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Hydrogenation of olefins in aqueous phase, catalyzed by polymer-protected rhodium colloids: kinetic study

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Abstract

Highly water-soluble polymer such as PVP was used to stabilize colloidal suspensions of active rhodium particles and to perform catalytic hydrogenation of oct-1-ene in a two liquid phase system. The effects of various parameters on the stability and activity of these nanoparticles under more or less severe conditions have been investigated. Experiments show that PVP–Rh colloids can be reused twice or more at 50°C and 0.3 MPa without losing activity. Much higher turnover than with usual biphasic catalysis were performed. The MET micrographs of the catalytic phase of the PVP–Rh system, before and after hydrogenation shows two nanometer particles containing rhodium oxide and metallic rhodium. IR and NMR spectroscopy analysis of the colloids shows geminal and terminal Rh–CO species with a preponderance of the geminal ones. The kinetics of biphasic hydrogenation and simultaneous isomerisation of oct-1-ene have been studied in the presence of ethanol cosolvent, using low concentrations of PVP–Rh colloids. The rate was found to be first order with respect to catalyst and olefin concentrations and hydrogen pressure. A kinetic model was fitted to the observed data, and was found to predict the rates with a good agreement. The activation energy was found to be as low as 3.4 kcal/mol suggesting the reaction to be limited by diffusion of oct-1-ene through the protective polymer layer. © 2001 Published by Elsevier Science B.V.

Keywords: Hydrogenation; Rhodium colloids; Stability; Kinetics

1. Introduction

Two liquid phase catalysis, employed in industry since its discovery in 1975, presents the advantage of easier catalyst separation, which reduces operation costs (catalyst being generally expensive) and/or avoids contamination of fine chemicals manufacture [1]. The most common procedure uses water-soluble catalysts made of transition metals coordinated to hydrophilic phosphines. Only cobalt and rhodium complexes are used on a commercial scale. Thus, a large variety of liquid olefins have been hydrogenated under very mild conditions (25°C, $P_{H_2} = 1$ atm) with a mixture of $RhCl_3$ and *m*-trisulfonated triphenylphosphine as its tri-sodium salt (TPPTS) in a 3:1 molar ratio [2]. In all cases, rapid and quantitative oxidation of the water-soluble phosphine was observed, leading to the formation of ligand protected colloids and black inactive metallic aggregates [3,4]. During the past decade, transition metal colloids were revealed as very efficient catalysts for various reactions, such as hydrogenation [4–7], hydrosilylation [8], hydroformylation [9] and some photocatalytic reactions [10]. Two liquid phase catalytic systems involving aqueous suspensions of colloidal metals, scarcely studied, are of great interest, provided that the colloidal particles remain stable in the aqueous phase during the whole catalytic process [2]. Such a condition may be achieved by the proper

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choice of protective colloidal agents which must be highly water-soluble, such as some polymers, e.g. poly(*N*-vinyl-2-pyrrolidone), “PVP” [11], polyvinyl alcohol, “PVA” [12], and polyvinyl acetate, “PVAc” [13] just to name a few. The kinetics of the selective hydrogenation of cyclooctadiene using PVP–Pd colloids in a homogeneous medium and of cyclopetadiene using colloidal palladium supported on chelate resin have been reported and rate models have been proposed [11,14]. In this paper, we first show under what conditions PVP can stabilize rhodium particles efficiently and secondly, analyze the kinetics of the hydrogenation and isomerisation of oct-1-ene in a biphasic liquid–liquid system using these PVP–Rh colloids.

2. Experimental

The experiments were carried out in a $5.0\times10^{-4}\,m^3$ 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. 1).

The precursor catalyst used was $RhCl_3.3H_2O$ (Acros). The polymer used was PVP (K15, MW: 10000) (Acros). Hydrogen was obtained from AGA, France. Oct-1-ene was provided by Acros Organics (99% purity), and absolute ethanol by Prolabo (Rectapur).

In a typical procedure, polymer-protected rhodium colloids were prepared according to the method reported by Hirai et al. [12]. Known amounts of $RhCl_3.3H_2O$ and PVP in a fixed mass ratio (polymer:Rh = 25:1) were added to an alcoholic solution. The mixture was refluxed for 3 h to obtain a dark-brown solution. Finally, oct-1-ene was added to the aqueous phase into the reactor. The content was heated to the desired temperature. After the thermal equilibrium was attained, the void space in the reactor was carefully flushed with hydrogen then pressurized to the selected level. The reaction was started by switching the stirrer on. The catalytic aqueous phase was recycled in order to test the stability of the system.

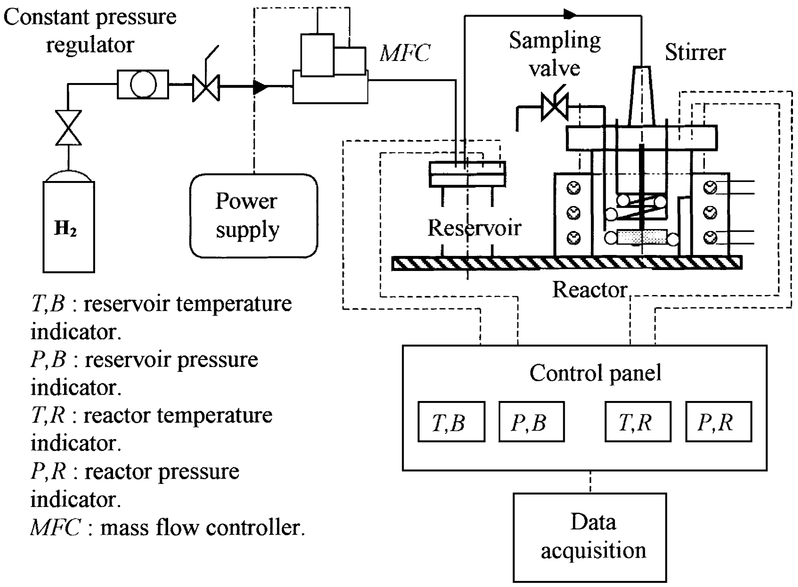

Fig. 1. Schematic representation of the experimental set-up.

Table 1
Influence of PVP stabilizer at various metal concentrations on the stability of rhodium colloids (50°C, 0.3 MPa, 50 wt.% ethanol, 2750 rpm, polymer:Rh = 25:1 (w/w))[a]

Experiment No.	$[Rh]_0$ (mol/m^3)	$[Rh]_1$ (mol/m^3)	$[Rh]_2$ (mol/m^3)	TOF_0 (s^{-1})	TOF_1 (s^{-1})	Literature TOF (s^{-1})
1	0.064	0.057	0.049	19.10	20.23	3.50[b]
2	0.095	0.090	0.070	18.73	19.05	0.023[c]
3	0.177	0.152	0.152	8.15	11.68	–
4	0.191	0.184	0.184	13.45	14.40	–
5	0.379	0.359	0.253	10.55	13.44	–

[a] $[Rh]_0$, $[Rh]_1$ and $[Rh]_2$ are concentrations in the aqueous phase before the reaction, after the first run and after the second run, respectively (30 min each run). TOF_0 [$mol_{octane}\, mol_{Rh}^{-1}\, s^{-1}$] and TOF_1 are turnover numbers according to $[Rh]_0$ and $[Rh]_1$ (calculated at initial times).

[b] 3 MPa, 323 K and 0.0597 mol/m^3 of a complex rhodium catalyst, oct-1-ene [17].

[c] 0.3 MPa, 298 K, 3 mol/m^3 of a complex rhodium catalyst, 1-hexene [18].

Analysis of the organic phase was performed, for kinetics by gas–liquid chromatography (HP-5890) in FFAP capillary column of 25 m length, whereas samples of the aqueous phase containing rhodium colloids were passed through an oxidizing flame in a Varian (AA-275 series) atomic absorption spectrophotometer for determination of the metal concentration. On the other hand, carbon monoxide was bubbled through the catalytic phase (fresh and used in catalysis) before analysis in Perkin Elmer 1710 infrared Fourier transform and Bruker AC-200 nuclear magnetic resonance spectrometers, in order to verify the presence of colloids in the solution and to check that no modification of these particles occurred during the reaction. Transmission electron microscopy (TEM) observations and examinations of the colloids just after their preparation and during the hydrogenation reaction were made on a Philips SEM-30 ST with 300 kV accelerated voltage.

3. Stability of PVP–Rh colloids

Colloids of rhodium prepared according to the literature were used in the hydrogenation of oct-1-ene. The results are summarized in Table 1 in terms of rhodium concentrations and corresponding turnover frequencies (TOF).

As shown in Table 1, under the operation conditions and at low rhodium concentrations in the aqueous phase (<0.191 mol/m^3) more stable colloids were obtained. In fact, after a slight diminution of the concentration in the first run, [Rh] remains unchanged. A very small quantity of fine and black deposit was observed at the interface between the two liquids after the first run. Nevertheless, reuse of the aqueous phase without those particles did not have any influence on the activity of the system. Besides, we can remark the existence of a deviation point when rhodium concentration is between 0.095 and 0.177 mol/m^3. Mass transfer control can be expected in the region beyond the rhodium concentration of 0.1 mol/m^3, where the independence of the reaction rate to the stirrer speed could not be achieved under 3000 rpm, the maximum stirrer speed.

CO chemisorption studies on the PVP-stabilized rhodium colloids (before and after use as catalyst for stability analysis) by IR spectroscopy show three main IR absorption bands which can be assigned to two different Rh–CO species: geminal $Rh(CO)_2$ (2059 and 1981 cm^{-1}) and terminal Rh–CO (2017 cm^{-1}). The geminal $Rh(CO)_2$ represents oxidized $Rh^{(I)}$ species, whereas the frequencies for the terminal CO are typical for $Rh^{(0)}$. Investigations were made by Bönnemann et al. [15] for surfactant-stabilized rhodium colloids. Geminal (2064 and 1988 cm^{-1}), terminal (2000 cm^{-1}) and bridged (1854 cm^{-1}) CO species were observed. Geminal bands represent very finely dispersed particles. This was illustrated by Yates et al. [16]. In the same way, ^{13}C NMR analyses of the samples in deuterated water proved the existence of two thin peaks at 179.84 and 179.98 ppm corresponding to $Rh(CO)_2$ (Fig. 2). These results were confirmed by TEM images where very finely dispersed particles of a mean diameter of 2.063 nm were observed.

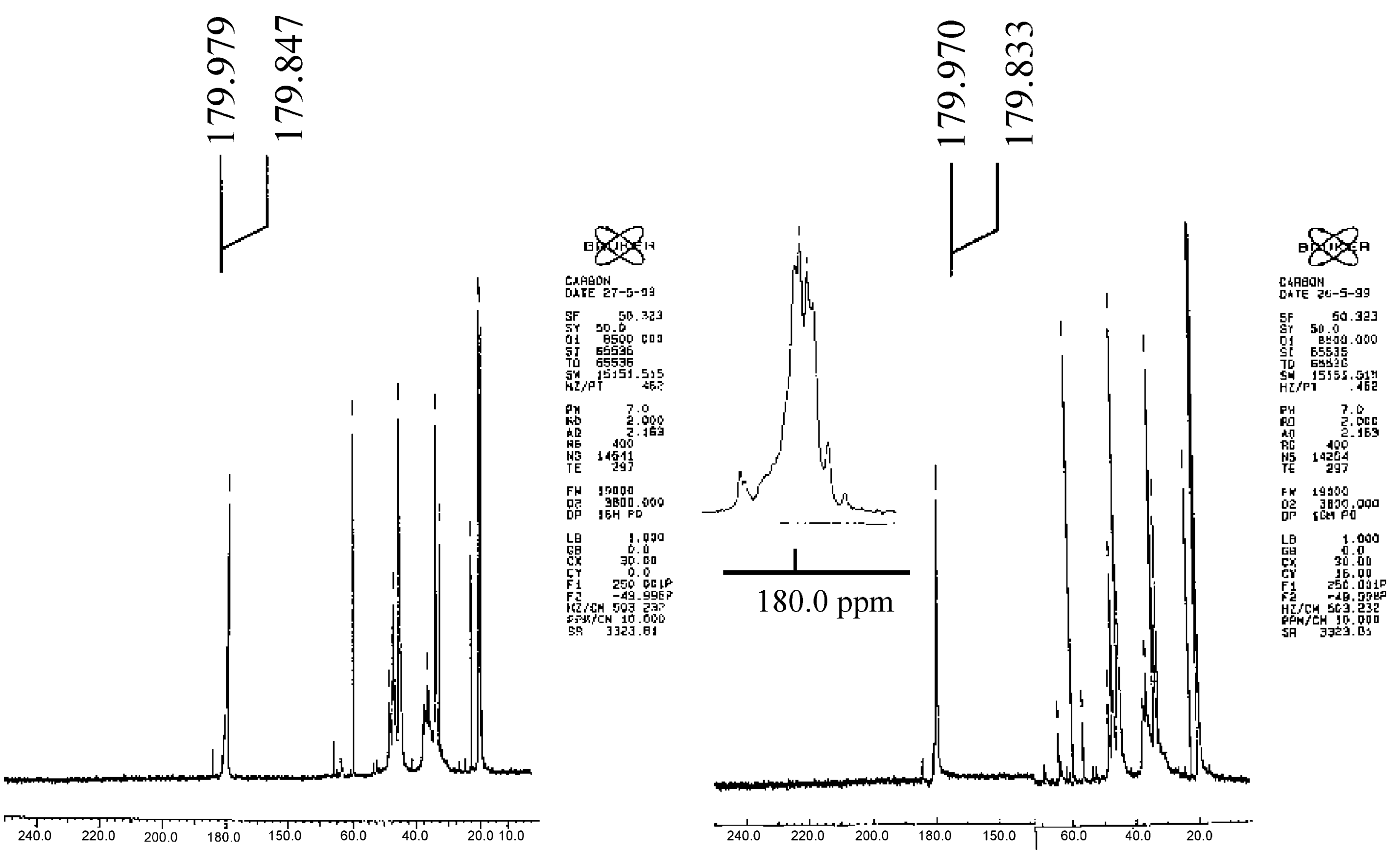

Fig. 2. ^{13}C NMR spectra of adsorbed CO on a PVP-stabilized rhodium colloid before (left side) and after (right side) hydrogenation reaction of oct-1-ene.

4. Kinetic study

4.1. *Effect of oct-1-ene concentration*

Experiments were carried out to investigate the effect of oct-1-ene concentration in the aqueous phase on the rate of reaction at 303 and 323 K, hydrogen pressure of 0.3 MPa and catalyst concentration of 0.095 mol/m^3. The variation of oct-1-ene concentration in the catalytic phase can be achieved by using different octane/oct-1-ene ratios. This method was preferred to that employed by Hablot et al. [19] which consists in adding different quantities of ethanol in the aqueous phase, involving simultaneous changes of hydrogen solubility in the aqueous phase. In our case, a first order dependence of the reaction rate with respect to the concentration of oct-1-ene in the catalytic aqueous phase was clearly proven as presented in Fig. 3. The same result was obtained by Hirai et al. [14] in the hydrogenation of cyclopentene in a homogeneous alcoholic phase, catalyzed by resin supported palladium colloids.

4.2. *Effect of rhodium concentration*

The catalyst concentration was varied by diluting the colloidal mixture. The effect of the concentration of the catalyst on the rate was studied at a hydrogen pressure of 0.3 MPa and a constant olefin concentration. Fig. 4 indicates that the rate of reaction is enhanced with the catalyst concentration with a first order dependence at low rhodium concentrations ([Rh] < 0.095 mol/m^3).

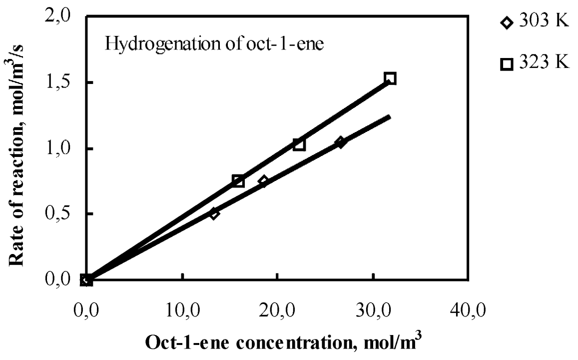

Fig. 3. Effect of oct-1-ene concentration in the catalytic aqueous phase on the rate of the reaction. [Rh]: 0.095 mol/m^3, P_{H_2}: 0.3 MPa, PVP/Rh: 25/1, volumes: octane + oct-1-ene : 0.28 × 10^{-4} m^3, aqueous phase (50 wt.% ethanol): 1.0 × 10^{-4} m^3.

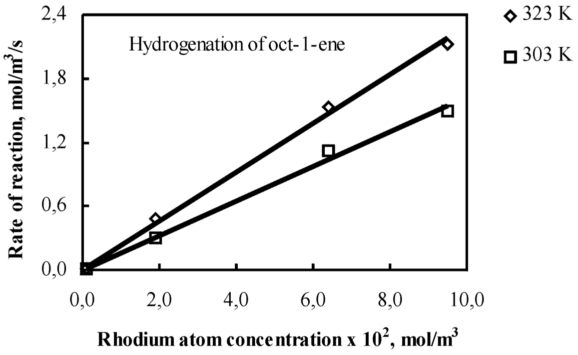

Fig. 4. Effect of catalyst concentration on the rate of the reaction. P_{H_2}: 0.3 MPa, PVP/Rh: 25/1, aqueous phase:1.0 × 10^{-4} m^3 (50 wt.% ethanol), organic phase (oct-1-ene): 0.28 × 10^{-4} m^3.

This type of behavior 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.

4.3. *Effect of hydrogen pressure*

The effect of hydrogen pressure on the rate of reaction was studied at a catalyst concentration of 0.095 mol/m^3 at 303 and 323 K. The rate of the reaction as shown in Fig. 5 was enhanced by increasing the hydrogen pressure with a first order dependence.

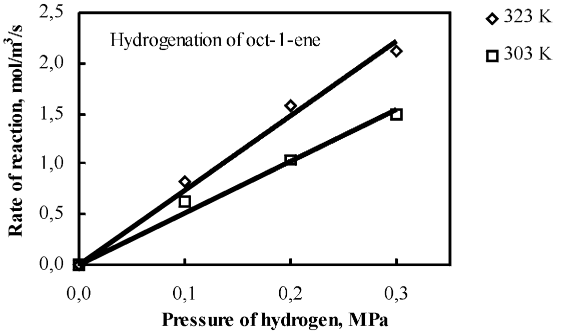

Fig. 5. Effect of hydrogen pressure on the rate of the reaction. [Rh]: 0.095 mol/m^3, PVP/Rh: 25/1, aqueous phase: 1.0 × 10^{-4} m^3 (50 wt.% ethanol), organic phase (oct-1-ene): 0.28 × 10^{-4} m^3.

5. Kinetic model

The kinetic data observed were used for the development of a rate model. According to the results, the rate R for oct-1-ene hydrogenation can be expressed in the following form:

$$R = k_1[\mathrm{Rh}]P_{\mathrm{H}_2} \tag{1}$$

where k_1 is the rate constant. Nevertheless, this model does not represent what happens during the reaction. Kinetic parameters optimization was performed for different reaction schemes, using the time dependent concentrations. It can be concluded that three parallel reactions take place: hydrogenation of oct-1-ene, its isomerisation and hydrogenation of the isomers. We have finally selected the following simplified scheme:

$$\text{Oct-1-ene} + \mathrm{H_2} \xrightarrow{k_1} \text{Octane}$$

$$\text{Oct-1-ene} \xrightarrow{k_2} \text{Isomers of oct-1-ene}$$

$$\text{Isomers of oct-1-ene} + \mathrm{H_2} \xrightarrow{k_3} \text{Octane}$$

The parameters were determined by a convenient routine of optimization using the complete hydrogenation runs during time and not only initial rates. The optimized mechanistic model was found to be in good agreement with experimental results. The results of the kinetics of the isomerisation of oct-1-ene and the hydrogenation of the isomers are introduced here, show in the same way as presented earlier, first order dependencies with respect to rhodium atom concentration, pressure of hydrogen and substrate aqueous phase concentrations. The data required in the optimization program such as hydrogen and oct-1-ene solubility in the aqueous phase were determined experimentally [20]. The comparison between experimental data and optimized model is presented in Figs. 6 and 7. The parameter values obtained are presented in Table 2.

The activation energy calculated from the temperature dependence of the rate constants (at 303, 313

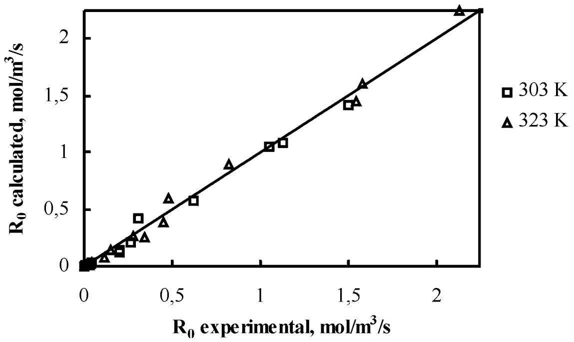

Fig. 7. Comparison between experimental and calculated values of the rate of octane formation.

Table 2
Rate parameters

Parameter (m^3/mol/s)	303 K	323 K
$k_1 \times 10^{-3}$	0.3030	0.3828
$k_2 \times 10^{-4}$	0.3760	0.8426
$k_3 \times 10^{-4}$	0.2470	0.2545

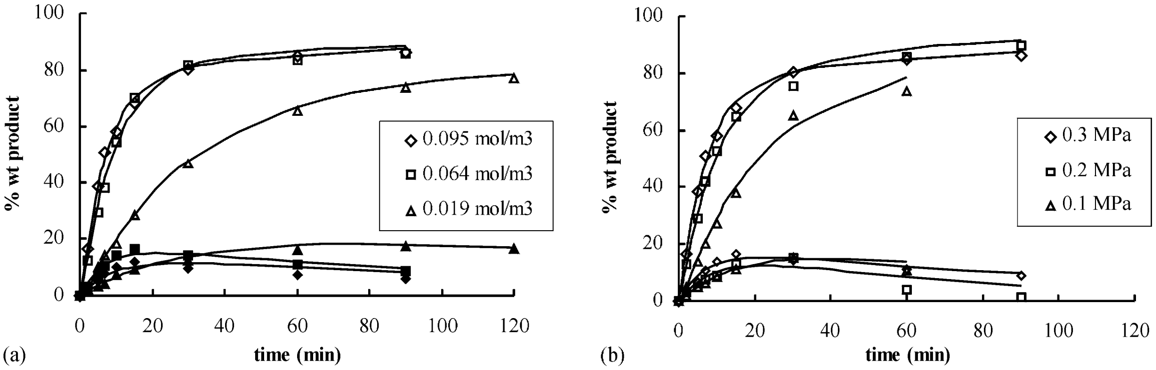

Fig. 6. Influence of catalyst concentration (left side) and hydrogen pressure (right side) on octane and isomers formation. Comparison between experimental values and calculations based on step by step liquid–liquid equilibria.

and 323 K), using the Arrhenius equation was found to be 3.4 kcal/mol for the hydrogenation of oct-1-ene and 4.9 kcal/mol for the isomerisation of oct-1-ene (8.0 kcal/mol was obtained by Hirai et al. [14] for the hydrogenation of cyclopentene).

6. Conclusion

The effect of various parameters on the stability of Rh nanoparticles under more or less severe conditions has been studied. The polymer-stabilized rhodium colloidal system shows very attractive performances. Remarkably high values of the turnover numbers were obtained here in, comparison with those obtained with classical complex catalysts in a biphasic liquid–liquid system. The presence of ethanol in the medium is of great interest as a foam-controlling agent. In addition, the loss of rhodium in the organic phase did never exceed 2 ppm.

The kinetics of hydrogenation of oct-1-ene with its parallel isomerisation and hydrogenation of the isomers have been investigated in biphasic media using PVP–Rh colloids. The effect of different parameters like concentration of olefin and catalyst, and pressure of hydrogen was investigated in the temperature range 303–323 K. The rate was found to be first order with rhodium concentration, hydrogen pressure and oct-1-ene concentration. A simplified kinetic model was conveniently optimized. The activation energies were very low, especially for the main reaction of oct-1-ene hydrogenation, 3.39 kcal/mol, suggesting severe diffusional limitations in the layer of polymer around the colloidal particles.

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