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Gas–liquid–liquid reaction engineering: hydroformylation of 1-octene using a water soluble rhodium complex catalyst

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Abstract

Hydroformylation of 1-octene was studied in a two-phase system using [RhCl(1,5-COD)]$_2$ complex catalyst and the trisodium salt of tri(*m*-sulfophenyl) phosphine (TPPTS) as a water soluble ligand. The reaction was carried out in a batch reactor at pressures between 1.5 to 2.5×10^3 kPa and temperatures of 333 and 343 K. Ethanol was added as a cosolvent to enhance the octene solubility in the aqueous phase and a buffer solution of sodium carbonate and bicarbonate was used to eliminate the formation of acetals. The hydroformylation products were n-nonanal and 2-methyl nonanal with a selectivity to linear aldehyde of about 80%. The reaction is first order with respect to octene and catalyst concentrations. The dependence on the carbon monoxide pressure was found to be complex with an enhancement at low partial pressures and an inhibition rate at high pressures. The reaction rate increased with the hydrogen partial pressure. A thermodynamic analysis concerning the solubilities of octene and gases in the reaction medium was studied and a semiempirical kinetic model was used to describe the rate of reaction.

1. Introduction

Hydroformylation of olefins is an important commercial process for the production of aldehydes and alcohols. Homogenous catalysts are widely used for this reaction. An important drawback of this process is the difficulty of separating the products from the catalyst and from any solvent. Therefore the use of a heterogeneous catalyst is preferred to overcome this difficulty. One method of preparing such a catalyst is to heterogenize a homogeneous catalyst onto an insoluble polymer support [1]. However, this approach has found no application in major industrial processes because of problems of catalyst leaching and deactivation. The other alternative is the use of a two-phase system (aqueous–organic) with a water soluble complex catalyst. This method provides a suitable means by separating the reaction product in the organic phase from the catalytic aqueous phase immediately after the reaction [2].

Kuntz [3] prepared the trisodium salt of tri(*m*-sulfophenyl) phosphine (TPPTS) by sulfonation of triphenylphosphine with oleum followed by neutralization. The complex [RhCl(1,5-COD)]$_2$ (where 1,5-COD is 1,5-cyclo-octadiene) is highly insoluble in water, however, displacement of the COD ligand with the TPPTS affords a new complex [RhCl(TPPTS)$_n$] which is actually soluble in water. This complex is successfully used as a catalyst precursor for the preparation of butyraldehyde from propylene by Ruhrchemie [4]. This biphasic process requires a low pressure of syngas but is limited to the hydroformylation of lower olefins.

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The use of water soluble complex catalyst for the hydrogenation of 1-octene was investigated by Hablot et al. [5] using $[RhCl(1,5\text{-}COD)]_2$/TPPTS. The other type of catalyst like $RhCl_3 \cdot 3H_2O$/TPPMS (monosulphonated phosphine) was investigated by Dror and Manassen [6] for the hydrogenation of cyclohexene. Both 1-octene and cyclohexene have very low solubility in water. The use of a cosolvent is necessary for enhancing the rate of reaction. The role of cosolvent such as methanol, ethanol, dimethyl acetamide, etc. is to enhance the solubility of reactants in the aqueous phase.

Monteil [7] has investigated the hydroformylation of 1-octene with $[Ru(m\text{-}S^tBu)(CO)(TPPTS)]_2$ as a catalyst. The author compared the different cosolvents: ethanol, acetone, acetonitrile and methanol. The highest reaction rate was obtained with ethanol. However, during the reaction ethanol can react with the nonanal to yield acetals.

Chaudhari et al. [8] have also discussed the use of cosolvent to enhance the rate of the hydroformylation reaction in biphasic media.

Recently Horvarth and Rabai [9] have used a biphasic system consisting of organic and fluorous phases (fluorocarbon rich) for the hydroformylation reaction using special phosphine soluble in the fluorous phase. The limitations of solubility encountered in aqueous–organic systems are expected to be overcome in such biphasic system.

This paper presents investigations on the kinetics of hydroformylation of 1-octene in the biphasic medium by using $[RhCl(1,5\text{-}COD)]_2$/TPPTS with ethanol as a cosolvent. In order to eliminate formation of acetals, a buffer solution of sodium carbonate and bicarbonate in the aqueous phase was used.

2. Experimental

Hydroformylation of 1-octene was carried out in a 6.0×10^{-4} m^3 batch reactor (Autoclave Engineer) with aqueous phase as a continuous phase and organic phase being a dispersed phase.

The reactor was equipped with a heating device such that the temperature could be controlled within ± 1 K. The gas-induced agitation was effected by a magnetic transfer system with a Rushton turbine.

The catalyst was formed in situ by adding $[RhCl(1,5\text{-}COD)]_2$ with TPPTS in water. $[RhCl(1,5\text{-}COD)]_2$ was obtained from Fluka and TPPTS from Rhône Poulenc was used as a 30% solution in water. The CO and H_2 were procured from AGA. The molar ratio of phosphorous to rhodium used was equal to 8. The reactions were carried out at 333 and 343 K and at a constant pressure of syngas from 1.5 to 2.5×10^3 kPa. The gas consumption was recorded during the reaction and the liquid phase was analysed by gas chromatography with a FFAP capillary column. The stirring speed of 23.3 rps was sufficient to ensure the chemical regime.

3. Results and discussion

3.1. Addition of cosolvent

A preliminary experiment carried out with a small concentration of octene in the aqueous phase indicated a very low conversion of octene. The reaction rate was clearly limited by the solubility of octene in the aqueous phase. In order to enhance the solubility of octene, ethanol was used as a cosolvent. However, due to the presence of nonanal formed during the reaction, a transfer of ethanol from the aqueous phase to the organic phase occurred. On the other hand, ethanol reacts with nonanal to form acetals. Therefore the use of an organic solvent such as octane is necessary to maintain the constant volume of two phases during the reaction. The formation of acetals could be avoided by adding a buffer solution of sodium carbonate and bicarbonate ($pH \approx 10$). The principal products of the reaction were n-nonanal and 2-methyl octanal with selectivity of n-nonanal $\approx 80\%$. The hydrogenation of octene to octane was neglected and the formation of a small amount

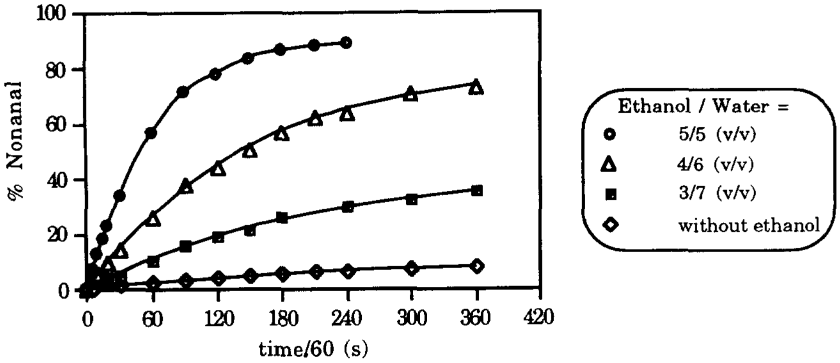

Fig. 1. Effect of cosolvent on the formation of nonanal. Catalyst: 1.0×10^{-4} kg, temperature: 343 K, pressure: 2.0×10^{3} kPa (CO/H_2 = 1/1); TPPTS/Rh: 8/1; aqueous phase: 2.0×10^{-4} m^3; organic phase: 0.5×10^{-4} m^3 (octene/octane = 3/7).

of octene isomers was observed. No condensation product was observed during the reaction.

Fig. 1 shows the effect of the ethanol in the aqueous phase on the reaction rate. The formation of nonanal is enhanced significantly with the enhancement of cosolvent.

3.2. Octene and gas solubility in the aqueous phase

A ternary diagram of the octene–water–ethanol system was established with the UNIFAC prediction [10] and compared with the experimental results [11] at 298 K. As a general result, UNIFAC gave a good prediction for the system studied.

By adding ethanol and water in equal proportions, the octene solubility could be enhanced to the order of 10^4 times that in the absence of ethanol. An equilibrium of a quartenary mixture of water–ethanol–octene–octane was calculated with the UNIFAC prediction using Prophy software of ENSIGC. The interaction parameters in the UNIFAC were calculated from the Magnussen parameters [12]. The results of the simulation are presented in Fig. 2 which depicts octene solubility in the aqueous phase.

The addition of the cosolvent to the aqueous phase also modified the hydrogen and carbon monoxide solubility. The solubility of these gases in several compositions of aqueous phase were measured in the reactor with the physical absorption method. The solubility observed increased with the addition of ethanol. The effect of cosolvent is greater for carbon monoxide than for hydrogen. In contrast to literature reports [13] on the solubility of hydrogen and carbon monoxide in a mixture of water–ethanol, a minimum solubility was not found. A similar observation was reported by Dake and Chaudhari in the carbon monoxide–water–ethanol system [14]. Hablot et al. [5,10] has made a model based on the correlation of Hildebrand et al. [15] modified by Lemcoff [16]. A minimum solubility of hydrogen in a mixture of water–ethanol was obtained by this model. In order to extend the use of solubility data, the experimental results were correlated with the O'Connell–Prausnitz equation [17]. The model was found to be in good agreement with the experimental results as presented in Fig. 3.

3.3. Effect of octene concentration

Experiments were carried out to investigate the effect of octene concentration on the rate of reaction at 333 and 343 K. The variation of octene concentration in the aqueous phase can be achieved by the addition of a different quantity of ethanol in the aqueous phase. Nevertheless this involves also changes of hydrogen and carbon monoxide solubilities in the aqueous phase. As a result only a rough estimate was provided as indicated in Fig. 4, a first order reaction with respect to octene concentration was observed at 333 and 343 K.

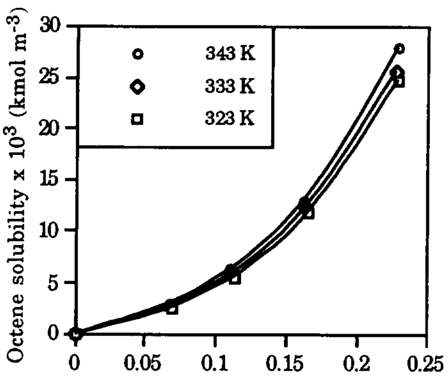

Fig. 2. Octene solubility in the aqueous phase.

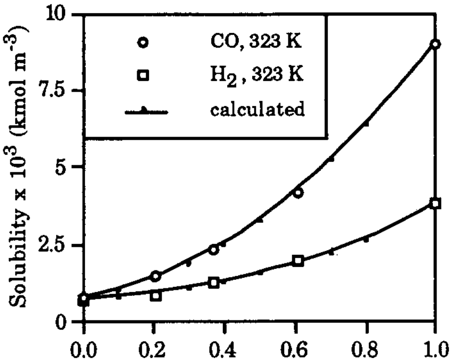

Fig. 3. Solubility of hydrogen and carbon monoxide in the aqueous phase.

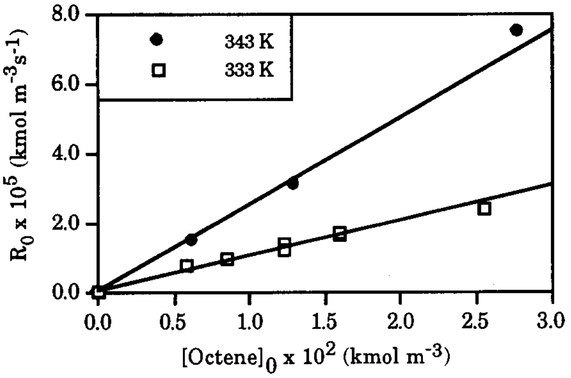

Fig. 4. Effect of octene concentration on the rate of reaction. Catalyst: 1.0×10^{-4} kg, pressure: 2.0×10^3 kPa (CO/H$_2$ = 1/1); TPPTS/Rh: 8/1; aqueous phase: 2.0×10^{-4} m^3; organic phase: 0.5×10^{-4} m^3 (octene/octane = 2/8; 3/7; 4/6).

It should be noted that the change in octene concentration in aqueous phase can also be achieved by changing the ratio of octene to octane in the organic phase. Same trends were observed in this case proving the overall effects of hydrogen and carbon monoxide solubilities were negligible.

3.4. *Effect of catalyst concentration*

The effect of catalyst concentration on the reaction rate is presented in Fig. 5. These experiments were carried out by maintaining a constant ratio of phosphorous to rhodium (equal to 8). Fig. 5 indicates that the rate of reaction is enhanced with the catalyst concentration with a first order dependence. Such classical behaviour was, however, not found when the reaction was investigated in the absence of buffer solution in the same range of catalyst concentration. A negative order was observed probably due to catalyst instability.

3.5. *Effect of hydrogen pressure*

The effect of hydrogen partial pressure on the rate of reaction was studied at a constant partial pressure of carbon monoxide at 333 and 343 K. The rate of reaction was enhanced by increasing hydrogen pressure (Fig. 6). The same complex catalyst was used in the hydrogenation of octene-1 in a two-phase system at 323 K and a pressure up to 10 MPa with the same equipment without buffer solution [3]. In contrast to the obtained hydrogenation data, the reaction is not first order with respect to hydrogen. This observation can be

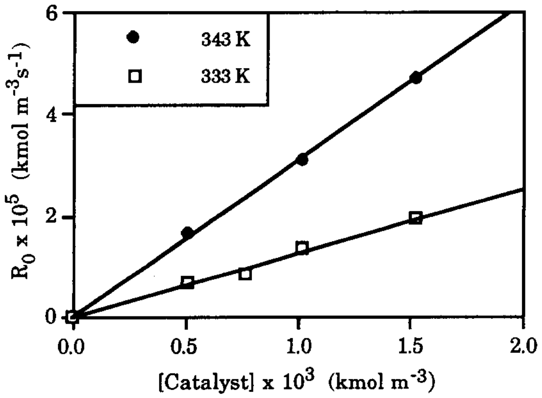

Fig. 5. Effect of catalyst concentration on the rate of reaction. Catalyst: (0.5–1.5) $\times 10^{-4}$ kg, pressure: 2.0×10^3 kPa (CO/H$_2$ = 1/1); TPPTS/Rh: 8/1; aqueous phase: 2.0×10^{-4} m^3; organic phase: 0.5×10^{-4} m^3 (octene/octane = 3/7).

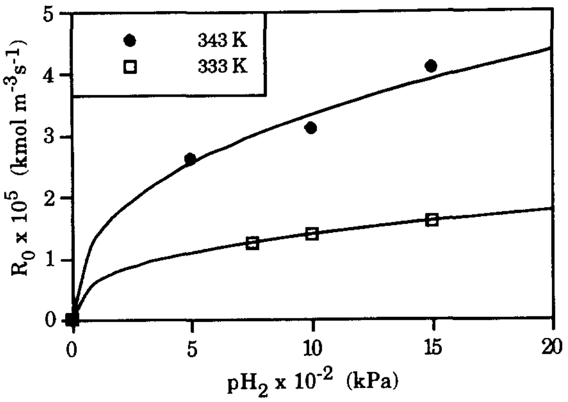

Fig. 6. Effect of partial pressure of hydrogen on the rate of reaction. Catalyst: 1.0×10^{-4} kg, pressure: $(1.5\text{–}2.5) \times 10^3$ kPa ($p_{CO} = 1.0 \times 10^3$ kPa); TPPTS/Rh: 8/1; aqueous phase: 2.0×10^{-4} m^3; organic phase: 0.5×10^{-4} m^3 (octene/octane = 3/7).

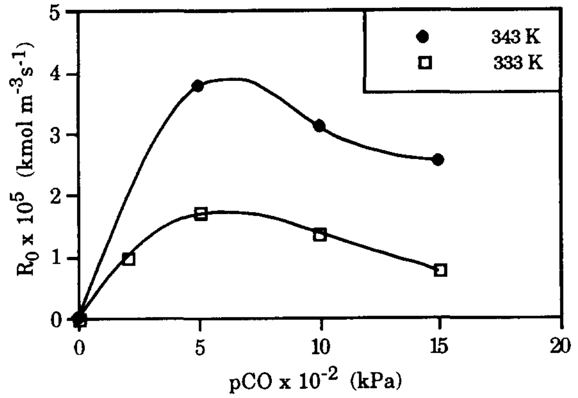

Fig. 7. Effect of carbon monoxide partial pressure on the rate of reaction. Catalyst: 1.0×10^{-4} kg, pressure: $(1.5\text{–}2.5) \times 10^3$ kPa ($p_{H_2} = 1.0 \times 10^3$ kPa); TPPTS/Rh: 8/1; aqueous phase: 2.0×10^{-4} m^3; organic phase: 0.5×10^{-4} m^3 (octene/octane = 3/7).

Table 1
Rate parameters

Parameter	333 K	343 K
$k \times 10^{-5}$, m^9 kmol^{-3} s^{-1}	1.571	7.441
$K_{H_2} \times 10^{-2}$, m^3 kmol^{-1}	1.967	2.185
$K_{CO} \times 10^{-2}$, m^3 kmol^{-1}	1.133	1.886

explained by the presence of carbon monoxide as well as sodium carbonate and bicarbonate which may modify the active catalytic species.

3.6. *Effect of carbon monoxide pressure*

The effect of carbon monoxide pressure on the reaction rate was investigated at two different temperatures — 333 and 343 K, respectively. As shown in Fig. 7 the reaction rate first increases with the enhancement of carbon monoxide partial pressure and then decreases with increasing carbon monoxide partial pressure. This observation is typical of hydroformylation kinetics in the homogenously catalysed systems with rhodium complex catalyst.

4. Kinetic model

The effect of different parameters on the rate of reaction was found to be complex. For the purpose of kinetic modeling, it is important to develop a suitable rate model to describe the intrinsic kinetics of the hydroformylation reaction. The semiempirical model proposed by Deshpande and Chaudhari [18] for homogenous catalysis was used since a rate model based on the mechanism of hydroformylation in a two-media has not been developed. The equation used for this model was based on the general trends obtained in this investigation.

$$R_0 = k\frac{[\text{octene}]_0[\text{cat.}][H_2][CO]}{(1+K_{H_2}[H_2])(1+K_{CO}[CO])^2}$$

The parameters in the equation were determined by the routine of optimization. The values obtained are presented in Table 1.

The model was found to be in good agreement with the observed results within an error of ±6% as shown in Fig. 8.

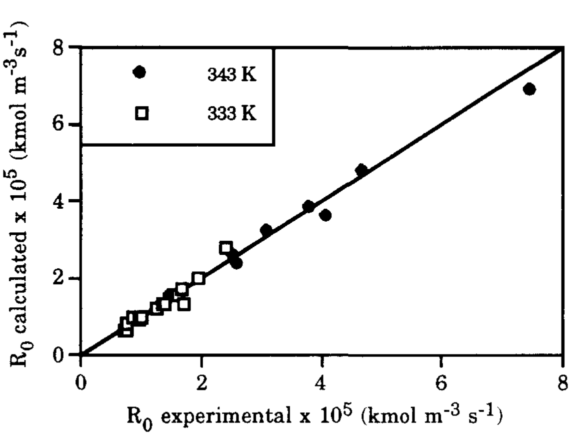

Fig. 8. Comparison between experimental and calculated values of the reaction rate with a semiempirical kinetic model.

5. Conclusions

Hydroformylation using a coordination complex in a biphasic liquid medium was proved to be efficient in as much that cosolvent was sufficiently added to enhance olefin solubility in the catalytic aqueous phase. This is specially true for higher olefins. The effect of cosolvent addition on liquid–liquid and gas–liquid equilibria was studied both experimentally and theoretically by UNIFAC simulations and was found to be in good agreement.

A kinetic study based on initial reaction rates and using the thermodynamic models has proved that the reaction rate obeys a similar law to that in homogenous liquid medium.

To manage such a biphasic hydroformylation, the remaining problems are catalyst stability and control, especially when chlorine is involved in the precursor, and the gas–liquid and liquid–liquid mass transfer involved in the complex gas–liquid–liquid medium.

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