectivity 2-methylpentanal decreases slightly from 91% (in 6 h) to 80% (in 12 h) since the selectivity of 2-methylpentenal and propanal increases. The possible reason may be due to deactivation of the Rh-component of the multi-functional catalytic system after that period which is suppose to be responsible for the conversion of 2-methylpenetenal to 2-methylpentanal. Moreover, the selectivity of propanal also decreases sharply during that period, indicates the ceasing of the hydroformylation activity, because hydroformylation reaction also seeks for Rh-component of the multi-functional catalytic system.

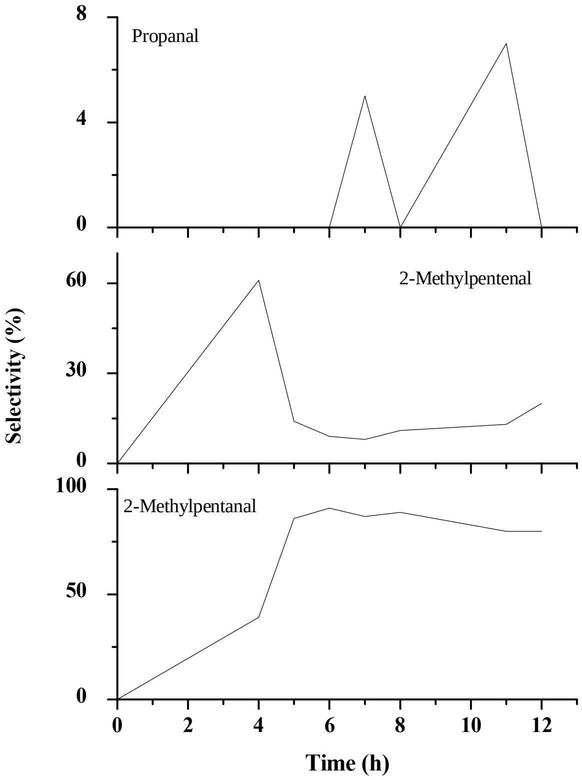
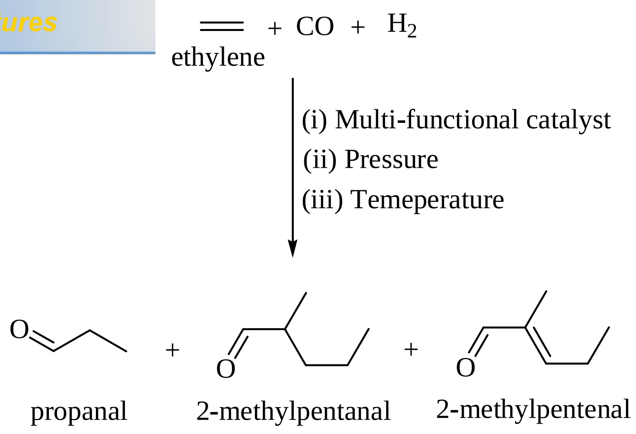


Figure 5.12. Kinetic studies of preparation of $C_{2(n+1)}$-aldol derivatives from ethylene using HF+HT(3.5) catalytic system.

Reaction conditions: Partial pressure of ethylene = 10 bar, partial pressure of CO = 5 bar, partial pressure of H_2 = 15 bar, total pressure of the reaction (P) = 30 bar, HF+HT(3.5) = 700 mg, T = 150^0C, t = 12 h, RPM = 1000 and solvent (volume) = Toluene (50 ml).



Scheme 5.5. The products obtained with ethylene as a substrate

armar, R.V. Jasra, *Chemical Weekly*, July 8 (2003) 173, July 15 (2003) 181.

2. J. J. Spivey, M. R. Gogate, Research Triangle Institute, *USEPA Grant*, Pollution Prevention in Industrial Condensation Reactions (1996).
3. M. Tomoyuki, O. Yasukazu, F. Koichi, E. Hiroki, T. Akio, *Jpn. Pat.*, 11269118 (1999).
4. C. R. Greene, *US Pat*., 3278612 (1966).
5. R. Giannandrea, P. Mastrorilli, G. Zaccaria, C. F. Nobile, *J. Mol. Catal. A: Chem.*, **109** (1996) 113.
6. V.K. Srivastava, H.C. Bajaj, R.V. Jasra, *Catal. Commun.*, **4** (2003) 543.
7. W. T. Reichle, *J. Catal.*, **94** (1985) 547.
8. K. K. Rao, M. Gravelle, J. S. Valente, F Figueras, *J. Catal.*, **173** (1998) 115.
9. D.D. Perrin, W.L.F. Armarego, D.D. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pegamon Press, p. 249.
10. D. Evans, G. Yagupsky, G. Wilkinson, *J. Chem. Soc. (A)*, (1968) 2660.
11. B.M. Choudary, M.L. Kantam, C.R.V. Reddy, K.K. Rao, F. Figueras, *J. Mol. Catal. A: Chem.*, **146** (1999) 279.
12. F. Basile, G. Fornasari, V. Rosetti, F. Trifirò, A. Vaccari, *Catal. Today*, **91–92** (2004) 293.