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Hydroformylation of linalool in a supported aqueous phase catalyst by immobilized rhodium complex: kinetic study

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Abstract

In this paper, we report on the kinetics of linalool hydroformylation using supported aqueous phase catalysis (SAPC). Hydroformylation of linalool by SAPC has been carried out in the presence of toluene as the solvent and using $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2] = [D2]$ as the catalyst supported on the silica DS50. The effects of temperature, pressure and concentrations of catalyst, water and linalool on the monoterpene conversion have been investigated. The rate was found to be first order with respect to catalyst and olefin concentrations and hydrogen and carbon monoxide pressure. A kinetic model was fitted to the observed data, and it was found to predict the rates with a good agreement. The activation energy was found to be as low as 14.5 kcal mol^{-1}.

Keywords: Hydroformylation; SAPC; Linalool

1. Introduction

The hydroformylation of higher olefins still remains a challenge for aqueous two-phase catalysis. The low solubility of higher olefins ($>C_7$) in the aqueous catalytic phase represents a serious problem in extending the technology to a broader variety of substrates. In supported aqueous phase catalysis (SAPC), the reaction proceeds at the interface between the organic phase and the immobilized aqueous phase in the pores of a hydrophilic support [1]. So, SAPC is very perspective due to its high capacity in the conversion, the selectivity and also the easy recovery of the catalyst from the organic phase.

Several positive responses to phytosanitary tests of aldehydes originating from various allyl- and propenylbenzene compounds lead to expect biological activity of aldehydes prepared by hydroformylation of monoterpenes [2]. Some of these aldehydes have previously been synthesized by homogenous hydroformylation in order to obtain perfumes. The monoterpenes are manufactured on a commercial scale from natural sources and at high tonnage from petrochemical (synthetic) sources. Specially, the most important natural source of linalool is "bois de rose oil" and lavander oil from which it is separated by distillation. The secondary lavander oil, which have lowest quality, contain 10–11% esters and approximately 90% alcohols, from which 60–70% linalool, 12–18% terpineol-4 and cineol-1,4 [3]. By far, more linalool is produced synthetically than from natural

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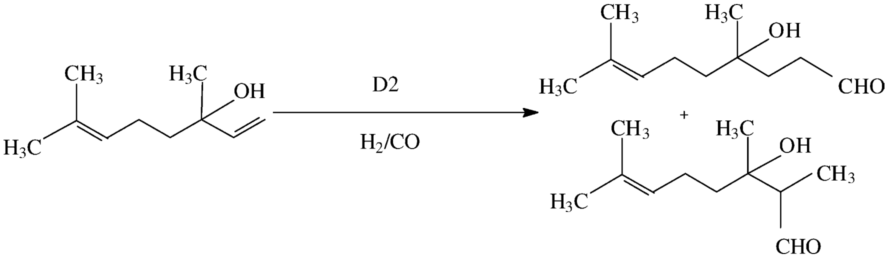

Fig. 1. Hydroformylation of the linalool.

sources [4]. Recently, Jáuregui-Haza et al. [5] have shown that the efficiency of SAPC to achieve hydroformylation of various monoterpenes strongly depends on the location of the double bond. External linear monoterpene (linalool) is fully transformed. Based on our previous work [5,6] here we analyse the kinetics of the hydroformylation of linalool by SAPC using $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2] = [D2]$ as catalyst (Fig. 1) and silica DS50 as support.

2. Experimental

The experiments were carried out in a 5.0×10^{-4} m^3 autoclave (Autoclave Engineers) equipped with a gas-inducing turbine with variable stirring speed up to 3000 rpm. The equipment was provided with automatic temperature control and pressure recording system. The temperature of the liquid in the reactor could be controlled within 1 °C. A fast and accurate pressure transducer (±1 kPa) was used to measure the variation of the reservoir pressure. The transducer signal was transmitted to an acquisition card and recorded on-line by a PC (Fig. 2).

Reagents and solvents were purchased from Aldrich, Acros and SDS, and used without further purification. Rhodium trichloride trihydrated was supplied by Acros. Tris(*m*-sodiumsulphonatophenyl)phosphine (TPPTS) is a generous gift from Rhône-Poulenc. Distilled, deionized water was used in all operations requiring water. All solvents, including water, were degassed by three freeze–pump–thaw cycles. The complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ was prepared as described by Kalck et al. [7]. Unless otherwise stated, all manipulations were performed under nitrogen or argon. The structure and purity of $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ and TPPTS were verified by NMR spectroscopy. Liquid phase ^{31}P NMR spectra were recorded on a Brüker AM 250 spectrometer (101.26 MHz) and on a Brüker AMX 400 (161.99 MHz) calibrated with H_3PO_4 as the external standard. Liquid phase ^1H and ^{13}C NMR were recorded on a Brüker AM 250 spectrometer (250.13 MHz for ^1H NMR spectra and 62.90 MHz for ^{13}C NMR spectra) and on a Brüker AMX 400 (400.14 MHz for ^1H NMR spectra and 100.62 MHz for ^{13}C NMR spectra) calibrated with TMS as external standard. Hydrogen and CO was obtained from AGA, France. The characterisation of the support was recently achieved (Table 1) [6].

In a typical run, the required amounts of TPPTS, $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ and the support DS50 were placed in the autoclave. The solids were covered with toluene, linalool and the quantity of permuted water necessary to reach the desired hydration percentage. Following this, the autoclave was closed, and the contents were flushed twice with nitrogen at working pressure. After stabilization of the temperature to a desired value, the autoclave was pressurized to the necessary pressure with syngas consisting of CO and H_2 in a desired ratio. Switching the stirrer on then started the reaction. The reaction was then

Table 1
Characteristics of the support

	DS50
BET surface (m^2/g)	488
Total porous volume (ml/g)	0.73
Mean diameter of the pores (Å)	59
Mean size of the particles (μm)	53
Water content (%)	8.5

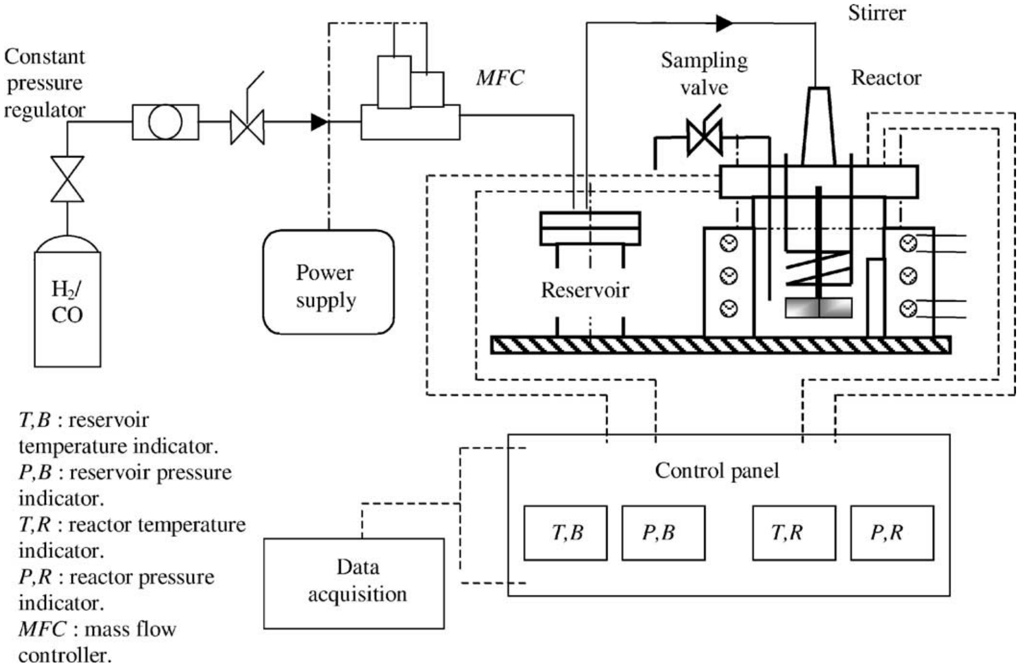

Fig. 2. Schematic representation of the experimental set-up.

continued at a constant pressure, by supply syngas from the reservoir vessel. Simultaneously, the pressure in the reservoir was measured continuously for the duration of the reaction (5 h). Samples of the liquid phase were withdrawn for time to time. The initial rates of reaction were then calculated in a region wherein the conversion of linalool was less than 15%, to ensure differential conditions. The molar ratio of rhodium to TPPTS used was 1:6 to ensure the optimal conditions for the stability of the catalytic complex, as shown for octene hydroformylation [6,7].

The organic phase was analysed by gas phase chromatography on a Carlo Erba HRGC 5160 chromatograph equipped with a flame ionization detector and a capillary column Alltech Econopac FFAP (30 m; 0.53 mm; 1.2 μm), $T_{\mathrm{det}} = 200\,^{\circ}\mathrm{C}$, $P_{\mathrm{H}_2} = 0.45$ bar.

3. Results and discussion

3.1. Preliminary results

The material balance and reproducibility were determined in preliminary experiments in which the amounts of linalool, products formed and the syngas consumed were compared. The consumption of linalool and syngas was found to be stoichiometrically consistent (>95% material balance) with the aldehydes, the only detected product. The selectivity in linear aldehyde did not change significantly during the reaction time. The selectivity was in the range of 70%. The experimental relative error for the reproducibility of conversion was found to be 5%.

The effect of agitation speed on the rate of hydroformylation was studied at the highest temperature, 363 K, to determine in which conditions gas–liquid mass transfer limitations can be ignored. It was found that, beyond a stirring speed of 1750 rpm the rate was independent of the agitation, indicating kinetic regime. Hence, all the reactions were conducted at an agitation speed of 1870 rpm.

In the case when SAPC takes place in the pores of the support, the optimum hydration yielding the best conversion was found to be very narrow [8–12]. Recently, it was shown that, with convenient supports, SAPC could be achieved with roughly stabilized conversion in a wide range of hydration during the

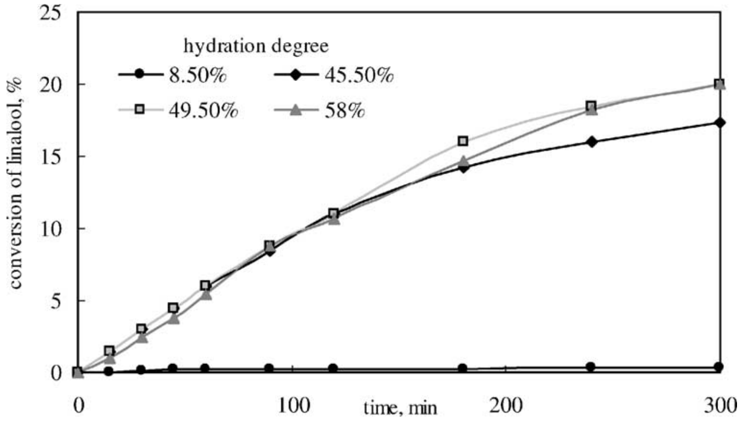

Fig. 3. Influence of hydration on the rate of conversion: $T = 353\,\mathrm{K}$; $P = 1\,\mathrm{MPa}$; $H_2/CO = 1$; $C_{\mathrm{cat}} = 36.04 \times 10^{-5}\,\mathrm{kmol/m^3}$; $C_{\mathrm{lin,0}} = 0.385\,\mathrm{kmol/m^3}$.

hydroformylation of 1-octene [6]. Then the influence of hydration degree of the support in the range 8.5–58% at 353 K was studied (Fig. 3). At hydration degree of 8.5% the reaction practically did not occur. The high improvement of the conversion begins with the total filling of the pores (corresponding to 45.5%) and then, the excess of water allows the catalyst to have enough mobility on the surface to improve consequently the yield on a interval ranging from 45.5 to 58%. This result follows the same behaviour obtained before for oct-1-ene [6]. Then, the water content of the support in all kinetic experiments was 49.5%. At these conditions, the pores of the silica DS50 are saturated in water and the reaction takes place at the external surface of the support.

In this work the catalyst activity will be given as the turnover frequency (TOF) for linalool, defined as the number of moles of the product obtained by the unit of moles of Rh in the unit of time, it means

$$\mathrm{TOF} = \left(\frac{\text{mol product}}{\text{mol Rh} \times \text{time}}\right)$$

The number of moles of the product was determined by GC (at 15 min from the beginning of the reaction the sample was withdrawn and analysed by GC). The total amount of Rh was calculated from the weight of catalytic complex added into the reactor. These initial values of TOF at 15 min correspond to the experiments carried out at different conditions of the hydroformylation. The initial TOF changed in the range of 22–459 h^{-1}. The TOF increases with increasing of temperature and pressure. This behaviour has been observed before when hydroformylation of olefins has been studied by homogeneous, biphasic, SAPC and heterogeneous catalysis.

The obtained values of TOF during the hydroformylation of linalool by SAPC were in the same order or higher than those observed in the hydroformylation of olefins by biphasic catalysis (5–10 h^{-1} [9,13,14]), by biphasic catalysis with cosolvent (100–136 h^{-1} [15–18]), by phase transfer catalysis with cyclodextrines (24 h^{-1} [19]) and by SAPC (50–432 h^{-1} [1,6–12]).

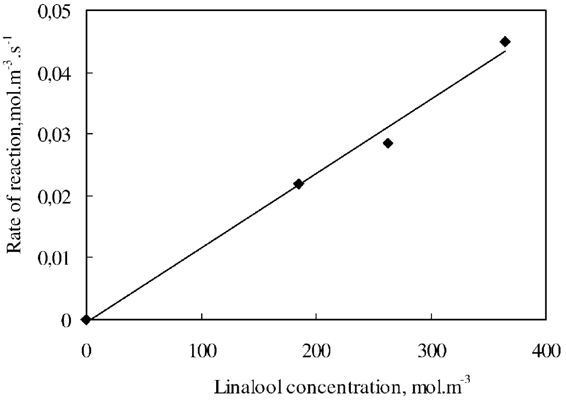

Fig. 4. Effect of linalool concentration on the rate of the reaction: $T = 363\,\mathrm{K}$; $P = 3\,\mathrm{MPa}$; $H_2/CO = 1$; $C_{\mathrm{cat}} = 36.04 \times 10^{-5}\,\mathrm{kmol/m^3}$.

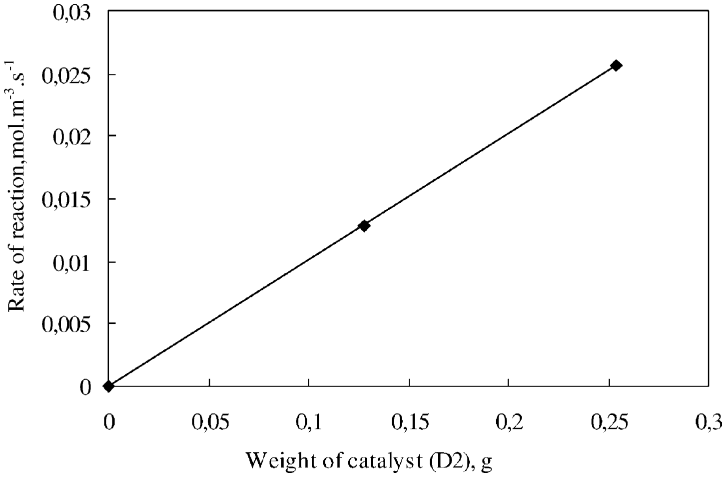

Fig. 5. Effect of catalyst concentration on the rate of the reaction: $T = 363\,\mathrm{K}$; $P = 1\,\mathrm{MPa}$; $H_2/CO = 1$; $C_{\mathrm{lin},0} = 0.385\,\mathrm{kmol/m^3}$.

3.2. Effect of linalool concentration

Experiments were carried out to investigate the effect of linalool concentration in the organic phase on the rate of reaction at 363 K, a hydrogen and CO total pressure of 3 MPa and a constant linalool to catalyst concentration ratio. The variation of linalool concentration in the organic phase can be achieved by using different linalool/toluene ratios. In our case, a first order dependence of the reaction rate with respect to the concentration of linalool in the organic phase was clearly proven as presented in Fig. 4.

3.3. Effect of catalyst concentration

The effect of the concentration of the catalyst on the rate was studied at a hydrogen and CO total pressure of 1 MPa; a constant temperature of 363 K and a constant linalool concentration. Fig. 5 indicates that the rate of reaction is enhanced with the catalyst concentration with a first order dependence. This type of behaviour is expected as far as mass transfer limitations are negligible and any increase in the catalyst concentration will proportionally enhance the concentration of the active catalytic species and hence the rate.

3.4. Effect of the total hydrogen and carbon monoxide pressure

The effect of total hydrogen and CO pressure on the rate of reaction was studied at a constant linalool and catalyst concentration at 363 K. The rate of the reaction, as shown in Fig. 6, was enhanced by increasing hydrogen and CO pressure with a first order dependence.

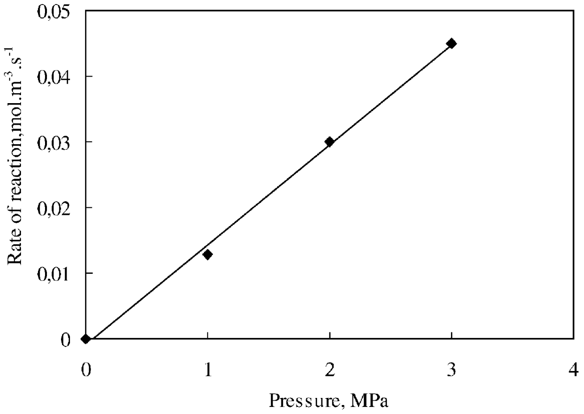

Fig. 6. Effect of the total hydrogen and CO pressure on the rate of the reaction.

4. Kinetic model

Since a rate model based on the mechanism of hydroformylation by SAPC has not been developed before, a empirical kinetic model was evaluated, taking into account the general trends observed in the experiments. The rate R for linalool hydroformylation

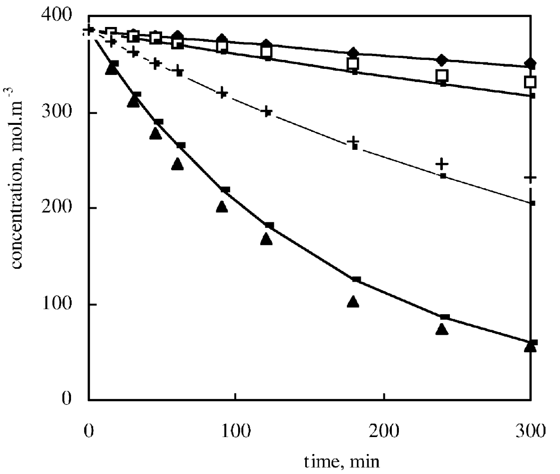

Fig. 7. Variation of the concentration of linalool. Comparison between experimental and calculated values: (—) calculated; (▲), (+), (☐), (◆): experimental.

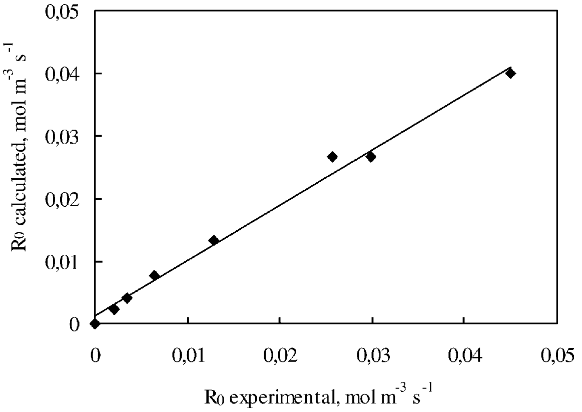

Fig. 8. Comparison between experimental and calculated values of the initial rate of the reaction.

can be expressed in the following form:

$$R = km_{\mathrm{D2}} C_{\mathrm{lin}} P \tag{1}$$

where k is the rate constant, m_{D2} the weight of catalytic complex D2, C_{lin} the concentration of linalool and P the total syngas pressure. Regression of the experimental data to the rate model was performed using a corrected Newton's algorithm. The procedure calculates the values of the parameters of kinetic model, which minimize the average standard error of estimation (S.E.E.)

$$\text{S.E.E.} = 100 \sum_{i=1}^{n} \frac{|R_i^{\mathrm{pred}} - R_i^{\mathrm{obs}}|}{R_i^{\mathrm{obs}}} \tag{2}$$

where R_i^{obs} are the elements of the vector containing the given experimental initial rate and R_i^{pred} the corresponding values calculated by the model being studied and n the number of data points. The comparison between experimental data and the optimized model is presented in Fig. 7. Fig. 8 presents the comparison between calculated and experimental initial rate of reaction. The standard error of estimation was

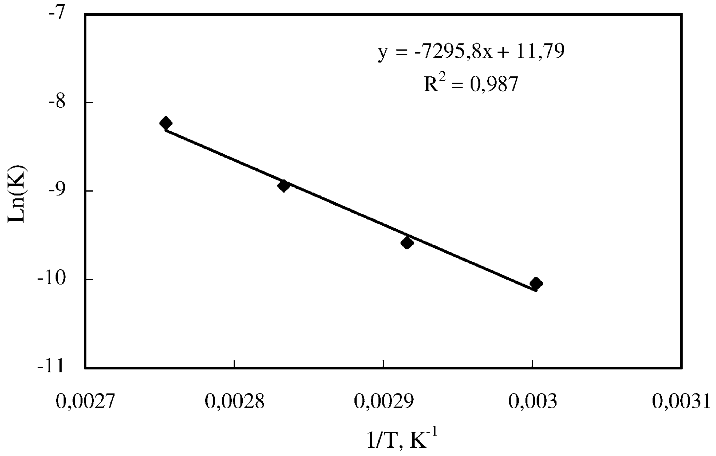

Fig. 9. Plot of ln(k) vs. 1/T for hydroformylation of linalool by SAPC.

less than 5% at all studied temperatures, which is within the range of the experimental error.

The activation energy calculated from the temperature dependence of the rate constant (at 333, 343, 353 and 363 K), using the Arrhenius equation was found to be 14.5 kcal mol^{-1} for the hydroformylation of linalool. The plot is presented in Fig. 9. This rather low value could be connected to diffusion limitations inside the pores or near the aqueous catalytic layer.

5. Conclusions

The kinetics of hydroformylation of linalool has been studied in the presence of hydrosoluble complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ supported on silica DS50. With this support the reaction rate is not sensitive to support hydration within a large range over complete filling of the pores. The effects of different parameters like concentrations of linalool and catalyst and total pressure of equimolar CO and hydrogen on the rate of reaction was studied in a temperature ranging from 333 to 363 K. The rate was found to be first order with respect to the three investigated variables. An empirical rate equation has been proposed. The kinetic model showed good fitting with the experimental data. The kinetic parameter has been evaluated for different temperatures. The activation energy was found to be 14.5 kcal mol^{-1}.

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