Water soluble RuCl₂(TPPTS)₃ complex as a catalyst for the hydroformylation and hydrogenation of alkenes

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Abstract

RuCl₂(TPPTS)₃ [TPPTS: P(m-C₆H₄SO₃Na)₃] catalyzed liquid phase hydroformylation and hydrogenation of 1-hexene was carried out in aqueous phase at different temperature and pressure. The catalyst was found to be more active towards hydrogenation even under hydroformylation conditions. It also gave 10–25% isomerized products. The hydrogenation yield (70-80%) remains almost similar under studied experimental conditions. Increase in hydroformylated products with the increase in reaction pressure from 10 to 90bar was observed. The catalyst is found to be selective towards n-heptanal at 125°C and n-heptanol at 175°C, although product yield is very low.

Keywords: Water soluble, hydroformylation, hydrogenation, 1-hexene, ruthenium, TPPTS

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1. Introduction

Hydroformylation of olefins with CO and H₂ is an important commercial process for the production of aldehydes and alcohols. Homogeneous catalysts such as $Co_2(CO)_8$ and HRh(CO)(PPh₃)₃ are widely used for this reaction. A striking drawback of this process is the difficulty in separating and recovering catalysts from the mixture of reaction products and solvent, especially for expensive catalysts made from noble metals. Therefore, it is preferred to use heterogeneous catalysts to overcome this difficulty. The biphasic (aqueous-organic) hydroformylation of propylene has been successfully commercialized to produce butyraldehyde using water-soluble rhodium complexes as the catalyst. This technique provides a simple method for

the separation of the reaction products in the organic phase from the catalyst in the aqueous phase immediately after the reaction [1,2]. When it is applied to the hydroformylation of higher olefins, the reaction rate becomes very low for practical insolubility of higher olefins in the aqueous phase [3–6]. However, the addition of co solvent or surfactant enhances the reaction rate [6-8]. The biphasic hydroformylation of higher olefins occurs in a typical gas-liquidliquid system. The nature of new catalytic complexes and ligands will certainly determine the intrinsic activity and selectivity of such catalysts. However, an equally important factor is the effectiveness of contact between gas and liquid reactants and the catalyst contained in certain phase, as being demonstrated in

the case of propylene hydroformylation in a gas-liquid system [9]. It largely depends on the hydrodynamics of gas-liquid-liquid dispersion, interphase mass transfer, solubility and phase equilibrium. interfacial properties, as well as the intrinsic kinetics of the reaction concerned. Under the circumstances, the biphasic media, wherein the use of watersoluble catalyst is possible, are gaining significance [3-7]. The advances in the field of catalysis are leading towards the development and demand for tailor-made catalysts [10-18]. Furthermore, the replacement of hazardous organic solvents by eco-friendly water as reaction media is also advantageous for environmental safety and economical reasons. The development of water-soluble catalyst in this context assumes relevance. The watersoluble metal-phosphine complexes of rhodium for hydroformylation of alkenes showing good selectivity and activity under mild conditions are reported [18]. In this paper, we are reporting our results on the hydroformylation and hydrogenation water-soluble of 1-hexene using ruthenium-TPPTS complex.

2.Experimental

2.1 Materials

The tri sodium salt of tri (m-sulfophenyl)phosphine (TPPTS) was prepared in accordance with method described in the literature [19]. The syn-gas (99.8%) used was from Hydro Gas India Pvt. Ltd., India. All the alkenes and hydrocarbons used were from Aldrich Chemicals, USA .The Sodium salt of tri (m-sulfophenyl) phosphine oxide as an impurity was less then 5% and water content was less then 10%. Ethanol (99.5% pure) used was from Baroda Chemicals Industries Ltd, India and was further purified by journal literature method. RuCl₃ 3H₂O used in reaction was purchased from Johnson Matthey, England.

2.2 Instrumentation

All the reactions were performed in 100 ml PARR Reactor Model 4593. NMR measurements were done by Bruker advance DPX 200MHz FT-NMR and IR spectra has been recorded on by Perkin-Elmer spectrum GX FT-IR system and CHN analysis has been done on Perkin-Elmer C, H, N, S & O analyzer. Products were analyzed using SHIMADZU GC-17A gas chromatograph using flame ionization detector (FID) having 5% and 95%dimethylsiloxane diphenyl capillary column (60 m length, 0.25mm diameter). Column temperature was kept initially at 40°C for 5 min and then raised to 150°C at 10°C/min. Nitrogen was used as a carrier gas (1.2ml/min). GC calibration was done using standard decane solution

2.3 Synthesis

Water-soluble ruthenium complex, RuCl₂(TPPTS)₃, was prepared by taking 100mg of RuCl₃³H₂O in 7ml of ethanol to which 500mg of TPPTS dissolved in water was added and solution was stirred under reflux for three hours. The volume of the reaction mixture was reduced to minimum and cold acetone was added to precipitate the complex. The complex was filtered and washed with cold acetone and finally re-crystallized from water: acetone mixture.

2.4 Catalytic reaction

1mmol of catalyst, RuCl₂(TPPTS)₃, dissolved in 100 ml water and 2gm of substrate was taken in stainless steel PARR autoclave 300ml reactor. The reactor was flushed with nitrogen three times followed by flushing syn-gas twice at room temperature after which reactor was pressurized to 10-bar pressure with syn-gas. The reaction was brought to desired reaction temperature. The reaction was initiated by stirring and after desired reaction time; it was cooled and brought to normal atmospheric pressure. Separating funnel was used to separate cooled reaction mixture and organic layer was analyzed on GC.

3. Results & discussion

3.1 Synthesis & Characterization

NMR studies of Tris sodium salts of tri phenyl phosphine give singlet peak at of 31 P at -5.37 ppm indicating the sulfonation of tri phenyl phosphine without the formation of phosphine oxide (³¹PNMR peak for the OPPh₃ oxide appears at 34.4 spectrum shows ppm). IR peak corresponding to sulfonyl group observed at v_{so} at 1202 cm⁻¹ and 1048cm⁻¹ confirming the substitution of sulforvl group. The IR peaks at 721cm⁻¹ and 698cm⁻¹ indicate mono substitution on phenyl ring. Water-soluble complex was prepared by the reaction of RuCl₃ 3H₂O with tri sodium salt of tri(m-sulfophenyl)-Phosphine; TPPTS was characterized by physicochemical technique. The C, H, N analysis data obtained for ruthenium (II) complex RuCl₂(TPPTS)₃, is as: calc. (found) C: 63.3 (62.4); H: 4.3 (3.9). ³¹P NMR spectra of the isolated complex gave singlet at 57.78ppm indicating а equivalence all the three phosphorous of TPPTS. IR spectra of the isolated complex gave identical peaks as for the **TPPTS** ligand.

It was observed that at mild reaction pressure of 10-20 bar of syn-gas,

hydroformylation of 1-hexene gives more that 70% hexane, 20-25% isomerization reaction and less then 1% hydroformylation products (Table 1). This may be due to the formation of hydrido complex, HRuCl(CO)(TPPTS)₂ which favors the hydrogenation. Wilkinson et al., [20] have reported RuCl₂[PPh₃]₃ catalyzed hydroformylation of 1-hexene at 120 C and 100bar of syn gas pressure wherein they also got maximum hydrogenation product during the hydroformylation of 1hexene. The catalytic hydrogenation of 1hexene and 1-heptene using RuCl₂[PPh₃]₃ as catalyst was studied at 150°C and 10atmosphere pressure of hydrogen. The hydrogenation of 1-hexene and 1-heptene was found to be 100% under the studied reaction conditions.

One can conclude form the above that at the low pressure and in the presence of water as coordinating solvent, as shown in Scheme I, hydride transfer is favored, which leads to hydrogenation of olefin rather then hydroformylation. As shown in table 1, at the different temperatures (125-175°C) and syn-gas pressure of 10bar, conversion of 1-hexene decreases from 66 to 56% with increase in temperature. However, the selectivity for hvdrogenated product n-hexane. isomerized product 2-hexene and for aldehvde/ alcohol remains around 74-78%. 21-25% and less than 1% respectively. Hydroformylation reaction carried out at syn-gas pressure of 90bar (table 1) showed an increase in aldehyde/alcohol vield and decrease in isomerized products compared to that observed at low reaction pressure. However, the total conversion of 1-hexene does not increase markedly with increase in pressure. These results also show that with increase in temperature. the selectivity towards alcohol increases with

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decrease in selectivity for aldehyde from 8 to 2%.

	Product analysis in wt%				
Temperature	% Selectivity				Total
	Hexane	2-Hexene	Heptaldehyde	Heptanol	Conversion
			_	_	in wt%
b	74	25	0.6	0.2	66
125°C					
С	82	9	8	8	93
b	76	23	0.5	0.4	60
150°C					
с	80	10	6	4.8	94
b	78	21	0.2	0.5	56
175°C					
с	78	12	2.	8	94

Table 1: Hydroformylation of 1-Hexene by RuCl₂(TPPTS)₃ at different pressure temperature^a

^a Reaction conditions: [RuCl₂(TPPTS)₃] = 55 mg; 1-hexene: 23.04 mmol; decane: 0.5ml: water: 20 ml; 150°C, reaction time, 420 min; ^bInitial Syn-gas Pressure =10bar; ^cInitial Syn-gas Pressure = 90bar.



In the case of water-soluble catalysts, the reaction takes place in the water phase or at the organic-aqueous interface. Mass transfer effect, solubility of gaseous reactants as well as liquid-liquid equilibrium properties play significant role

in determining the reaction progress. The water soluble RuCl₂(TPPTS)₃ complex to be active catalyst found for hydrogenation under mild pressure, is explained in terms of formation of HRuCO(TPPTS)₂ complex and low solubility of CO in aqueous phase (0.16 x 10^{-4} mol fraction) compared that in the organic phase $(6-20 \times 10^{-4} \text{ mol fraction})$ [21]. A general mechanism is proposed for hydroformylation the as well as hydrogenation of 1-hexene catalyzed by RuCl₂(TPPTS)₃ and is given in Scheme-1. According to Scheme 1, complex RuCl₂(TPPTS)₃ interact with syn-gas to give intermediate HRuCl(CO)(TPPTS)₂ 2. Then olefin interacts with 2 to give species **3**. Now either hydride transfer take place (route 1) to give hydrogenated alkyl complex 4' or carbonyl insertion take place (route 2) to give CO inserted species 4.

As we are getting maximum hydrogenated product, it can be inferred that route 1 is more favored than route 2 under the employed experimental conditions. This may be due the strong $p\pi - d\pi$ back bonding interaction of CO with ruthenium center then week hydride – ruthenium interaction that makes the hydride more labile then CO.

4.Conclusions

Water soluble complex, RuCl₂(TPPTS)₃, was found to have low hydroformylation activity as well as high isomerization and hydrogenation activity. Low hydroformylation and high hydrogenation activity is attribute to the formation of intermediate compound, HRuCl(CO)(TPPTS)₂. The principal advantage of water-soluble catalyst is ease of separation of the product from the catalyst and long-term stability. The

industrial outlook for hydrogenation processes based on water-soluble catalysts, therefore, seems to be of promise.

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