



# Synthesis of 2-methylpentanol from ethylene in single pot using eco-friendly $\text{HRhCO}(\text{PPh}_3)_3$ supported on activated hydrotalcite as a multi-functional catalyst

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## ABSTRACT

The [Rh-complex/HT-Act] catalyst was synthesized by the impregnation of  $\text{HRhCO}(\text{PPh}_3)_3$  [Rh-complex] on the surface of activated hydrotalcite [HT-Act] and characterized by  $^{31}\text{P}$  NMR, FT-IR, P-XRD and TGA. The multi-functional potential of [Rh-complex/HT-Act] catalyst was evaluated for the selective synthesis of 2-methylpentanol from ethylene employing hydroformylation, aldol condensation and hydrogenation reactions in single pot. The catalytic activity of [Rh-complex/HT-Act] was studied in detail as a function of Mg/Al molar ratio of [HT-Act], reaction temperature, partial pressure of ethylene,  $\text{CO}:\text{H}_2$  ratio and nature of solvent used. The selectivity of 2-methylpentanol was observed to increase from 56 to 79% on increasing the Mg/Al molar ratio of [HT-Act] from 1.5 to 3.5. Polar solvent such as methanol showed 86% selectivity for 2-methylpentanol as compared to non-polar solvents. Kinetic profiles of the various products formed during the course of reaction were in agreement with the reaction pathway proposed to understand the role of each component of [Rh-complex/HT-Act] catalyst for the formation of 2-methylpentanol.

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## 1. Introduction

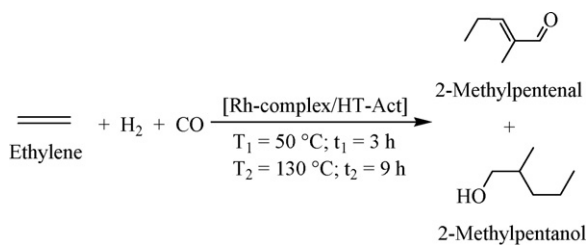
2-Methylpentenal and 2-methylpentanol are commercially important chemicals that find application in pharmaceuticals, fragrances, flavors, cosmetics and as an intermediate for the synthesis of various pharmacologically active compounds [1–3]. Commercially, 2-methylpentenal and 2-methylpentanol are synthesized by a process which involves hydroformylation, aldol condensation and hydrogenation reactions being carried out separately. In the first step, propanal is produced by the hydroformylation of ethylene using rhodium-based catalyst [4,5]. The propanal produced undergoes aldol condensation in the presence of liquid base like KOH or NaOH used in stoichiometric amount in the second step [1–3]. Under optimum reaction conditions, 95% conversion of propanal is achieved with 86% selectivity of 2-methylpentenal using a liquid base [1]. The third step involves hydrogenation of 2-methylpentenal (obtained by the condensation of propanal) to 2-methylpentanol in a fixed bed reactor using nickel or copper based catalyst [6,7]. The existing commercial process for the synthesis of 2-methylpentenal/2-methylpentanol from propanal is multi-steps process. Besides, this process has other drawbacks like the use of

KOH or NaOH in large stoichiometric amount, lower selectivity, separation of spent KOH/NaOH from post-synthesis reaction mixture, and disposal of spent liquid base. The alkali metal hydroxides require large amount of water for the neutralization and washing after the completion of reaction. Replacement of currently used homogeneous alkaline liquid by solid bases can result in the reusability of the catalyst and the minimization of waste stream [8]. It is desirable to find solid bases catalysts which could substitute liquid base and still possess the advantages of heterogeneous catalysis, i.e., ease of separation of the products, decreased corrosion of the reactor, and possible regeneration of the catalyst. Therefore, research efforts are directed to develop a catalytic process, which can produce 2-methylpentenal or 2-methylpentanol from ethylene in single pot with high selectivity employing eco-friendly re-usable catalyst (Scheme 1).

The potential of the ruthenium, palladium and copper containing hydrotalcite as a bi-functional catalyst has been reported in the literature for synthesis of methyl isobutyl ketone (MIBK) from acetone, nitriles and 2-methyl-3-phenyl-propanal via condensation of benzaldehyde with propanal and hydrogenation of condensed product in one pot [9–16]. In our earlier study, a novel idea was conceptualized to integrate the hydroformylation with aldol condensation and hydrogenation using an eco-friendly multi-functional catalyst prepared by impregnation and mechanical mixing of  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  on the surface of a solid base catalyst, as-synthesized hydrotalcite for one pot synthesis of  $\text{C}_8$  aldehydes and alcohol from propylene [17–20]. This catalyst showed excellent

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**Scheme 1.** Single pot synthesis of 2-methylpentenal and 2-methylpentanol from ethylene using [Rh-complex/HT-Act] as a multi-functional catalyst.

conversion of propylene and selectivity of  $C_8$  aldehydes/alcohol. Kinetic study for the one pot synthesis of  $C_8$  aldehydes and alcohol from propylene suggested that the overall rate of reaction depends on the aldol condensation step. If the rate of aldol condensation is higher, then the hydrogenation of hydroformylation products (butanal to butanol) could be suppressed. Therefore, in order to select highly active solid base catalyst for aldol condensation step various alkali ion-exchanged zeolites, modified synthetic talc, alumina, alkali impregnated alumina, as-synthesized and activated hydrotalcite of varied Mg/Al molar ratio were used as catalysts in a separate study by selecting propanal as a model reactant [21,22]. The activated hydrotalcite samples were observed to be more active solid base catalyst among all the studied catalysts. Higher conversion of propanal and selectivity of 2-methylpentenal was found using activated hydrotalcite of Mg/Al molar ratio of 3.5 as a catalyst due to higher basicity of hydrotalcite on its activation at 450 °C. Therefore, in the present study we have chosen activated hydrotalcite of varied Mg/Al molar ratio as a base component of the multi-functional catalyst. The multi-functional catalyst [Rh-complex/HT-Act] was synthesized by impregnation of a rhodium complex,  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  [Rh-complex], on the surface of activated hydrotalcite [HT-Act] and used as a catalyst for single pot synthesis of 2-methylpentanol from ethylene.

## 2. Experimental

### 2.1. Materials

Ethylene (99.6%), hydrogen (99.999%) and carbon monoxide (99.99%) were procured from Alchemie Gases and Chemicals Private Limited, India. Triphenylphosphine ( $\text{PPh}_3$ ; 99%), rhodium metal precursor ( $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ; 99.99%), formaldehyde ( $\text{HCHO}$ ) and sodium borohydride ( $\text{NaBH}_4$ ; 99%) were purchased from Sigma–Aldrich, USA. Magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ; 98.9%), aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ; 99.1%), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ; 99.9%), sodium hydroxide ( $\text{NaOH}$ ; 99.9%), toluene (99.9%) were purchased from s.d. Fine Chemicals Ltd., Mumbai, India. The double distilled milli-pore de-ionized water was used for the synthesis of catalyst.

### 2.2. Catalyst synthesis

#### 2.2.1. Synthesis of Rh-complex

A solution of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (7.6 mmol) in ethanol (70 ml) was added to a refluxing solution of triphenylphosphine (46.0 mmol) in 300 ml ethanol [23]. After 2 min, 10 ml solution of aqueous formaldehyde was added drop wise and color of the mixture was changed to yellow which indicates the formation of  $\text{trans-RhCl}(\text{CO})(\text{PPh}_3)_2$ . Addition of ethanolic solution of sodium borohydride (2.0 g) into this hot mixture yielded yellow crystals of  $\text{HRhCO}(\text{PPh}_3)_3$  [Rh-complex]. The yellow crystals were washed first with ethanol followed by diethyl ether to remove un-reacted rhodium metal and triphenylphosphine. Then the Rh-complex was dried in vacuum at room temperature for 8 h.

#### 2.2.2. Synthesis of [HT]

Hydrotalcite [HT] samples of varied Mg/Al molar ratio from 1.5 to 3.5 were synthesized by co-precipitation method [24]. Typically, for the synthesis of hydrotalcite sample with Mg/Al molar ratio = 3.5, an aqueous solution of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.34 mol) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.0971 mol) in 200 ml double distilled deionized water was prepared (solution A). A second solution (B; 200 ml) containing  $\text{Na}_2\text{CO}_3$  (0.21 mol) was prepared in another beaker. Solution A was slowly added to solution B in a round bottom flask of 1 l capacity under vigorous stirring at room temperature in around 2 h. Constant pH ( $9.5 \pm 0.5$ ) of the suspension was maintained by adding the 0.1 M NaOH solution. The content was aged at 70 °C for 16 h under auto-genous water vapor pressure. Precipitate formed was filtered and washed with hot distilled water until pH of the filtrate was reached to 7. The cake was dried in an oven at 80 °C for 14 h and ground to convert into powder form. The [HT] samples of varied Mg/Al molar ratios of 1.5–3.0 were synthesized as per above procedure having appropriate moles of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . The activation (calcination) of [HT] samples of varied Mg/Al molar ratio were carried out at 450 °C for 4 h in a muffle furnace and thus activated samples are represented as [HT-Act]. The freshly activated samples were used for the synthesis of multi-functional [Rh-complex/HT-Act] catalyst.

#### 2.2.3. Synthesis of [Rh-complex/HT-Act] catalyst

The [Rh-complex/HT-Act] catalyst was synthesized by dissolving 500 mg of Rh-complex and 1050 mg of triphenylphosphine into a round bottom flask having 10 ml toluene as a solvent. Appropriate amount of [HT-Act] (4 g) was added into the above solution at vigorous stirring under inert atmosphere. Slurry was stirred for 32 h at room temperature under nitrogen atmosphere. After 32 h, toluene was removed under vacuum and was a free-flowing light yellow powder obtained. This powder was stored under vacuum and used as a catalyst for synthesis of 2-methylpentanol from ethylene.

### 2.3. Characterization of catalyst

The  $^{31}\text{P}$  nuclear magnetic resonance (NMR) spectra of Rh-complex and [Rh-complex/HT-Act] catalyst were measured using Bruker Avance II-500 (FT-NMR-500 MHz) spectrometer.

Infrared (IR) spectra of Rh-complex, [HT], [HT-Act] and [Rh-complex/HT-Act] catalyst were recorded with a PerkinElmer Spectrum GX-Fourier transform infrared spectrometer (FT-IR) system in the region of 400–4000  $\text{cm}^{-1}$  using KBr pellets.

The powder X-ray diffraction (P-XRD) patterns of Rh-complex, [HT], [HT-Act] and [Rh-complex/HT-Act] were recorded on a Philips X'Pert MPD system equipped with XRK 900 reaction chamber, using Ni-filtered  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) over a  $2\theta$  range of 2–70°. The data were processed with Philips X'Pert (version 1.2) software.

Thermogravimetric analysis (TGA) of Rh-complex, [HT], [HT-Act] and [Rh-complex/HT-Act] were carried out using a Mettler TGA/SDTA 851e equipment in flowing nitrogen (flow rate = 50 ml/min) at a heating rate of 10 °C/min.

Surface area measurements of [HT-Act] and [Rh-complex/HT-Act] were carried out using ASAP 2010 Micromeritics, USA. The samples were activated at 80 °C for 4 h under vacuum ( $5 \times 10^{-2}$  mmHg) prior to  $\text{N}_2$  adsorption measurements. The specific surface area of the samples was calculated from  $\text{N}_2$  adsorption isotherms measured at 77.4 K using Brunauer, Emmett, Teller (BET) method.

### 2.4. Catalytic reaction

The synthesis of 2-methylpentanol from ethylene was carried out in 100 ml EZE-Seal stirred reactor supplied by Autoclave Engineers, USA. The desired amount of [Rh-complex/HT-Act] (HT-Act

to Rh-complex ratio (by weight)=8) was added into the autoclave reactor having 50 ml toluene as a solvent. The autoclave was flushed with nitrogen prior to introducing ethylene at 10 atm. Carbon monoxide (CO) and hydrogen (H<sub>2</sub>) were introduced in the reactor up to 40 atm pressure. The reactor was brought to 50 °C (T<sub>1</sub>) for hydroformylation of ethylene. The reaction was then initiated by starting the stirrer at 1000 rpm and kept at 50 °C for 3 h (t<sub>1</sub>) following which, the reaction temperature was raised to T<sub>2</sub> °C for 9 h (t<sub>2</sub>) to initiate aldol condensation of propanal and hydrogenation of condensed product. The reaction was continued at constant pressure by supplying CO and H<sub>2</sub> from the reservoir cylinders. After 12 h total reaction time (t), the reactor was cooled to ambient temperature by circulation of cold water in the coil provided inside the reactor. For kinetic studies liquid samples were withdrawn through a sampling valve at desired time intervals during the course of experiments.

### 2.5. Reaction product analysis

The analysis of product mixture was carried out by GC–MS (Shimadzu, GCMS-QP2010) and gas chromatography (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. Nitrogen gas was used as a carrier gas. The temperatures of injection port and FID were kept constant at 200 °C. The retention time of each compound was determined by injecting pure compound under identical GC conditions. The conversion of ethylene and selectivity of formed products were calculated by the reported methods [18,19]. Overall conversion of ethylene was found to be in the range of 96–100% except for the studies on the effect of partial pressure of ethylene on the selectivity of 2-methylpentanol. To ensure the reproducibility of the reaction, repeated experiments were carried out under identical reaction conditions. The obtained results including conversion and selectivity data were found to be reproducible in the range of ±5% variation.

## 3. Results and discussion

### 3.1. Characterization

<sup>31</sup>P NMR spectra of Rh-complex and [Rh-complex/HT-Act] are shown in Fig. 1. Appearance of the doublet at 43.41 ppm [ $J(\text{Rh-P}) = 154 \text{ Hz}$ ] in <sup>31</sup>P NMR spectrum of Rh-complex show that all the three phosphorous atoms are present in the equivalent environment and are in the equatorial position [23]. The hydride (H) and CO finds axial positions showing trigonal bipyramidal structure in the complex. The %C and %H for the Rh-complex are; calculated (found): %C = 71.9 (71.6); %H = 5.0 (5.1). The <sup>31</sup>P solid state NMR spectrum of [Rh-complex/HT-Act] catalyst shows two peaks at 41.42 and 52.79, confirming the impregnation of the Rh-complex on the surface of [HT-Act] without decomposition.

Formation of Rh-complex was also confirmed by the appearance of bands at 2037 cm<sup>-1</sup> for  $\nu$  (Rh-H) and 1964 cm<sup>-1</sup> for  $\nu$  (C=O) in the FT-IR spectrum of the Rh-complex (Fig. 2). The FT-IR spectra of [HT] and [HT-Act] matched well with the reported spectra in the literature which confirmed the formation of hydrotalcite [24]. The absorption band at 3442 cm<sup>-1</sup> in the FT-IR spectrum of [Rh-complex/HT-Act] catalyst is attributed to the H-bonding stretching vibrations of the OH group in the brucite-like layer. Slightly shift in the bands at about 2037 cm<sup>-1</sup> for  $\nu$  (Rh-H) and 1964 cm<sup>-1</sup> for  $\nu$  (C=O) was observed in the FT-IR spectrum of [Rh-complex/HT-Act] catalyst, again showed that the Rh-complex impregnated on the surface of [HT-Act] without decomposition. Appearance of the shoulders at 1645 and 1370 cm<sup>-1</sup> are the characteristic bands of

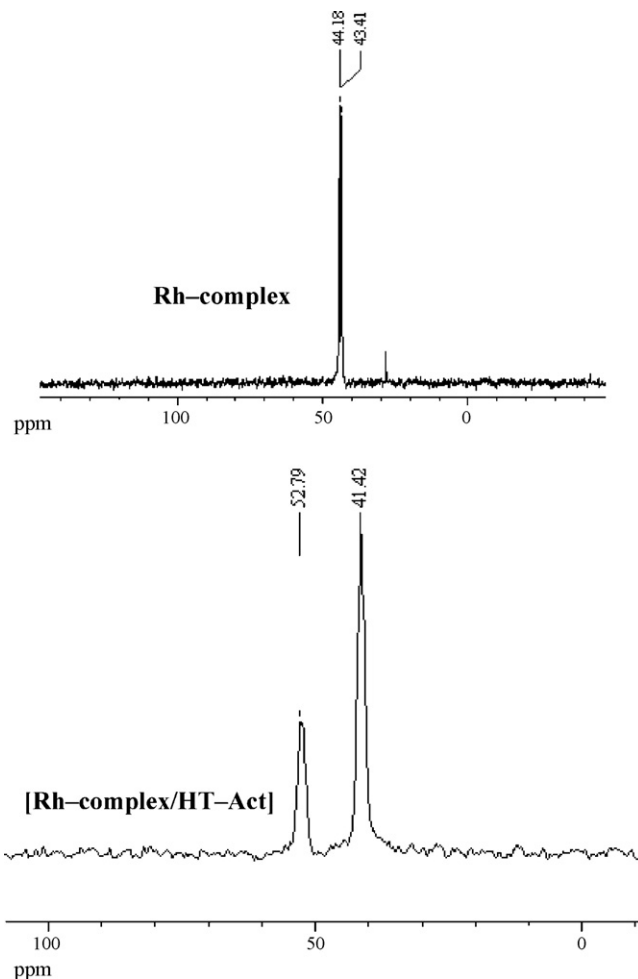


Fig. 1. (a) <sup>31</sup>P NMR of Rh-complex in C<sub>6</sub>D<sub>6</sub> and (b) solid state <sup>31</sup>P NMR of [Rh-complex/HT-Act].

H<sub>2</sub>O and CO<sub>3</sub><sup>2-</sup>. The low frequency region showed a band at about 506 cm<sup>-1</sup>, corresponding to the translation modes of hydroxyl groups, influenced by Al<sup>3+</sup> cations. The peak at the 693 cm<sup>-1</sup> ( $\nu_4$ ) is assigned to the in-plane carbonate bending [25].

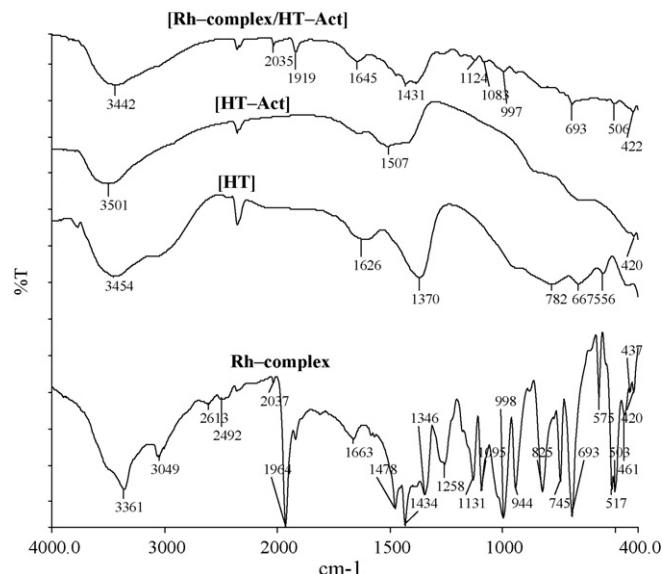


Fig. 2. FT-IR of Rh-complex, [HT], [HT-Act] and [Rh-complex/HT-Act].

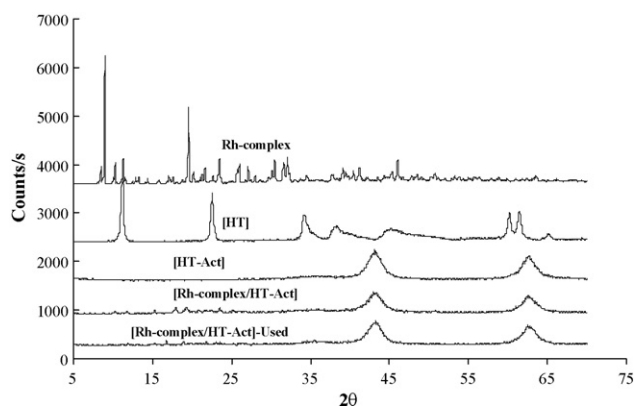


Fig. 3. P-XRD of Rh-complex, [HT], [HT-Act], [Rh-complex/HT-Act] and used [Rh-complex/HT-Act].

P-XRD patterns of [HT] showed sharp, intense and symmetric peaks at lower diffraction angles ( $2\theta = 10\text{--}25$ ) and broad asymmetric reflections at higher diffraction angles ( $2\theta = 30\text{--}50$ ), which are characteristics of hydrotalcite (Fig. 3) [24]. The P-XRD patterns of [HT-Act] consist of broadened peaks that can be assigned to a mixed oxide phase  $\text{Mg}(\text{Al})\text{O}_x$ , with diffraction lines at values very similar to that of MgO. The sharp peaks at  $2\theta = 8.5$  and  $20$  were observed in the P-XRD pattern of the P-XRD pattern of the Rh-complex and were present in the P-XRD pattern of [Rh-complex/HT-Act] catalyst. The P-XRD patterns of [Rh-complex/HT-Act] catalyst showed that the characteristic original planes of [HT-Act] are retained after impregnation of Rh-complex.

TGA data of Rh-complex, [HT], [HT-Act] and [Rh-complex/HT-Act] are shown in Fig. 4. Two stages of weight loss accompanied by an endothermic transformation were observed in the TGA of [HT]. The 16% weight loss was observed in the first stage between  $160$  and  $220^\circ\text{C}$  due to the loss of physically adsorbed water molecules, without collapse of the structure. The second weight loss (28%) was observed in the temperature range of  $300\text{--}450^\circ\text{C}$  and is attributed to the removal of condensed water molecules (hydroxyl group) and carbon dioxide from the carbonate anion present in the interlayer space of [HT]. The activated hydrotalcite [HT-Act] showed only 5% weight loss in the entire temperature range. The major weight loss (63%) of Rh-complex was observed in the temperature range of  $200\text{--}360^\circ\text{C}$  due to thermal decomposition of the Rh-complex. Only 5% weight loss of the [Rh-complex/HT-Act] catalyst was observed in temperature range of  $200\text{--}220^\circ\text{C}$  and increased up to 32% on increasing the temperature from  $250$  to  $570^\circ\text{C}$ . The major weight loss in the second stage is due to the thermal decomposition of the Rh-complex from [Rh-complex/HT-Act] catalyst. The TGA data shows that the [Rh-complex/HT-Act] can be used as a catalyst up to  $200^\circ\text{C}$  reaction temperature without thermal decomposition.

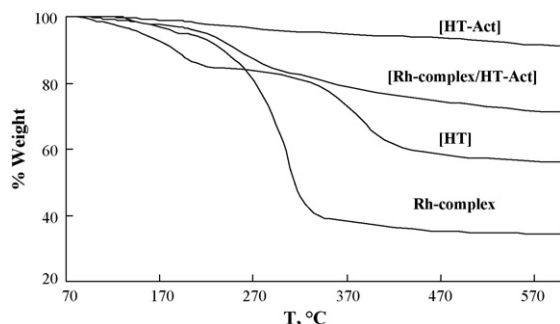
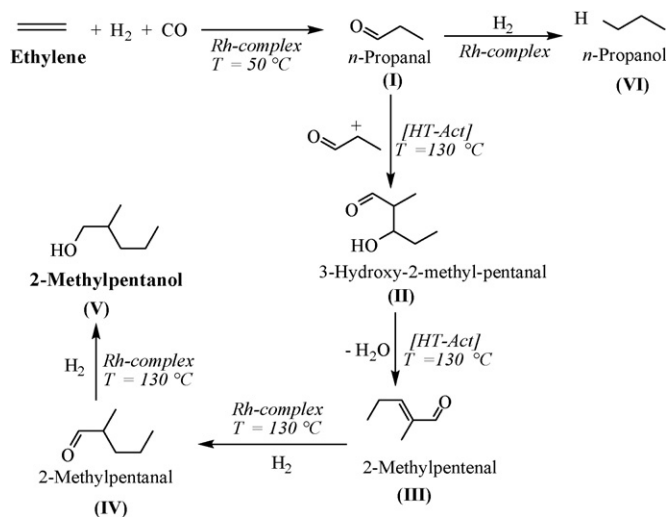


Fig. 4. TGA of Rh-complex, [HT], [HT-Act] and [Rh-complex/HT-Act].



Scheme 2. Reaction pathway for the synthesis of 2-methylpentanol from ethylene in one pot.

Surface area of [HT-Act] was calculated as  $197\text{ m}^2/\text{g}$  that decreased to  $144\text{ m}^2/\text{g}$  after impregnation of Rh-complex on the surface of [HT-Act]. The decrease in the surface area of [Rh-complex/HT-Act] is due to the coverage of the pores and external surface of hydrotalcite by the lower surface area [HF] complex on impregnation.

### 3.2. Reaction pathways for the synthesis of 2-methylpentanol from ethylene in one pot

Before discussion of the obtained results, it is worthwhile to understand the function of each constituent of the [Rh-complex/HT-Act] catalyst involved in the production of 2-methylpentanol from ethylene (Scheme 2). The reaction is initiated by the hydroformylation of ethylene to form propanal (I) catalyzed by Rh-complex of [Rh-complex/HT-Act] catalyst at  $50^\circ\text{C}$ . Then two molecules of (I) undergo condensation step to give 3-hydroxy-2-methylpentanal (II) catalyzed by [HT-Act] component of multi-functional catalyst and subsequently after removal of water molecule gave 2-methylpentenal (III). Reaction temperature for condensation step should be more than  $100^\circ\text{C}$  to obtain excellent selectivity of 2-methylpentanol [21]. The Rh-complex of the catalyst also plays an important role for hydrogenation of (III) to 2-methylpentanal (IV) and of (IV) to 2-methylpentanol (V). This hydrogenation step requires two hydrogen molecules and the reaction temperature similar to the condensation step. Thus, the Rh-complex of [Rh-complex/HT-Act] system catalyzes three reactions namely, hydroformylation, double bond ( $\text{C}=\text{C}$ ) hydrogenation and ( $\text{C}=\text{O}$ ) carbonyl hydrogenation during the one step preparation of 2-methylpentanol from ethylene. However, possibility of side reactions involved in the present studied conditions cannot be ignored. The most probable side reaction is the reduction of propanal to the propanol (VI) under the reaction conditions similar to the condensation step. The Rh-complex is efficient for the reduction of propanal in the presence of hydrogen. Potential of Rh-complex for hydrogenation of propanal was again confirmed by performing a separate experiment. Hence, in order to avoid this competitive side reaction, the amount and basicity of [HT-Act] component of [Rh-complex/HT-Act] catalyst must be sufficient enough to divert the reaction pathway in the direction of aldol condensation of propanal rather than hydrogenation of propanal. The condensation temperature ( $T_2$ ) and reaction conditions also played an important role for the diversion of reaction pathway from hydrogenation of propanal to condensation of propanal.

**Table 1**  
Effect of  $T_2$  (aldol temperature) on the selectivity of 2-methylpentenal and 2-methylpentanol.

Run	$T_2$ , °C	% selectivity <sup>a</sup>				
		2-Methylpentanol	2-Methylpentenal	Propanal	Propanol	3-Pentanone
1	60	0	46	49	0	5
2	80	2	52	40	0	6
3	100	8	54	25	5	8
4	130	79	0	4	7	10
5	150	64	0	0	23	13
6	180	55	0	0	28	17

<sup>a</sup> Reaction conditions: Ethylene = 10 atm, CO = 5 atm, H<sub>2</sub> = 15 atm, [Rh-complex/HT-Act] = 700 mg,  $T_1$  = 50 °C,  $t_1$  = 3 h and  $t_2$  = 9 h.

### 3.3. Catalytic activity of [Rh-complex/HT-Act] catalyst

In order to optimize the reaction parameters for one step synthesis of 2-methylpentanol from ethylene using [Rh-complex/HT-Act] catalyst, the experiments were carried out by varying the aldol condensation temperature ( $T_2$ ) at a fixed hydroformylation temperature ( $T_1$ ). The effect of Mg/Al molar ratio of [HT-Act] at constant [HT-Act]/Rh-complex ratio (8), partial pressure of ethylene, CO:H<sub>2</sub> ratio and nature of solvents on the selectivity of 2-methylpentanol was studied in detail by varying one variable at a time.

#### 3.3.1. Effect of aldol condensation temperature ( $T_2$ )

The condensation of propanal, which takes place after hydroformylation reaction (Scheme 2), is influenced by the temperature ( $T_2$ ). Experiments were conducted by varying  $T_2$  from 60 to 180 °C at constant Mg/Al molar ratio of [HT-Act] 3.5 (Table 1). The significant effect on the conversion of ethylene was not observed, therefore, the results are explained in terms of selectivity of products formed. The lower selectivity of 2-methylpentanol was observed at lower  $T_2$ , which increased on increasing the  $T_2$ . The selectivity of 2-methylpentanol was observed to increase from 0 to 79% on increasing the  $T_2$  from 60 to 130 °C. However, on further increasing the  $T_2$ , the selectivity of 2-methylpentanol was observed to decrease to 55%. The lower selectivity of 2-methylpentanol in the  $T_2$  range of 60–100 °C indicates that this temperature range is not suitable for hydrogenation of 2-methylpentenal to 2-methylpentanol. However, significant selectivity of 2-methylpentenal was observed, which shows that the condensation of propanal occurred at lower temperature also. The observed lower selectivity of 2-methylpentanol at higher  $T_2$  is due to the higher selectivity of propanol via hydrogenation of propanal. At higher  $T_2$ , hydrogenation reaction is predominant as compared to the condensation of propanal. As the  $T_2$  increased from the 60–180 °C, the selectivity of propanal was also observed to decrease which is attributed to the consumption of propanal for condensation and hydrogenation reactions. Similar trends in the selectivity of products were observed in our earlier reports for the one pot synthesis of C<sub>8</sub> aldehydes and alcohol from propylene [18,19]. As the effect of  $T_1$  on the ethylene hydroformylation reaction is well documented in the literature [4,5], therefore, we have not studied this effect on the hydroformylation of ethylene in the present manuscript. The 130 °C aldol temperature was selected as  $T_2$  for further study on optimization of reaction parameters for the synthesis of 2-methylpentanol from ethylene in one pot.

#### 3.3.2. Effect of Mg/Al molar ratio of [HT-Act]

The effect of Mg/Al molar ratio of [HT-Act] in the [Rh-complex/HT-Act] catalyst on the selectivity of 2-methylpentanol was studied by varying the ratio from 1.5 to 3.5 and the corresponding results are depicted in Table 2. The selectivity of 2-methylpentanol increased on increasing the Mg/Al molar ratio of [HT-Act]. The 56% selectivity of 2-methylpentanol obtained at the ratio of 1.5 was found to increase significantly up to 79% on

increasing the Mg/Al molar ratio to 3.5. At lower Mg/Al molar ratio, higher selectivity of propanol was observed. The selectivity of propanol was found to be 27% at Mg/Al = 1.5, which decreased to 7% on increasing the Mg/Al molar ratio to 3.5. The significant effect on the selectivity of propanal and 3-pentanone were not observed in the studied Mg/Al molar ratio.

The increase in the selectivity of 2-methylpentanol with increasing Mg/Al molar ratio of hydrotalcite is explained in terms of the increased basicity of [HT-Act] which enhances the aldol condensation reaction. Basicity of the hydrotalcite can be tuned by increasing the Mg/Al molar ratio or activation at appropriate temperature. The basicity of the [HT-Act] is mainly due to their O<sup>2-</sup> (Lewis basicity) and hydroxyl groups (Brønsted basicity; small amount) present in it. The increment of Mg-content in the [HT] increases the basic character of the hydrotalcite, which results into the increase of 2-methylpentanol selectivity. Higher selectivity of aldol derivatives was observed in the present study using [Rh-complex/HT-Act] catalyst as compared to the results reported earlier on the use of [HF/HT] as a multi-functional catalyst for one pot synthesis of C<sub>8</sub> aldol derivatives from propylene [19]. The higher selectivity of corresponding alcohol in the present report might be due to the enhanced basicity of the activated hydrotalcite as compared to the as-synthesized hydrotalcite in previous study along with the size of the reactants and products molecules. For the confirmation of enhanced basicity, we have carried out a reaction for the synthesis of 2-methylpentanol from ethylene in one pot using the multi-functional catalyst [HF/HT] reported earlier [19]. The selectivity of 2-methylpentanol was observed to 62% with 12% selectivity of propanol. The 14% propanal was still un-reacted using [HF/HT] catalyst system. These results clearly show that the [Rh-complex/HT-Act] catalyst is more active as compared to the [HF/HT] catalyst for the one pot synthesis reactions. To compare the observed results, the Rh-complex was impregnated on MgO [MgO to Rh-complex ratio (by weight)=8], which is known as a strong base catalyst as compared to activated hydrotalcite. The obtained Rh-complex/MgO was used as a multi-functional catalyst for one pot synthesis of 2-methylpentanol from ethylene under

**Table 2**  
Effect of Mg/Al molar ratio of [HT-Act] on the selectivity of 2-methylpentanol.

Run	Mg/Al molar ratio	% selectivity <sup>a</sup>			
		2-Methylpentanol	Propanal	Propanol	3-Pentanone
1	1.5	56	6	27	11
2	2.0	65	5	20	10
3	2.5	68	6	16	10
4	3.0	72	6	11	11
5	3.5	79	4	7	10
6 <sup>b</sup>	3.5	62	14	12	12
7 <sup>c</sup>	–	86	1	5	8

<sup>a</sup> Reaction conditions: Ethylene = 10 atm, CO = 5 atm, H<sub>2</sub> = 15, [Rh-complex/HT-Act] = 700 mg,  $T_1$  = 50 °C,  $t_1$  = 3 h,  $T_2$  = 130 °C and  $t_2$  = 9 h.

<sup>b</sup> [HF/HT] catalyst presented in Ref. [19].

<sup>c</sup> Rh-complex was impregnated on MgO (MgO to Rh-complex ratio=8 (by weight)).

**Table 3**  
Effect of partial pressure of ethylene on the selectivity of 2-methylpentanol.

Run	$P_{\text{ethy}}$ (atm)	% conversion	% selectivity <sup>a</sup>			
			2-Methylpentanol	Propanal	Propanol	3-Pentanone
1	3	100	45	10	38	7
2	5	100	55	20	20	5
3	7	100	61	14	18	7
4	10	99	79	4	7	10
5	14	95	71	5	13	11
6	17	89	67	6	15	12
7	20	80	64	5	20	11

<sup>a</sup> Reaction conditions: CO = 5 atm, H<sub>2</sub> = 15 atm, [Rh-complex/HT-Act] = 700 mg, T<sub>1</sub> = 50 °C, t<sub>1</sub> = 3 h, T<sub>2</sub> = 130 °C and t<sub>2</sub> = 9 h.

**Table 4**  
Effect of CO to H<sub>2</sub> ratio on the selectivity of 2-methylpentanal and 2-methylpentanol.

Run	$p_{\text{CO:H}_2}$	% selectivity <sup>a</sup>				
		2-Methylpentanol	2-Methylpentenal/2-methylpentanal	Propanal	Propanol	3-Pentanone
1	1:1	24	51	12	6	7
2	1:2	40	35	10	8	7
3	1:3	79	–	4	7	10
4	1:4	62	–	4	18	16
5	1:5	50	–	3	30	17

<sup>a</sup> Reaction conditions: Ethylene = 10 atm,  $p_{\text{CO+H}_2}$  = 30 atm, [Rh-complex/HT-Act] = 700 mg, T<sub>1</sub> = 50 °C, t<sub>1</sub> = 3 h, T<sub>2</sub> = 130 °C and t<sub>2</sub> = 9 h.

identical reaction conditions reported in Table 2. The selectivity of 2-methylpentanol was observed to 86% with 5% selectivity of propanol via hydrogenation of propanal. The selectivity of propanal and 3-pentanone were also observed to decrease. These results clearly showed that the increase in the basicity of multi-functional catalyst enhanced the selectivity of condensation products. A control experiment was also carried out by taking 30 mg Rh-complex and 700 mg [HT-Act] separately (without impregnation) into 50 ml toluene as a solvent and this mixture used for reaction under the identical conditions used for [Rh-complex/HT-Act] catalyst. After 12 h reaction time, 84% selectivity of 2-methylpentanol was observed which is higher than the observed selectivity (79%) using impregnated [Rh-complex/HT-Act] catalyst. The higher selectivity of 2-methylpentanol in a controlled experiment is due to—(i) Rh-complex is in homogeneous condition (soluble in toluene) and (ii) availability of all active basic sites of [HT-Act] for condensation reaction (since there is no Rh-complex impregnation, so all site of [HT-Act] are accessible for condensation reaction).

### 3.3.3. Effect of partial pressure of ethylene

The effect of partial pressure of ethylene on the selectivity of 2-methylpentanol was studied by varying the pressure from 3 to 20 atm at 130 aldol temperature (T<sub>2</sub>) by taking [HT-Act] of Mg/Al molar ratio 3.5 as a solid base constituent of multi-functional catalyst (Table 3). As the partial pressure of ethylene increased, the conversion of ethylene was observed to decrease. The conversion of ethylene was calculated as 100% at 3 atm which decreased to 80% at 20 atm pressure of ethylene. The selectivity of 2-methylpentanol was observed to increase up to 79% at 10 atm that decreased to 64% at 20 atm. The 38% selectivity of propanol was found when partial pressure of ethylene was 3 atm.

### 3.3.4. Effect of CO:H<sub>2</sub> ratio

The effect of CO to H<sub>2</sub> ratio (partial pressures) on the selectivity of aldol derivatives was studied by varying the ratio from 1:1 to 1:5 at constant pressure of  $p_{\text{CO+H}_2}$  = 30 atm using [Rh-complex/HT-Act] catalyst (Table 4). The lower selectivity of 2-methylpentanol was observed at lower CO:H<sub>2</sub> ratio. For example, on increasing the CO:H<sub>2</sub> ratio from 1:1 to 1:3, the selectivity of 2-methylpentanol increased from 24 to 79%. However, at 1:1 and 1:2 CO:H<sub>2</sub> ratio, formation of 2-methylpentanal and 2-methylpentenal

were observed due to insufficient hydrogen for hydrogenation of 2-methylpentenal to 2-methylpentanol in the studied reaction conditions. On further increase in the CO:H<sub>2</sub> ratio from 1:3 to 1:5, the selectivity of 2-methylpentanol decreased from 79 to 50%. The decrease in the selectivity of 2-methylpentanol at higher CO:H<sub>2</sub> ratio (above 1:3) is due to presence of excess hydrogen which assist the another side reaction, i.e., hydrogenation of propanal to propanol. On increasing the CO:H<sub>2</sub> ratio, the selectivity of 3-pentanone and propanol was observed to increase significantly. From these experiments, 1:3 is the optimum CO:H<sub>2</sub> ratio to obtained maximum selectivity of 2-methylpentanol.

### 3.3.5. Effect of solvent

The effect of the nature of solvents used for single pot synthesis of 2-methylpentanol from ethylene is presented in Table 5. Polar solvents like, methanol and *n*-butanol showed slightly higher selectivity for 2-methylpentanol as compared to non-polar solvent toluene. The selectivity of 2-methylpentanol was observed to be 86% for methanol as a solvent which decreased to 79% for toluene as a solvent. For *n*-hexane, selectivity of 2-methylpentanol was found to be 60%. Higher selectivity in case of polar solvents is attributed to the higher solubility of CO, H<sub>2</sub> and ethylene.

### 3.3.6. Reusability of [Rh-complex/HT-Act] catalyst

The spent [Rh-complex/HT-Act] catalyst after completion of reaction was filtered and washed with 100 ml toluene and dried in vacuum for 12 h. Then the material was used as catalyst for the one pot synthesis of 2-methylpentanol from ethylene in one pot and the results are shown in Table 6. The significant drop in

**Table 5**  
Effect of solvent on the selectivity of 2-methylpentanol.

Solvent	% selectivity <sup>a</sup>			
	2-Methylpentanol	Propanal	Propanol	3-Pentanone
Methanol	86	2	2	10
<i>n</i> -Butanol	83	3	4	10
Toluene	79	4	7	10
Benzene	74	6	8	12
<i>n</i> -Hexane	60	16	10	14

<sup>a</sup> Reaction conditions: Ethylene = 10 atm, CO = 5 atm, H<sub>2</sub> = 15 atm, [Rh-complex/HT-Act] = 700 mg, T<sub>1</sub> = 50 °C, t<sub>1</sub> = 3 h, T<sub>2</sub> = 130 °C and t<sub>2</sub> = 9 h.

**Table 6**  
Reusability of [Rh-complex/HT-Act] catalyst.

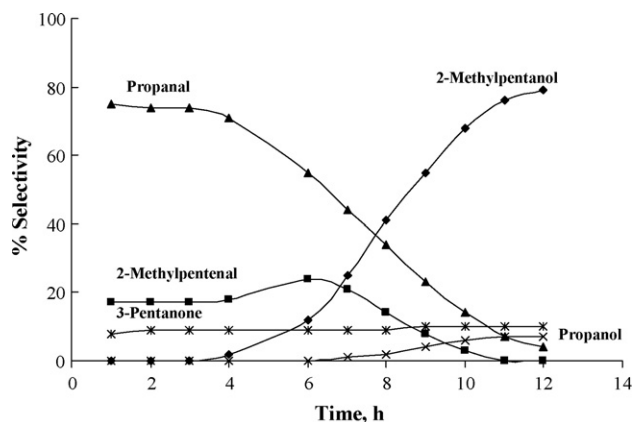
Cycles	% conversion	% selectivity <sup>a</sup>			
		2-Methylpentanol	Propanal	Propanol	3-Pentanone
First	99	79	4	7	10
Second	98	66	13	7	14
Third	94	57	20	15	8
Fourth	87	34	24	33	9

<sup>a</sup> Reaction conditions: Ethylene = 10 atm, CO = 5 atm, H<sub>2</sub> = 15 atm, T<sub>1</sub> = 50 °C, t<sub>1</sub> = 3 h, T<sub>2</sub> = 130 °C and t<sub>2</sub> = 9 h.

the conversion of ethylene was not observed up to third cycles and decreased to 87% in the fourth cycle. The selectivity of aldol derivatives gradually decreased in each cycle of reusability. The selectivity of 2-methylpentanol decreased from 79 to 34% at the end of fourth cycle. This indicates the deactivation of basic component [HT-Act] of [Rh-complex/HT-Act] catalyst, which is used for condensation of propanal. Therefore, the reaction is forwarding towards hydrogenation of propanal rather than the condensation step. This is also confirmed by the observed higher selectivity of propanal and propanol at the end of each cycle. The decrease in the conversion of ethylene at fourth cycle also indicates that the leaching or deactivation of Rh-complex from [Rh-complex/HT-Act] catalyst. These results clearly suggest that the [Rh-complex/HT-Act] catalyst is active for hydroformylation and hydrogenation reactions up to third cycle, but activity decreased significantly for the aldol condensation of propanal.

### 3.4. Reaction kinetic profile

In order to have an insight into the kinetic profile and rates of the products formed during the synthesis of 2-methylpentanol, which could provide significant information for the stages of the formation of various products with time and to understand the reaction pathways, time dependent experiments were conducted with the catalyst systems [Rh-complex/HT-Act] at 130 °C, the temperature at which maximum selectivity for 2-methylpentanol was obtained. The kinetic profile of the products formation during the synthesis of 2-methylpentanol in one pot gives significant information with respect to time to understand the actual reaction pathway for the formation of various products at different stages. The hydroformylation of ethylene catalyzed by Rh-complex of [Rh-complex/HT-Act] catalyst was completed in 3 h and maximum formation of propanal takes place up to 2 h (Fig. 5). Simultaneously, formation of 2-methylpentenal was also observed by aldol condensation of propanal at 50 °C catalyzed by [HT-



**Fig. 5.** Effect of reaction time on the formation of products during synthesis of 2-methylpentanol from ethylene in one pot using [Rh-complex/HT-Act] as a catalyst.

Act] component of multi-functional catalyst. After 3 h, reaction temperature was increased from 50 to 130 °C. Formation of 2-methylpentanol was started after 4 h and increased gradually. Linear increase in the selectivity of 2-methylpentanol after 6 h was observed which indicates that the condensation and hydrogenation of condensed product is faster during this reaction time period. The selectivity of 2-methylpentenal was also increased on increasing the reaction temperature, which indicates faster aldol condensation reaction at higher temperature. Linear decrease in the selectivity of propanal was observed due to its continuous consumption for condensation reaction. As the reaction time increased, selectivity of 2-methylpentanol increased continuously up to 12 h, with decrease in the selectivity of the 2-methylpentenal, due to the simultaneous consumption of the 2-methylpentenal into 2-methylpentanol. Almost complete consumption of 2-methylpentenal for 2-methylpentanol was observed within 10 h via hydrogenation reaction catalyzed by Rh-complex of multi-functional catalyst. Significant changes in the selectivity of 3-pentanone was not observed throughout the reaction. The formation of propanol was also observed after 7 h via hydrogenation of propanal.

From the comparison point of view, the rate of reaction was calculated for hydroformylation of ethylene, aldol condensation of *n*-propanal and hydrogenation of 2-methylpentenal by conducting experiments separately taking ethylene, *n*-propanal and 2-methylpentenal as a reactant under reaction conditions identical to those used for one pot synthesis of 2-methylpentanol from ethylene (Table 7). The rate of reaction for hydroformylation of ethylene, aldol condensation of *n*-propanal and hydrogenation of 2-methylpentenal were found to be  $16.4 \times 10^{-2}$ ,  $9.8 \times 10^{-2}$  and  $5.2 \times 10^{-2}$  M/h, respectively, when the all three reactions were performed separately in the reaction conditions similar to those of one pot synthesis of 2-methylpentanol. The rate of reaction for ethylene hydroformylation was found to be  $14.3 \times 10^{-2}$  and  $5.1 \times 10^{-2}$  M/h for the formation of 2-methylpentanol in the single pot synthesis of 2-methylpentanol from ethylene using [Rh-complex/HT-Act] as a catalyst. The rate of condensation reaction was calculated as  $4.8 \times 10^{-2}$  M/h due to the basic solid component (activated hydrocalcite) of the multi-functional catalyst. The higher rate of reaction for the hydrogenation reaction as compared to the aldol condensation step showed the faster hydrogenation of 2-methylpentenal to achieve higher selectivity. Generally, lower reaction rate were observed in case of single pot synthesis of 2-methylpentanol from ethylene using [HF/HT-Act] catalyst as compared to the separate reaction performed by taking individual reactants shows the complexity of the reaction for various subsequent reactions and side

**Table 7**

Rate of individual reactions involved for one pot synthesis of 2-methylpentanol from ethylene using [Rh-complex/HT-Act] as a catalyst.

Run	Catalyst	Reaction <sup>a</sup>	Rate $\times 10^2$ M/h
1	[Rh-complex/HT-Act] <sup>b</sup>	Hydroformylation	16.4
2	[Rh-complex/HT-Act] <sup>c</sup>	Hydrogenation <sup>f</sup>	9.8
3	[Rh-complex/HT-Act] <sup>d</sup>	Aldol condensation	5.2
4	[Rh-complex F/HT-Act] <sup>e</sup>	Hydroformylation	14.3
		Aldol condensation	4.8
		Hydrogenation <sup>f</sup>	5.1
		Hydrogenation <sup>g</sup>	0.7

<sup>a</sup> Reaction conditions: Ethylene = 10 atm, CO = 5 atm, H<sub>2</sub> = 15 atm.

<sup>b</sup> [Rh-complex/HT-Act] catalyst = 700 mg, T<sub>1</sub> = 50 °C for 3 h.

<sup>c</sup> [Rh-complex/HT-Act] catalyst = 700 mg, 2-methylpentenal = 0.4 M, T<sub>2</sub> = 130 °C for 9 h.

<sup>d</sup> [Rh-complex/HT-Act] = 700 mg, *n*-propanal = 0.4 M, T<sub>2</sub> = 130 °C for 9 h.

<sup>e</sup> [Rh-complex/HT-Act] = 700 mg, T<sub>1</sub> = 50 °C for 3 h, T<sub>2</sub> = 130 °C for 9 h.

<sup>f</sup> Formation of 2-methylpentanol.

<sup>g</sup> Rate for formation of propanol.

reactions in the one pot. However, significant difference in the rate of reaction was not observed for the hydroformylation of propylene and aldol condensation of *n*-butanol steps in one pot reaction as compared to the separate reaction performed by taking individual reactants using [HF/HT-Act] catalyst.

#### 4. Conclusions

Multi-functional catalyst [Rh-complex/HT-Act] was synthesized by impregnation of Rh-complex on the surface of [HT-Act] of varied Mg/Al molar ratio and its multi-functional potential was evaluated for single pot selective synthesis of 2-methylpentanol from ethylene. <sup>31</sup>P NMR spectrum of [Rh-complex/HT-Act] catalyst showed that the [Rh-complex] was impregnated on [HT-Act] without decomposition. The Mg/Al ratio of [HT], aldol condensation temperature  $T_2$ , CO:H<sub>2</sub> ratio and partial pressure of ethylene showed pronounced effect on the selectivity of 2-methylpentanol. As the Mg/Al molar ratio of [HT-Act] increased from 1.5 to 3.5, the selectivity for 2-methylpentanol also increased from 56 to 79% due to the enhancement in the basicity of catalyst. The selectivity of 2-methylpentanol was observed to increase from 0 to 79% on increasing the aldol temperature ( $T_2$ ) from 60 to 130 °C. On further increase in the  $T_2$  up to 180 °C, the selectivity of 2-methylpentanol decreased to 55% due to the hydrogenation of propanal to propanol. As the partial pressure of ethylene was increased up to 10 atm, the selectivity of 2-methylpentanol was observed to increase. The polar solvents showed higher selectivity of 2-methylpentanol as compared to non-polar solvents. The [Rh-complex/HT-Act] catalyst is reusable for hydroformylation and hydrogenation reactions even at the end of third cycle, but not active for the aldol condensation of propanal. The reaction pathway and role of each component of multi-functional catalyst [Rh-complex/HT-Act] for the synthesis of 2-methylpentanol is discussed with the help of the kinetic profile of the reaction with time.

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#### References

- [1] A.D. Godwin, R.H. Schlosberg, F. Hershkowitz, M.G. Maturro, G. Kiss, K.C. Nadler, P.L. Buess, R.C. Miller, P.W. Allen, H.W. Deckman, R. Caers, E.J. Mozeleski, R.P. Reynolds, US Pat. 6,307,093 B1 (2001).
- [2] W. Schoenlebe, H. Hoffmann, W. Lengsfeld, DE Pat. 2,727,330 (1979).
- [3] P.Y. Blanc, A. Perret, F. Teppa, Helv. Chim. Acta 47 (1964) 567–575.
- [4] D. Frohning, C.W. Kohlpaintner, in: B. Cornils, W.A. Hermann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Wiley-VCH, Weinheim, 2000, pp. 29–104.
- [5] V.K. Srivastava, D.U. Parmar, R.V. Jasra, Chem. Weekly July 8 (2003) 173–178 and July 15 (2003) 181–190; Oxo Chemical Report, SRI International, January 2003.
- [6] H.G. Lueken, U. Tanger, W. Droste, G. Ludwig, D. Gubisch, US Pat. 4,968,849 (1990).
- [7] T. Mori, K. Fujita, H. Hinoishi, US Pat. 5,550,302 (1996).
- [8] J.J. Spivey, M.R. Gogate, Pollution Prevention in Industrial Condensation Reactions, Research Triangle Institute, USEPA Grant, 1996; G.J. Kelly, F. King, M. Kett, Green. Chem. 4 (2002) 392–399.
- [9] D. Tichit, C. Gerardin, R. Durand, B. Coq, Topics Catal. 39 (2006) 89–96.
- [10] F. Winter, M. Wolters, A.J. van Dillen, K.P. de Jong, Appl. Catal. A: Gen. 307 (2006) 231–238.
- [11] K. Motokura, D. Nishimura, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. 126 (2004) 5662–5663.
- [12] Y.Z. Chen, C.M. Hwang, C.W. Liaw, Appl. Catal. A: Gen. 169 (1998) 207–214.
- [13] D. Tichit, M. de, J.M. Ortiz, D. Francova, C. Gerardin, B. Coq, R. Durand, F. Prinetto, G. Ghiotti, Appl. Catal. A: Gen. 318 (2007) 170–177.
- [14] D. Tichit, B. Coq, S. Cerneaux, R. Durand, Catal. Today 75 (2002) 197–202.
- [15] M. de, J.M. Ortiz, D. Tichit, P. Gonzalez, B. Coq, J. Mol. Catal. A: Chem. 201 (2003) 199–210.
- [16] A.A. Nikolopoulos, B.W.L. Jang, J.J. Spivey, Appl. Catal. A: Gen. 296 (2005) 128–136.
- [17] R.V. Jasra, V.K. Srivastava, R.S. Shukla, H.C. Bajaj, S.D. Bhatt, US Pat. 7,294,745 B2 (2007).
- [18] V.K. Srivastava, S.K. Sharma, R.S. Shukla, R.V. Jasra, Catal. Commun. 7 (2006) 879–884.
- [19] S.K. Sharma, V.K. Srivastava, R.S. Shukla, P.A. Parikh, R.V. Jasra, New J. Chem. 31 (2007) 277–286.
- [20] V.K. Srivastava, S.K. Sharma, R.S. Shukla, R.V. Jasra, Ind. Eng. Chem. Res. 47 (2008) 3795–3803.
- [21] S.K. Sharma, P.A. Parikh, R.V. Jasra, J. Mol. Catal. A: Chem. 278 (2007) 135–144.
- [22] H.A. Patel, S.K. Sharma, R.V. Jasra, J. Mol. Catal. A: Chem. 286 (2008) 31–40.
- [23] D. Evans, G. Yagupsky, G. Wilkinson, J. Chem. Soc. (A) (1968) 2660–2665.
- [24] F. Cavani, F. Trifiro, A. Vaccari, Catal. Today 11 (1991) 173–301.
- [25] S. Abello, F. Medina, D. Tichit, J. Pérez-Ramírez, J.C. Groen, J.E. Sueiras, P. Salagre, Y. Cesteros, Chem. Eur. J. 11 (2005) 728–739.