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Supported aqueous phase catalysis: a new kinetic model of hydroformylation of octene in a gas–liquid–liquid–solid system

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Abstract

The kinetics of the $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ catalyzed hydroformylation of 1-octene by supported aqueous phase catalysis has been investigated under mild conditions (0.5–1 MPa, 353–373 K). The effect of 1-octene and catalyst concentration and partial pressure of hydrogen and carbon monoxide on the rate of reaction has been studied. The rate was found to be first-order with respect to catalyst concentration and partial order with respect to partial pressure of hydrogen. However, when partial pressure of carbon monoxide and 1-octene concentration increased, the rate showed a typical case of substrate-inhibited kinetics. A rate equation has been proposed, considering that each particle of supported aqueous phase catalyst is a microreactor, where the reaction takes place at the aqueous/organic interface. The kinetic model showed the good agreement with the experimental data, being the average relative error of estimation less than 7%. The kinetic parameters have been evaluated for different temperatures. The activation energy was found to be 71 kJ/mol.

Keywords: Hydroformylation; Gas–liquid–liquid–solid system; Supported aqueous phase catalysis

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1. Introduction

Among the several attempts to heterogenize the homogeneous catalysts, only the biphasic catalysis is successfully used in the industry [1,2]. But its use is limited due to poor solubilities of reactants in water [1,3]. The recent report about the possibility of supported aqueous phase catalysis (SAPC) [4] to take place in the external surface of the support [5] opens the way to apply SAPC at commercial scale.

On the other hand, the hydroformylation of olefins by SAPC is an example of a gas–liquid–liquid catalytic reaction on the solid phase, in which reaction of two gaseous reactants with liquid-phase olefin occurs in the presence of a water-soluble catalyst in the liquid–liquid interface on the hydrophilic support [5–7]. In this case, the rate of reaction will be governed by several factors like dissolution of CO, H_2 and olefins in both organic and aqueous phases, the solubility of these components, their partition coefficients, and the intrinsic kinetics of the reaction. The most important of these factors is the knowledge of kinetics, essential to understanding of the reaction mechanism and the elucidation of the rate-controlling step [3]. However, limited information is available on the kinetics of hydroformylation of olefins by SAPC [8–11].

In this paper, we report some important features of the kinetics of the hydroformylation of oct-1-ene under mild conditions (0.5–1 MPa, 80–100 °C), using

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$[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ as catalyst, by SAPC when the reaction occurs at the external surface of the support (silica Degussa Sipernat 50). Three kinetic models were evaluated for this purpose, and the best model was selected based on the minimum average error. The kinetic parameters have been evaluated for different temperatures.

2. Experimental

Reagents and solvents were purchased from Aldrich and SDS, and used without further purification. Rhodium trichloride trihydrated is a generous loan from Engelhardt-Comptoir Lyon-Alemand-Louyot. Tris(*m*-sodiumsulphonatophenyl)phosphine (TPPTS) is a generous gift from Hoechst (Ruhrchemie). Distilled, deionized water was used in all operations requiring water. All solvents, including water were degassed by three freeze-pump-thaw cycles. The complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ (Fig. 1) was prepared as described by Kalck et al. [12]. 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 [5]. The silica Degussa Sipernat 50 (DS50) was used to prepare SAPC catalyst. The detailed physical characterization of the silica DS50 has been reported before [13].

Catalytic tests were carried out in a high-pressure stirred stainless steel reactor of 500 ml capacity supplied by Autoclave Engineers. The experimental setup was described elsewhere [14,15]. 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, oct-1-ene 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. The reaction was then started by switching the stirrer on. The reaction was then 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 1-octene was less than 15%, to ensure differential conditions. The water content of the support in all experiments was 49.3%. At these conditions, the pores of the silica DS50 are saturated in water and then, the reaction takes place at the external surface of the support [5,16]. The molar ratio of rhodium to TPPTS used was 1:6 to ensure the optimal conditions for the stability of the catalytic complex [5,12].

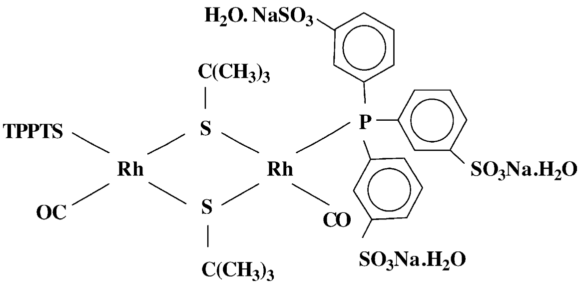

Fig. 1. The structure of the catalytic complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$.

The organic phase was analyzed 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), $T_{det} = 200\,^{\circ}C$, $P_{H_2} = 0.45$ bar.

3. Results and discussion

3.1. Solubility data

For interpretation of kinetic data, knowledge of the concentration of the gaseous reactants in the reaction medium is essential. The solubility of CO and H_2 in water, toluene, 1-octene and nonanal in the range of 298–363 K is available in the literature [14,17–21]. The solubility at 373 K was determined experimentally [16] by the absorption method as a function of gas pressure in the solvent [22] with an accuracy of 2–6%. The solubility values of CO and H_2 in pure toluene, octene and nonanal were further used for calculating the solubility of these gases in a mixture of solvents by using the method described by Hildebrand and Scott [23].

3.2. Preliminary results

The material balance and reproducibility were determined in preliminary experiments in which the amounts of 1-octene, products formed and the syngas consumed were compared. A typical concentration–time profile of CO, H_2, 1-octene and products as a function of time is shown in Fig. 2. There was roughly a 10 min induction period before any product of hydroformylation was observed. The precise reason for an induction period is not yet known, however, we believe the phenomenon is a complex one and could be due to the stabilization of the active form of the supported aqueous phase catalyst. The consumption of 1-octene and syngas was found to be stoichiometrically consistent (>96% material balance) with *n*-nonanal and 2-methyloctanal, the only formed products. The selectivity in lineal aldehyde did not change significantly during the study as function of the time. The linearity was in the range of 78–82%. No hydrogenation, isomerization and oxidation products were observed. The experimental relative error for the reproducibility of conversion was found to be in the range 4–7%.

The effect of agitation speed on the rate of hydroformylation was studied at 353 and 373 K to verify the significance of mass transfer. 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 1850 rpm.

Table 1
Range of conditions for kinetic study of the hydroformylation of 1-octene by SAPC on DS50 using the hydrosoluble complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$

Concentration of catalyst (kmol/m^3)	1.52×10^{-4} to 1.03×10^{-3}
Initial concentration of 1-octene (kmol/m^3)	0.195–6.372
Partial pressure of hydrogen (MPa)	0.15–0.55
Partial pressure of carbon monoxide (MPa)	0.15–0.55
Temperature (K)	353–373
Reaction volume (m^3)	3.5×10^{-4}

3.3. Initial rate data

In order to study the kinetics of the hydroformylation of 1-octene by SAPC on DS50 using the hydrosoluble complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$, several experiments were carried out in the range of conditions as shown in Table 1.

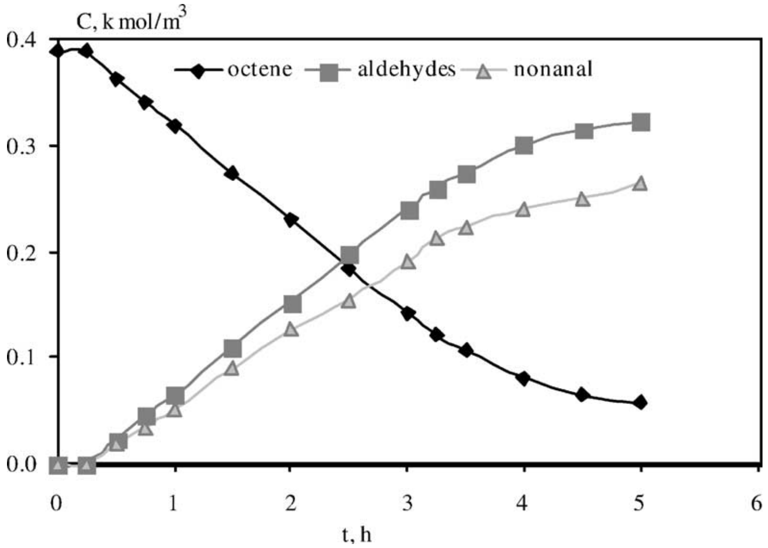

Fig. 2. Typical concentration–time profile for the hydroformylation of 1-octene by SAPC on silica DS50 ($T = 373$ K; $P = 1$ MPa; $H_2/CO = 1$; $C_{cat} = 3.71 \times 10^{-4}$ kmol/m^3; $C_{oct,0} = 0.389$ kmol/m^3).

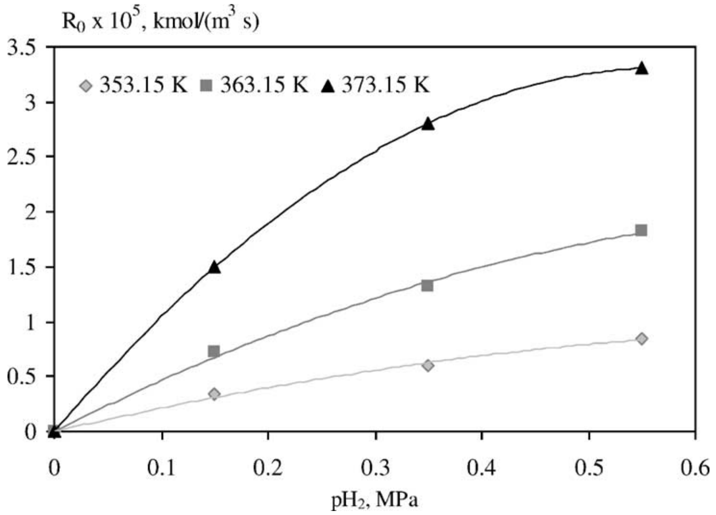

Fig. 3. Effect of P_{H_2} on initial rate of hydroformylation ($P_{CO} = 0.35$ MPa; $C_{cat} = 3.71 \times 10^{-4}$ kmol/m^3; $P/Rh = 6$; $C_{oct,0} = 0.39$ kmol/m^3).

The effect of partial pressure of hydrogen (P_{H_2}) on the rate of reaction was studied at constant partial pressure of carbon monoxide (P_{CO}) of 0.35 MPa and a catalyst concentration (C_{cat}) of 3.71×10^{-4} kmol/m^3. The results are shown in Fig. 3. The initial rate is positively dependent on the partial pressure of hydrogen with a partial order. The similar behavior was observed by Purwanto [14], Deshpande et al. [15] and Lekhal [19] when studied the biphasic hydroformylation of 1-octene in presence of cosolvent. It is probable that in the case of SAPC, as is also reported earlier in biphasic catalysis [24] there are other interaction possible with solvent which may lead to a partial order dependence of hydrogen as observed.

The effect of the partial pressure of CO on the rate of hydroformylation of octene ($P_{H_2} = 0.35$ MPa; $C_{cat} = 3.71 \times 10^{-4}$ kmol/m^3) is shown in Fig. 4. The rate first increased with increasing P_{CO} passed through a maximum, with substrate-inhibited kinetic at higher partial pressure of carbon monoxide. The negative effect of CO concentration on the rate of hydroformylation has been previously well established, in particular, for homogeneous [25–27], biphasic systems [14,15,19,28] and in SAPC [6,8]. Any further increase in CO after the maximum will cause the formation of inactive Rh species [28], and hence lower rates of reaction will be observed.

The effect of the concentration of the catalytic complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ was studied at P_{CO} and P_{H_2} of 0.5 MPa each and a constant 1-octene concentration of 0.39 kmol/m^3. The reaction rate of olefin hydroformylation by SAPC increased with an increase of the catalyst concentration, in the range under investigation, with a first-order behavior as shown in Fig. 5. This type of behavior is expected since an increase in the catalyst concentration will enhance the concentration of the active catalytic species and hence the rate.

The influence of initial 1-octene concentration on reaction rate was studied at a P_{CO} and P_{H_2} of 0.5 MPa and a catalyst concentration of 3.71×10^{-4} kmol/m^3. The results are shown in Fig. 6 as a plot of rate versus initial concentration of olefin at 353–373 K. The rate was found to increase with an increase in concentration up to a certain limit, beyond which it decreased with increasing octene concentration. This substrate-inhibited kinetics has been observed here for the first time in the hydroformylation of octene using a water-soluble Rh-complex, and is consistent at all the temperatures studied. However, a similar behavior was reported when the hydroformylation of 1-hexene in homogeneous system was investigated [27].

3.4. Kinetic model

The kinetic modeling of hydroformylation of olefins by SAPC has not been studied before. For the first time it was developed a kinetic model for

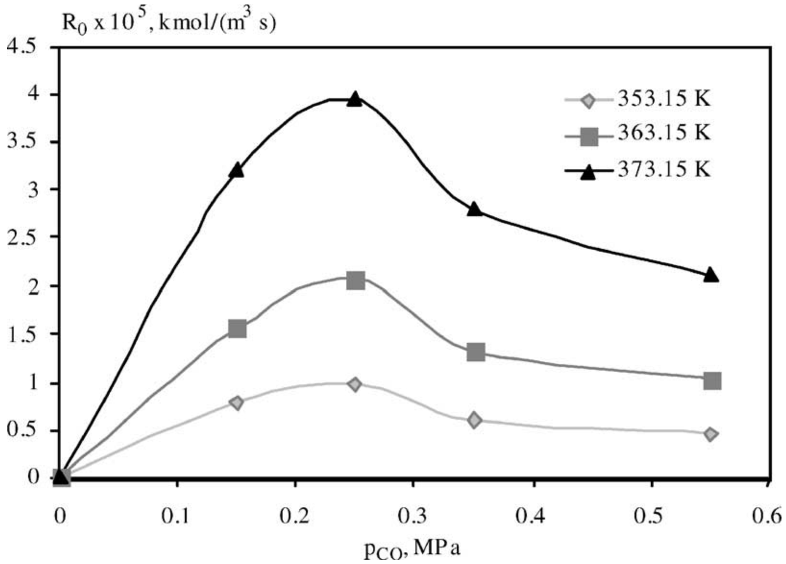

Fig. 4. Effect of P_{CO} on rate of hydroformylation ($P_{H_2} = 0.35$ MPa; $C_{cat} = 3.71 \times 10^{-4}$ kmol/m^3; P/Rh = 6; $C_{oct,0} = 0.39$ kmol/m^3).

1-octene hydroformylation by SAPC, when reaction occurs at the external surface of the silica support. For developing the rate model it was assumed that:

1. Reaction takes place in the organic–aqueous interface, as it was suggested by Horváth in SAPC [7]. In this case, it can be considered that the hydrosoluble complex remain mainly in the aqueous phase thanks to the sulfonated groups, but the rhodium can emerge with carbonyl groups to the organic part of the organic–aqueous interface [7].
2. Each particle of the support is a microreactor. Kalck et al. [29,30] and Tsang et al. [31] proposed that supported aqueous phase catalysts can be considered as microreactor or nano-reactors where

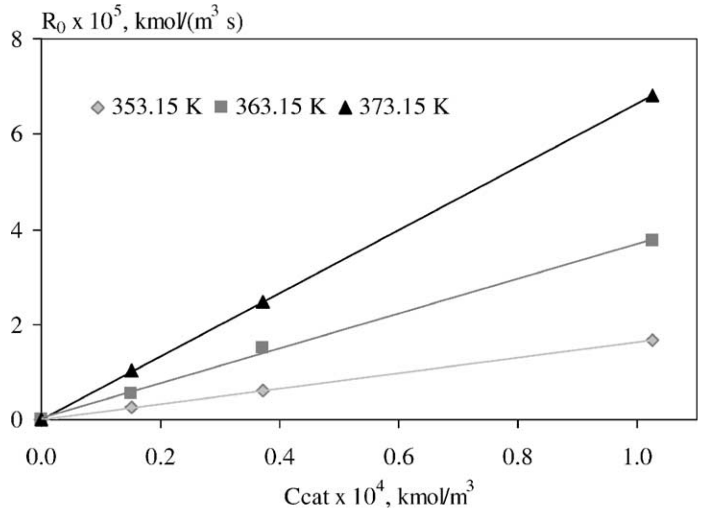

Fig. 5. Effect of catalyst concentration on rate of 1-octene hydroformylation ($P = 1$ MPa; P/Rh = 6; $C_{oct,0} = 0.39$ kmol/m^3).

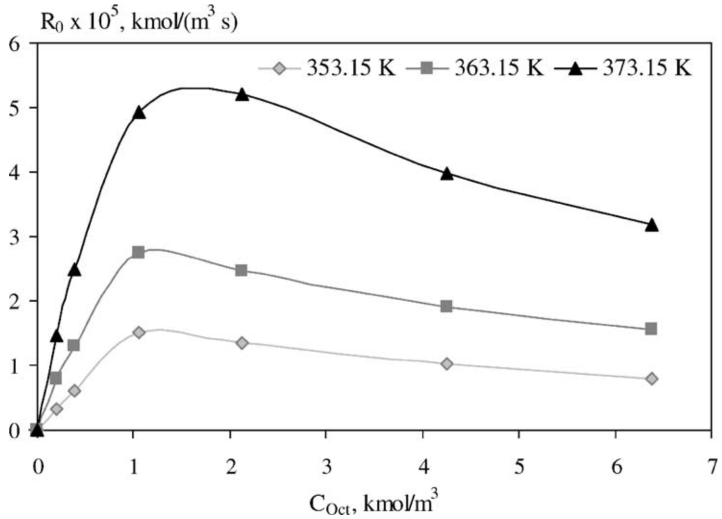

Fig. 6. Effect of initial concentration of 1-octene on rate of hydroformylation ($P = 1\,\text{MPa}$; $H_2/CO = 1$; $C_{cat} = 3.71 \times 10^{-4}\,\text{kmol/m}^3$; $P/Rh = 6$).

mass transfer and chemical reaction are improved if compare with classical biphasic systems. For this reason, we considered that all particles of support are spheres with a radius r_p, a hydration radius r_{H_2O} and a radius of organic phase in the aqueous–organic interface r^i_{org} (Fig. 7).

3. Taking into account that catalytic complex remains “anchored” in the aqueous phase, it was

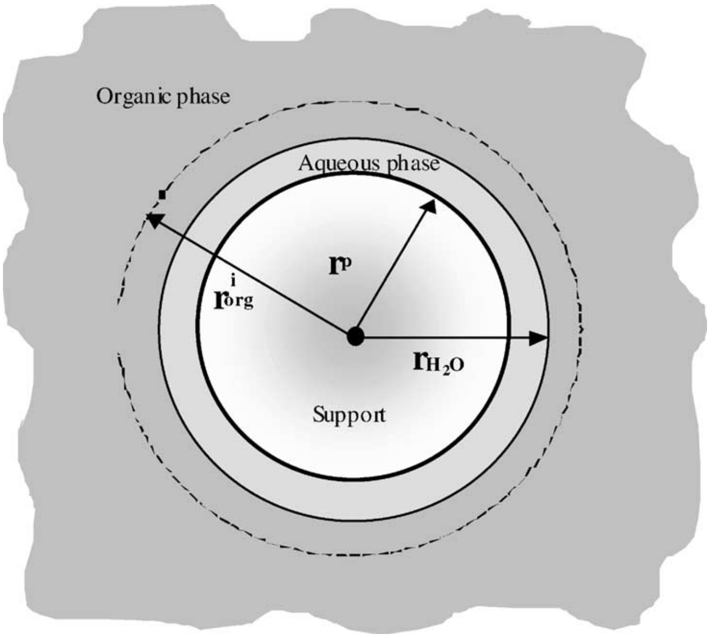

Fig. 7. A particle of the support as a microreactor in SAPC.

estimated that thickness of organic part of the aqueous phase is about 19.5 Å, value which corresponds to the largest lineal dimension of $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ complex.

4. The mass transfer is not limiting in the range of studied conditions. Then, the concentration of hydrogen, carbon monoxide and 1-octene is the same at the organic part of aqueous–organic interface and in bulk organic phase.

From these conditions, the concentration of reactants in the organic layer of aqueous–organic interface change in the next ranges:

- Hydrogen concentration: 5.69×10^{-2} to 4.64×10^{-2} kmol/m^3.
- Carbon monoxide concentration: 1.27×10^{3} to 2.17×10^{-2} kmol/m^3.
- Catalyst concentration: 4.83×10^{-3} to 3.26×10^{-3} kmol/m^3. In this case, the concentration was recalculated, from assumed conditions, considering that the catalytic rhodium is placed inside the spheres delimited by r^i_{org} (Fig. 7). The higher developed interface in SAPC explain why the hydroformylation of heavy alkenes ($C \geq 4$) takes place with high conversions if compare with biphasic catalysis [4–11]. Then, the proposed strategy for modeling considers the role of the inert support in increasing the contact between catalyst and reagents at the interface.

Since a rate model based on the mechanism of hydroformylation by SAPC has not been developed before, three different semiempirical kinetic models were evaluated, taking into account the general trends observed in the experiments:

$$R_0 = \frac{kC_{H_2}C_{CO}C_{cat}C_{oct}}{(1 + K_A C_{H_2})^l\,(1 + K_B C_{CO})^m} \tag{1}$$

$$R_0 = \frac{kC_{H_2}C_{CO}C_{cat}C_{oct}}{(1 + K_B C_{CO})^m\,(1 + K_D C_{oct})^n} \tag{2}$$

$$R_0 = \frac{kC_{H_2}C_{CO}C_{cat}C_{oct}}{(1 + K_A C_{H_2})^l\,(1 + K_B C_{CO})^m\,(1 + K_D C_{oct})^n} \tag{3}$$

The model (1) was used for describing the kinetics of the hydroformylation of 1-octene by biphasic catalysis [14,15]. This model did not consider the inhibition for the substrate. The model (2), proposed by Deshpande and Chaudhari [27], for the hydroformylation of 1-hexene considering the substrate inhibition when the concentration of olefin and carbon monoxide increased. However, the rate of reaction was found to be first-order with respect to catalyst concentration and partial pressure of hydrogen. The last model (3), proposed in this work for the specific case of the hydroformylation of 1-octene by SAPC differs of the model (2) in the one term, which considers the partial order of reaction with respect to partial pressure of hydrogen.

For the evaluation of the rate parameters, an optimization sequential routine was used. For this purpose, the guess values of the constants l, m and n in the denominator were first obtained using the sets of initial rate data in which only a single parameter was varied [27]. The average calculated values of l, m and n were 1, 3 and 3.63, respectively. Regressions of the experimental data to the rate models were performed using a corrected Newton algorithm. The procedure calculates the values of the isotherm parameters, which minimize the average standard error of estimation (SEE):

$$\text{SEE} = 100 \sum_{i=1}^{n} \frac{\left|\boldsymbol{R}^{\text{pred}}_{0,i} - \boldsymbol{R}^{\text{obs}}_{0,i}\right|}{\boldsymbol{R}^{\text{obs}}_{0,i}} \tag{4}$$

where $\boldsymbol{R}^{\text{obs}}_{0,i}$ is the elements of the vector containing the given experimental initial rate and $\boldsymbol{R}^{\text{pred}}_{0,i}$ the corresponding values calculated by the model being studied and n is the number of data points.

The selection of the most adequate model was performed using Fisher's test. The model selected exhibited the highest value of the Fisher parameter F_{calc} [32]:

$$F_{\text{calc}} = \frac{(n - l)\sum_{i=1}^{n}\left(\boldsymbol{R}^{\text{obs}}_{0,i} - \overline{\boldsymbol{R}^{\text{obs}}_{0}}\right)^2}{(n - 1)\sum_{i=1}^{n}\left(\boldsymbol{R}^{\text{obs}}_{0,i} - \boldsymbol{R}^{\text{pred}}_{0,i}\right)^2} \tag{5}$$

where $\overline{\boldsymbol{R}^{\text{obs}}_{0}}$ is the mean value of the vector of observed initial rates and l the number of adjusted parameters of the model.

Table 2 summarizes the results of the nonlinear regression analysis. The model (1) was discarded because the predicted rates were in poor agreement with the experimental values. Regarding to the values of the sum of squares (SS), the SEE and the calculated

Table 2
Comparison of different rate models proposed for the hydroformylation of 1-octene by SAPC (in models 1–3: $l = 1$; $m = 3$; $n = 3.63$)

Model	T (K)	k ($m^9\,kmol^{-3}\,s$)	K_A ($m^3\,kmol^{-1}$)	K_B ($m^3\,kmol^{-1}$)	K_D ($m^3\,kmol^{-1}$)	SS × 10^{10} ($kmol^2\,m^{-6}\,s^{-2}$)	F_{cal}	SEE (%)
1	353	99.4	58.5	112.6	–	6.89	0.31	74.09
	363	429.0	174.8	106.7	–	28.22	0.30	73.82
	373	1301.6	211.8	118.6	–	99.64	0.31	71.78
2	353	50.6	43.8	–	0.194	0.26	8.21	10.16
	363	99.7	39.6	–	0.240	0.65	13.05	10.61
	373	238.4	48.9	–	0.205	1.96	15.63	9.92
3	353	60.5	38.0	35.6	0.192	0.21	9.34	6.53
	363	113.6	36.5	32.7	0.220	0.47	16.19	6.58
	373	221.3	36.0	34.0	0.207	1.20	23.19	6.41

Fisher parameter it can be concluded that the best fit was obtained for the model proposed in this work (3) with a SEE less than 7% at all studied temperatures, which is within the range of the experimental error.

The activation energy calculated from the temperature dependence of the rate constants for the empirical model, using the Arrhenius equation was found to be 71 kJ/mol. This value is in the range of activation energy reported by other authors for the hydroformylation of 1-octene with different Rh-complexes by homogeneous, biphasic and SAPC: 68–75 kJ/mol [8,14,15,33].

4. Conclusions

The kinetics of hydroformylation of 1-octene has been investigated in the presence of hydrosoluble complex $[Rh_2(\mu\text{-S}^t\text{Bu})_2(CO)_2(TPPTS)_2]$ by SAPC at the external surface of the support DS50. The effects of different parameters like concentrations of 1-octene and catalyst and partial pressures of CO and hydrogen on the rate of reaction was studied in a temperature rate 353–373 K. A kinetic model has been proposed, considering that each particle of supported aqueous phase catalyst is a microreactor, where the reaction takes place at the aqueous/organic interface. The rate model proposed in this work was found to predict the experimental data within ±7% error at all temperatures. The kinetic parameters have been evaluated for different temperatures. The activation energy was found to be 71 kJ/mol.

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