l importances of the alkene hydroformylation reaction for
s have a glowing past and its continuous growth is an evidence of bright future. Today, Asia, with 32% contributions to the world production of oxo products, is the main producers followed by North America and Western Europe with 23% and 31% respectively. This commercial significance of oxo products has inspired many research strategies for enhancing catalyst activity, application of various solvent medium and immobilization of the homogeneous catalysts on solid support for easy separation of catalysts form the products mixture. The developments of the hydroformylation catalysts have been central to the growth of the oxo products. Typically, the general formula of hydroformylation catalysts is $[HM(CO)_xL_y]$, where M is a transition metal atom, especially platinum group metals and L is a modified ligand.

Rhodium and cobalt are the commercially used metals with rhodium for lower alkene and cobalt for higher alkene hydroformylation. Triphenylphosphine (PPh_3), carbon monoxide (CO) and water-soluble sulfonated triphenylphosphine (TPPTS) are commercially employed ligands. The rigorous analysis of the developments on the hydroformylation catalysts show that the research contributions focused on the development of metals and the tailor-made ligands to improve the process parameters of the oxo process. Among the metals, although the ruthenium metal finds third position after rhodium and cobalt in relative activity orders of metals. However, the possible exact reasons for the low activity of the ruthenium metal are not known. On the other hand, the use of ligand other than triphenylphosphine (PPh_3) is rare. Therefore, our study is focused on studying the reasons of the low activity of the ruthenium metal and applicability of triphenylarsine ($AsPh_3$) as ligand in hydroformylation reactions. Additionally, 2-ethylhexanol is commercially important products for the preparation of value-added products, however; its production form propylene is a three-step process involving the use of hazardous liquid base like KOH in one of the steps. In the present study, the attempts have been made to synthesize 2-ethylhexanol and/or 2-ethylhexanal from propylene in a single step under hydroformylation reaction conditions using multi-functional catalyst via non-hazardous route. The conclusions of the present studies have been summarized below;

In order to understand the reason for the low activity of ruthenium metal in hydroformylation reactions, the homogeneous hydroformylation of propylene has been

phenylphosphine)ruthenium(II), $RuCl_2(PPh_3)_3$, catalyst in
$Cl_2(PPh_3)_3$ catalyst was observed along with the separation of solids, which precipitated out during the course of reaction under employed reaction conditions. The solids which have been precipitated were characterized and identified as dicarbonylchlorohydridobis(triphenylphosphine)ruthenium(II), $HRuCl(CO)_2(PPh_3)_2$ and dicarbonyldichlorobis(triphenylphosphine)ruthenium(II), $RuCl_2(CO)_2(PPh_3)_2$. The crystal structure of one of the complexes was also determined by single crystal X-ray diffraction which shows the *cis* form of $RuCl_2(CO)_2(PPh_3)_2$ complex. The isolated complexes $HRuCl(CO)_2(PPh_3)_2$ and $RuCl_2(CO)_2(PPh_3)_2$ were observed inactive for hydroformylation of propylene. Hence, the formation and precipitation of the intermediate complexes, $HRuCl(CO)_2(PPh_3)_2$ and $RuCl_2(CO)_2(PPh_3)_2$ during the course of reaction, was concluded to be one of the possible reasons for the low hydroformylation activity for the complex $RuCl_2(PPh_3)_3$ under studied experimental reaction conditions. Additionally, the kinetic, equilibrium and thermodynamic investigations of interaction of $RuCl_2(PPh_3)_3$ complex with CO in mixed aqueous media have also been carried out. In mixed aqueous, water and 1,4 dioxane 1:1 (v/v) solvent, dissolved CO reacts with $RuCl_2(PPh_3)_2$ complex to form $RuCl_2(CO)(PPh_3)_2$ complex. The $RuCl_2(PPh_3)_3$ complex dissociates to $RuCl_2(PPh_3)_2(S)$ complex which subsequently coordinates with CO to form $RuCl_2(CO)(PPh_3)_2$ complex at λ_{max} 430 nm in the ionic strength range of (0.5-5.0) $x10^{-2}$ mol dm^{-3} KCl at atmospheric pressure of CO in the temperature range 283-313 K. The kinetics of complexation of $RuCl_2(PPh_3)_2(S)$ complex with carbon monoxide indicated first order dependence in terms of concentration of complex $RuCl_2(PPh_3)_2(S)$ complex and carbon monoxide. The activation parameters ($\Delta H^{\#}$ = 35.9±2.5 $kJmol^{-1}$ and $\Delta S^{\#}$ = -122.0±6.0 $JK^{-1}mol^{-1}$) corresponding to the rates of complexation to form $RuCl_2(CO)(PPh_3)_2$ complex and thermodynamic parameters (ΔH^0 = -33.5 ± 4.5 kJ mol^{-1}, ΔS^0 = -25 ± 8 $JK^{-1}mol^{-1}$ and ΔG^0_{303} = -25.7 ± 2.0 $kJmol^{-1}$) corresponding to the formation constants were found to be favorable for the complexation reaction.

A comparative study on transition metal-catalyzed hydroformylation of 1-hexene and ethylene using rhodium, cobalt, ruthenium and palladium complexes of triphenylphosphine, triphenylarsine and triphenylantimony as catalysts. The catalytic activities of the ligands with the studied metals vary in the order: $Ph_3P \approx Ph_3As > Ph_3Sb$

tion. The hydroformylation activity of M/$AsPh_3$ systems r under few experimental conditions than that of M/PPh_3 systems. The only significant difference observed in 1-hexene hydroformylation, which makes M/PPh_3 systems better than M/$AsPh_3$ systems, was the higher normal/iso (n/iso) ratio of heptanal for M/PPh_3 systems. It was concluded that the possible reasons for both, the higher activity and lower n/iso ratio of aldehydes which were observed for $AsPh_3$ ligands is due to the lower value σ-donor/π-acceptor ratio of $AsPh_3$ ligand followed by PPh_3 and $SbPh_3$ ligand.

The kinetics of homogeneous hydroformylation of 1-hexene with $RhCl(AsPh_3)_3$ catalyst has been carried out since the catalytic activity of $RhCl(AsPh_3)_3$ complex was found to be comparable with itôs analogue, $RhCl(PPh_3)_3$ complex. The rate increased on increasing catalyst concentration up to $20.0x10^{-5}$ mol/L followed by a decrease and then saturation obtained. At lower concentrations, the rates were increased on increasing 1-hexene followed by substrate-inhibited kinetics at higher concentration ranges. The dependence of partial pressure of hydrogen showed first order kinetics. The rates were found to be increased with increasing the partial pressure of carbon monoxide up to a certain limit and after that followed inhibition. The dependence agitation speed of stirrer indicated that a moderate speed of 100 rpm is sufficient for the hydroformylation reaction. During the study of thermal deactivation, $RhCl(AsPh_3)_3$ catalyst system is observed to be more susceptible towards the temperature and time of the pre-heat treatment than $RhCl(PPh_3)_3$. The activation energy and the entropy of activation were calculated as 42.74 kJ/mol and -0.22±1 kJ/K mol respectively. The following nonlinear semi-empirical kinetic model representing the data was found to be the best with 11.6 % error (ϕ_{min}) between experimental and calculated rates.

$$\text{rate} = \frac{4008.22.[H_2]^{0.75}[CO][\text{catalyst}]^{0.35}[\text{1-hexene}]}{((1 + 102.0[CO] + 10.99.\text{1-hexene})^{3}.\text{1-hexene})}$$

A multi-functional catalyst system have been developed for preparation of $C_{2(n+1)}$-aldol derivatives from C_n-alkene (where, n = 2-10) in a single step under hydroformylation reaction conditions. The emphasis has been given to propylene due to the relatively more commercial significances of 2-ethylhexanol and 2-ethylhexanal, s of propylene. Industrial production of $C_{2(n+1)}$-aldol a three stage process which included use of hazardous liquid base KOH or NaOH. A novel eco-friendly multi-functional catalyst system has been developed with the use of metal complex $HRh(CO)(PPh_3)_3$ and solid base Mg-Al hydrotalcite by following methods;

(i) uniform mixing of the metal complex $HRh(CO)(PPh_3)_3$ with the solid base hydrotalcite of different Mg/Al ratio

(ii) impregnation of the metal complex $HRh(CO)(PPh_3)_3$ onto the surface of solid base hydrotalcite of different Mg/Al ratio

These two catalytic systems have been studied under various reaction conditions. The selectivity of $C_{2(n+1)}$-aldol derivative from C_n-alkene was observed to be upto 87% in some of the studies. It was observed that higher selectivity of aldol products can be obtained with higher, Mg/Al ratio of hydrotalcites, reaction temperature and weight of catalytic system. Moreover, it was also observed with the multi-functional catalytic system that the selectivity of aldol products decreases on increasing the chain length of starting alkenes. The kinetic experiment with the use of KOH liquid base and with solid base hydrotalcites showed a comparable trend of the formation of aldol products with time.