



Catalytic conversions in green aqueous media: Highly efficient biphasic hydrogenation of benzene to cyclohexane catalyzed by Rh/TPPTS complexes

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ABSTRACT

Exceptionally, high catalytic activities (TOF > 204,000 h⁻¹) have been achieved in the hydrogenation of benzene to cyclohexane catalyzed by water-soluble Rh/TPPTS complexes [TPPTS = P(C₆H₄-*m*-SO₃Na)₃] in green aqueous/organic two-phase systems. The influence of several operating parameters on the biphasic benzene hydrogenation reaction was investigated. A great advantage of this reaction is that the highest catalytic activity was achieved at a low volume ratio of aqueous/benzene phase of 0.4. Rh/TPPTS catalytic complexes, which are stable toward sulfur-containing compounds, were easily recovered by a simple phase separation, and recycling experiments showed that the catalytic activity remained high in five consecutive runs.

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1. Introduction

The hydrogenation of benzene to cyclohexane is one of the most important industrially practiced aromatic compounds hydrogenation reactions [1]. Millions of tonnes of benzene are hydrogenated to cyclohexane per year, and about 90% of world's production of cyclohexane is used for manufacturing nylon 6 and nylon 6.6, which are about 90% of all polyamides. Nowadays, almost the whole world's production capacity of cyclohexane is manufactured by the route of the hydrogenation of benzene. However, despite its apparent simplicity, the hydrogenation reaction of benzene has evolved through many variations and has given rise to many different processes. The successful industrial hydrogenation of benzene suitable for petrochemical cyclohexane production requires the resolution of three major critical problems: (i) the reaction is strongly exothermic with a $\Delta H_f^{0(473\text{ K})}$ of $-214.2\text{ kJ mol}^{-1}$, (ii) the cyclohexane must be pure, and (iii) the low stability of heterogeneous catalysts *e.g.*, nickel catalysts which require extremely pure benzene feedstocks with less than 1 ppm sulfur in order to remain effective in the liquid phase under mild conditions. The strongly exothermic hydrogenation reaction requires careful con-

trol of temperature, pressure and residence time in order to achieve quantitative conversion of benzene at very high cyclohexane selectivity. Thus, significant formation of methylcyclopentane, which is favored at higher temperatures, has to be suppressed together with other by-products such as methylpentane, *n*-hexane, *n*-pentane and methane obtained by isomerization and hydrocracking side reactions. These undesired by-products can be separated from the cyclohexane product only by complicated separation methods such as rectification, extraction and by molecular sieves [1].

A large number of industrial processes for the heterogeneous catalytic hydrogenation of benzene to cyclohexane have been developed, which are carried out in the liquid or in the gas phase. Among the well-known liquid phase benzene hydrogenation processes are the Mitsubishi, Sinclair and Institut Franais du Ptrole (IFP) process [1]. The IFP process uses a Raney nickel heterogeneous catalyst in a bubble column reactor at temperatures between 200 and 230 °C under 50 bar. The main drawbacks with this process are due to the fact that the Raney nickel catalyst possesses a low stability toward sulfur-containing compounds unavoidable in benzene feedstock and that the catalyst is pyrophoric to a greater or less extent. Benzene feedstock requires deep desulfurization to a sulfur content of <1 ppm, which considerably increases the cost of the whole process. Well-known gas phase

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benzene hydrogenation processes were developed by UOP (Hydrar process), DSM, Toray, Arco and Houdry under forcing conditions (400–600 °C, $P_{H_2} = 30$ bar) and short residence times [1]. Furthermore, IFP has developed a homogeneous catalytic process for the hydrogenation of benzene to cyclohexane by Ziegler-type catalysts based on triethylaluminium with a nickel or cobalt salt [2]. In a typical patent example [2d], benzene was quantitatively hydrogenated to cyclohexane using a catalyst prepared from a mixture of nickel stearate and triethylaluminium at 180 °C and 7 bar H_2 pressure within 2-h reaction time. The nature of such Ziegler-type catalysts is poorly defined, which in the case of nickel does not give solids on ultracentrifugation and it is highly probable that the catalyst solution contains transition metal hydrides or alkyl species stabilized with coordination to the aluminium metal [2].

A general trend is to reduce the quantities of benzene in gasoline and of other aromatics in diesel fuel because of their known toxic properties [3]. The benzene content in gasoline depends largely on the reformate component in that gasoline, which could be hydrogenated to cyclohexane. However, this hydrogenation reaction cannot be performed in a mixture of hydrocarbons containing toluene and xylenes. This mixture must be first fractionated to isolate the cut of benzene, which could then be hydrogenated. More and more environmental regulations governing diesel fuel specifications are set up to limit the aromatic content to low levels and therefore new catalytic processes for aromatics hydrogenation in middle distillates are receiving increasing attention [3]. The hydrogenation of aromatic compounds is more difficult to be achieved than hydrodesulphurization and hydrodenitrogenation over conventional hydrotreating catalysts under conditions that are normally used for lowering sulfur and nitrogen levels. The hydrogenation of polyaromatics to monoaromatics occurs even at low severity but the monoaromatics stay nearly unchanged. The hydrogenation of monoaromatics is the key step for the production of low aromatic diesel fuel. Several heterogeneous hydrotreating catalytic processes were developed for deep aromatic hydrogenation in diesel fuel such as by IFP, Shell, Criterion jointly with Lummus Crest Inc. (SynSat process) and Haldor Topsøe [3].

Trisulfonated triphenylphosphine (TPPTS) catalytic complexes of transition metals are water-soluble, which provides for their facile recovery from organic products by a simple phase separation in aqueous/organic biphasic industrial catalytic processes [4]. Interest in this concept of heterogenization of homogeneous catalysis employing aqueous/organic two-phase systems has been further stimulated by increasing environmental constraints because catalysis in aqueous media obviates the need for conventional organic toxic solvents, and water is a non-toxic, non-inflammable, safe, inexpensive, abundantly available and a green solvent [4,5]. Moreover, the large heat capacity of water makes it an excellent medium to perform exothermic reactions more safe and selective, which is especially important in industrial large-scale exothermic catalytic processes [4,5]. Rh/TPPTS catalysts have found important industrial applications such as in the biphasic Ruhrchemie/Rhône-Poulenc process for the hydroformylation of lower olefins [4]. A great number of biphasic catalytic hydrogenation reactions of benzene in aqueous/organic two-phase systems have been described in the literature. Usually, these biphasic reactions are either catalyzed by nanoparticles and clusters when the catalysts stay in the aqueous phase or catalyzed by homogeneous complexes, which are soluble in the upper organic phase [6]. Many transition metal catalytic complexes originally assigned as homogeneous in the hydrogenation of aromatics have subsequently been shown to be heterogeneous catalytic metal particles [7]. In contrast, there are only a few reports on the hydrogenation of benzene catalyzed by water-soluble transition metal complexes modified with sulfonated phosphines in aqueous/organic two-phase systems, and all of these catalytic complexes exhibited low activities [8–12]. Par-

mar et al. [8] developed the hydrogenation of benzene to cyclohexane catalyzed by Ru/TPPTS complexes, which exhibited a low catalytic activity of TOF = 0.6 h⁻¹; and after addition of ZnCl₂, the rates were improved to TOF = 1.6 h⁻¹ in aqueous/organic two-phase systems. Dyson et al. [9] obtained a higher activity of TOF = 488 h⁻¹ using Ru/TPPTS catalysts in the aqueous/organic biphasic hydrogenation of benzene to cyclohexane. Ellis et al. [10] applied Ru₃(CO)₁₁(TPPTS) clusters in the biphasic hydrogenation of benzene to cyclohexane, which exhibited an activity of TOF = 45 h⁻¹ with, however, decomposition of the cluster to colloidal ruthenium catalytic active species. Suárez et al. [11] showed that Ru/TPPTS catalytic complexes (TPPTS = disulfonated triphenylphosphine) are capable to hydrogenate benzene to cyclohexane with an activity of TOF = 60 h⁻¹ in aqueous/organic biphasic media. Baricelli et al. [12] disclosed that W/TPPTS catalysts (TPPTS = monosulfonated triphenylphosphine) could hydrogenate benzene to cyclohexane with a low catalytic activity of TOF = 0.4 h⁻¹ under basic biphasic conditions and, interestingly, W/TPPTS catalysts are not capable to hydrogenate the aromatic ring of styrene, which after hydrogenation only of the side olefinic moiety yields ethylbenzene [12]. The TOFs in references [8–12] are calculated as per mole of benzene molecules per mole of transition metal per hour. Furthermore, Baricelli et al. [13] showed that W/TPPTS catalysts similarly hydrogenate only the side olefinic groups of styrene and allylbenzene to give ethylbenzene and propylbenzene, respectively, and the aromatic moieties remain intact in micellar aqueous/organic biphasic media. We now report on the hydrogenation of benzene to cyclohexane using highly active, selective and stable water-soluble Rh/TPPTS catalytic complexes in aqueous/organic two-phase systems, which may yield a new industrial process for the production of cyclohexane where the green and safe aqueous medium provides the means for quantitative recovery and recycling of the catalytic complex by a simple phase separation [14].

2. Experimental

2.1. Materials

Benzene was purchased from Panreac Quimica SA, which contains 4 ppm of sulfur compounds and was used without any further purification. Distilled demineralized water was deoxygenated in an ultrasound bath under vacuum for 2 h. During the deoxygenation, the flask was disconnected from the vacuum, and the aqueous solvent was saturated with argon; this procedure was repeated several times. RhCl₃·3H₂O, Brij-30, Brij-35 and dodecyltrimethylammonium chloride (DTAC) were purchased from Acros Organics and used without any further purification. Hydrogen (quality 5.0) was purchased from Air Liquide Hellas A.E.B.A. (Athens) and was used without further purification. TPPTS was prepared according to literature procedures [15] and isolated with purity higher than 98%. The remainder of the water-soluble ligand consisted of TPPDS.

2.2. Typical hydrogenation procedure

In 10 ml deaerated distilled demineralized water, 2.63 mg (0.01 mmol) RhCl₃·3H₂O and 18.5 mg (0.03 mmol) TPPTS, (TPPTS/Rh molar ratio = 3) were dissolved under argon. Immediately this aqueous catalyst solution, having a rhodium concentration of 100 ppm, with 2.34 g (30 mmol) of benzene which results a two-phase system were charged into an Autoclave Engineers autoclave (100 ml) which was previously purged with argon. In the reaction mixture, the molar ratio of C=C units/Rh was 9000. After a number of pressurising–depressurising cycles with hydrogen to remove last traces of air oxygen, the autoclave was pressured, and contents

were heated with stirring (stirring rate = 670 rpm). At the reaction temperature of 120 °C, the hydrogen partial pressure was 30 bar and the reaction time 10 min. After the reaction, the autoclave was cooled to room temperature, vented of hydrogen and the reaction mixture removed. The upper organic layer was easily separated from the lower aqueous layer containing the catalyst and dried over sodium sulfate. The organic layer containing the products was analyzed by gas chromatography (GC) and ^1H NMR spectrometry after addition of *n*-dodecane as standard, and the results obtained are summarized in Table 1, entry 1/5.

2.3. Analysis of TPPTS ligand and of the hydrogenation reaction mixture

The purity of the TPPTS ligand [15] was determined by quantitative $^{31}\text{P}\{^1\text{H}\}$ NMR analysis in D_2O at 25 °C. $\delta_{\text{TPPTS}} = -5.4$ ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, referenced to external 85% H_3PO_4) and ^1H NMR (300 MHz) spectra were recorded on a Varian Unity Plus 300/54 spectrometer. The cyclohexane hydrogenation product was identified by comparison of GC and NMR analytic data with data for authentic sample. GC analyses of the benzene hydrogenation mixtures were run on a Shimadzu GC-14B equipped with a flame ionization detector (FID) and a HP-Innowax capillary column (30 m \times 0.251 mm i.d. \times 0.50 μm film thickness), which was purchased from Agilent Technologies. Carrier gas was N_2 at 50 kPa. The oven temperature was 85 °C. The injector and detector temperatures both were set at 240 °C.

2.4. Dynamic light scattering

Measurements were conducted with a Series 4700 Malvern system composed of a PCS5101 goniometer with a PCS stepper motor controller, a Cyonics variable power Ar^+ laser, operating at 488 nm, a PCS8 temperature control unit, a RR98 pump/filtering unit and a 192 channel correlator for the accumulation of the data. The correlation functions were analyzed by the cumulant method and CONTIN software. Measurements were carried out at 45°, 90° and 135°.

3. Results and discussion

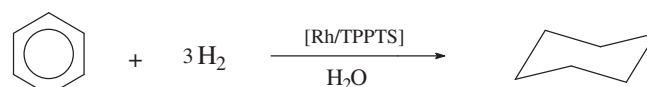
3.1. Hydrogenation of benzene to cyclohexane catalyzed by Rh/TPPTS complexes in aqueous/organic two-phase systems

First, we investigated the influence of operating parameters such as temperature, TPPTS/Rh molar ratio, hydrogen partial pressure, volume ratio of the aqueous/benzene phase, C=C units/Rh

molar ratio and the pH value on the hydrogenation of benzene to cyclohexane (Scheme 1) catalyzed by highly active water-soluble Rh/TPPTS complexes in aqueous/organic two-phase systems. Furthermore, we studied the Rh/TPPTS-catalyzed hydrogenation of benzene to cyclohexane in the presence of non-ionic surfactants added above their critical micelle concentration (CMC) in order to get information regarding mass transfer limitations resulting from the low solubility of benzene in water. The solubility of benzene in pure water is 1.1 g/L [6d]. Moreover, we recovered water-soluble Rh/TPPTS catalytic complexes in active form by a simple phase separation of the bottom aqueous phase from the upper organic layer and recycling experiments of the aqueous catalyst phase were performed to prove that the catalytic activity and selectivity to cyclohexane remained high in several consecutive runs.

3.1.1. Effect of temperature and the TPPTS/Rh molar ratio

The biphasic hydrogenation reaction of benzene catalyzed by water-soluble Rh/TPPTS complexes started immediately with H_2 consumption without to be observed any induction period. No pre-reduction of the Rh/TPPTS catalyst, therefore, was carried out and only made sure that the reaction conditions were well chosen in order to obtain reproducible results. All the benzene hydrogenation experiments were performed systematically without a prior pre-reduction of the Rh/TPPTS catalyst. Table 1 presents the activity and selectivity of the water-soluble Rh/TPPTS catalyst in the hydrogenation of benzene to cyclohexane in aqueous/organic two-phase systems as a function of reaction temperature and of the molar ratio of the TPPTS ligand to the $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ precursor. At a reaction temperature of 80 °C, molar ratios of C=C units/Rh = 9000 and of TPPTS/Rh = 3, a rhodium concentration of 100 ppm in water, a volume ratio of the aqueous/benzene phase = 2.2 and 30 bar hydrogen partial pressure, the catalytic activity was low to give a turnover frequency (TOF) of 25,200 h^{-1} with, however, quantitative selectivity to cyclohexane (Table 1, entry 1/1). The TOFs quoted in this work are calculated as per mole of hydrogenated C=C units of benzene per mole of Rh per hour and are indicated in the tables. The catalytic activity increases with incrementing temperature up to 130 °C to give TOF values up to



Scheme 1. Rh/TPPTS-catalyzed hydrogenation of benzene to cyclohexane in aqueous/organic two-phase systems.

Table 1
Effect of temperature and the P/Rh molar ratio on the biphasic hydrogenation of benzene catalyzed by Rh/TPPTS complexes in the absence of added organic solvents.^a

| Entry | Catalyst precursor | C=C/Rh molar ratio | T (°C) | P/Rh molar ratio | P_{H_2} (bar) | Conv. (mol%) | Selectivity cyclohexane (mol%) | TOF ^b (h^{-1}) |
|-------|--------------------------------------------------------|--------------------|--------|------------------|------------------------|--------------|--------------------------------|--------------------------------------|
| 1/1 | $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ | 9000 | 80 | 3 | 30 | 47 | 100 | 25,200 |
| 1/2 | $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ | 9000 | 90 | 3 | 30 | 56 | 100 | 30,150 |
| 1/3 | $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ | 9000 | 100 | 3 | 30 | 86 | 100 | 46,600 |
| 1/4 | $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ | 9000 | 110 | 3 | 30 | 91 | 100 | 49,300 |
| 1/5 | $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ | 9000 | 120 | 3 | 30 | 89 | 100 | 48,100 |
| 1/6 | $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ | 9000 | 120 | 3 | 30 | 98 | 100 | 53,000 |
| 1/7 | $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ | 15,000 | 120 | 3 | 50 | 77 | 100 | 69,000 |
| 1/8 | $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ | 15,000 | 120 | 4 | 50 | 88 | 100 | 79,050 |
| 1/9 | $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ | 15,000 | 120 | 5 | 50 | 87 | 100 | 78,250 |
| 1/10 | $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ | 15,000 | 120 | 8 | 50 | 83 | 100 | 74,800 |
| 1/11 | $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ | 15,000 | 120 | 12 | 50 | 68 | 100 | 60,700 |
| 1/12 | $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ | 15,000 | 120 | 16 | 50 | 53 | 100 | 47,800 |

^a Reaction conditions: $t = 10$ min; 2.63 mg (0.01 mmol) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$; 10 ml deaerated distilled demineralized water; $[\text{Rh}] = 100$ ppm; pH of the aqueous catalyst phase after the reaction = 2.8–3.5; entries 1/1–1/6: 2.34 g \approx 2.67 ml (30 mmol) benzene, $V_{\text{H}_2\text{O}}/V_{\text{benzene}}$ (ml/ml) = 3.7; entries 1/7–1/12: 3.90 g \approx 4.46 ml (50 mmol) benzene, $V_{\text{H}_2\text{O}}/V_{\text{benzene}}$ (ml/ml) = 2.2; stirring rate = 670 rpm.

^b Defined as mole of hydrogenated C=C units of benzene per mole of Rh per hour.

53,000 h⁻¹ with quantitative selectivity to cyclohexane (entries 1/2–1/6). The Rh/TPPTS-catalyzed hydrogenation of benzene is influenced by the molar ratio of added TPPTS ligand to the RhCl₃·3H₂O precursor. As expected, the highest catalytic activity (TOF = 79,050 h⁻¹) was obtained at low TPPTS/Rh molar ratios i.e., of 4 (entry 1/8), whereas at increasing ligand/metal molar ratios the catalytic activity dramatically decreases to give at a ratio of TPPTS/Rh = 16 a TOF value of only 47,800 h⁻¹ (entries 1/9–1/12). This lower catalytic activity at higher TPPTS/Rh molar ratios could probably be rationalized by assuming that a competition between the free TPPTS ligand and the C=C units of benzene for a coordination site on rhodium takes place which may lead to a retardation in the activation of the benzene hydrogenation reaction.

3.1.2. Effect of hydrogen pressure, the volume ratio of aqueous/benzene phase and the C=C units/Rh molar ratio

To study the dependence of hydrogen partial pressure on the Rh/TPPTS-catalyzed biphasic hydrogenation of benzene, a series of reactions were carried out by varying the pressure over the range of 30–80 bar at 120 °C keeping the molar ratios of C=C/Rh (15,000) and P/Rh (3), the volume ratio of the aqueous/benzene phase (2.2) and the rhodium concentration (100 ppm) constant. A beneficial effect of dihydrogen partial pressure was shown in

the biphasic benzene hydrogenation reaction since the catalytic activity increased from TOF = 55,900 h⁻¹ to TOF = 86,800 h⁻¹ with increasing pressure from 30 to 80 bar (Table 2, entries 2/1–2/5). The effect of the volume ratio of the aqueous/benzene phase in the biphasic benzene hydrogenation reaction catalyzed by water-soluble Rh/TPPTS complexes in the absence of any added organic solvents is shown in Table 3. Surprisingly, the highest catalytic activity (TOF = 136,700 h⁻¹) was achieved at a low volume ratio of the water/benzene phase of 0.4 (entry 3/4), which is a great advantage of this biphasic catalytic hydrogenation reaction resulting in substantial reactor volume savings due to small amount of aqueous solvent required for effective conversion of considerable large quantities of the benzene feedstock. At higher and lower volume ratios of the aqueous/benzene phase, the catalytic activity decreased to give at a volume ratio of 4.4 a TOF value of 48,200 h⁻¹ (entry 3/1) and at a ratio of 0.3 a TOF of 135,700 h⁻¹ (entry 3/5). The catalytic activity of biphasic benzene hydrogenation reaction increases with increasing C=C units/Rh molar ratios from 9000 up to 24,000 to give TOF values from 53,000 up to 136,700 h⁻¹ (Table 4 entries 4/1–4/3). Raising the C=C units/Rh molar ratio higher has a negative effect on the reaction rate in the biphasic hydrogenation of benzene to give at a molar ratio of C=C units/Rh = 60,000 a TOF value of only 38,800 h⁻¹ (entry 4/6).

Table 2
Effect of hydrogen partial pressure on the biphasic hydrogenation of benzene catalyzed by Rh/TPPTS complexes in the absence of added organic solvents.^a

| Entry | Catalyst precursor | C=C/Rh molar ratio | P _{H2} (bar) | Conversion (mol%) | Selectivity of cyclohexane (mol%) | TOF ^b (h ⁻¹) |
|-------|--------------------------------------------|--------------------|-----------------------|-------------------|-----------------------------------|-------------------------------------|
| 2/1 | RhCl ₃ ·3H ₂ O/TPPTS | 15,000 | 30 | 62 | 100 | 55,900 |
| 2/2 | RhCl ₃ ·3H ₂ O/TPPTS | 15,000 | 50 | 77 | 100 | 69,000 |
| 2/3 | RhCl ₃ ·3H ₂ O/TPPTS | 15,000 | 60 | 87 | 100 | 78,700 |
| 2/4 | RhCl ₃ ·3H ₂ O/TPPTS | 15,000 | 70 | 92 | 100 | 83,200 |
| 2/5 | RhCl ₃ ·3H ₂ O/TPPTS | 15,000 | 80 | 96 | 100 | 86,800 |

^a Reaction conditions: T = 120 °C; t = 10 min; 2.63 mg (0.01 mmol) RhCl₃·3H₂O; 18.5 mg (0.03 mmol) TPPTS (P/Rh molar ratio = 3); 10 ml deaerated distilled demineralized water; [Rh] = 100 ppm; pH of the aqueous catalyst phase after the reaction = 2.8–3.5; addition of 3.90 g ≈ 4.46 ml (50 mmol) benzene (C=C/Rh molar ratio = 15,000), V_{H2O}/V_{benzene} (ml/ml) = 2.2; stirring rate = 670 rpm.

^b Defined as mole of hydrogenated C=C units of benzene per mole of Rh per hour.

Table 3
Effect of the volume ratio of the aqueous/benzene phase in the Rh/TPPTS-catalyzed biphasic hydrogenation of benzene in the absence of added organic solvents.^a

| Entry | Catalyst precursor | C=C/Rh molar ratio | V _{H2O} /V _{benzene} (ml/ml) | H ₂ O (ml) | Benzene (ml) | Conv. (mol%) | Select. C ₆ H ₁₂ (mol%) | TOF ^b (h ⁻¹) |
|-------|--------------------------------------------|--------------------|------------------------------------------------|-----------------------|--------------|--------------|-----------------------------------------------|-------------------------------------|
| 3/1 | RhCl ₃ ·3H ₂ O/TPPTS | 15,000 | 4.4 | 20 | 4.5 | 53 | 100 | 48,200 |
| 3/2 | RhCl ₃ ·3H ₂ O/TPPTS | 15,000 | 2.2 | 10 | 4.5 | 83 | 100 | 74,800 |
| 3/3 | RhCl ₃ ·3H ₂ O/TPPTS | 15,000 | 1.1 | 5 | 4.5 | 92 | 100 | 82,500 |
| 3/4 | RhCl ₃ ·3H ₂ O/TPPTS | 24,000 | 0.4 | 3 | 7.1 | 48 | 100 | 136,700 |
| 3/5 | RhCl ₃ ·3H ₂ O/TPPTS | 30,000 | 0.3 | 3 | 8.9 | 38 | 100 | 135,700 |

^a Reaction conditions: T = 120 °C; except entries 3/4 and 3/5, T = 130 °C; P_{H2} = 50 bar; except entries 3/4 and 3/5, P_{H2} = 80 bar; t = 10 min; except entries 3/4 and 3/5, t = 5 min; 2.63 mg (0.01 mmol) RhCl₃·3H₂O; 49.8 mg (0.08 mmol) TPPTS (P/Rh molar ratio = 8); except entries 3/4 and 3/5, 24.6 mg (0.04 mmol) TPPTS (P/Rh molar ratio = 4); pH of the aqueous catalyst phase after the reaction = 2.8–3.5; stirring rate = 670 rpm.

^b Defined as mole of hydrogenated C=C units of benzene per mole of Rh per hour.

Table 4
Effect of the C=C units/Rh molar ratio on the Rh/TPPTS-catalyzed biphasic hydrogenation of benzene in the absence of added organic solvents.^a

| Entry | Catalyst precursor | C=C/Rh molar ratio | Conversion (mol%) | Selectivity cyclohexane (mol%) | TOF ^b (h ⁻¹) |
|-------|--------------------------------------------|--------------------|-------------------|--------------------------------|-------------------------------------|
| 4/1 | RhCl ₃ ·3H ₂ O/TPPTS | 9000 | 98 | 100 | 53,000 |
| 4/2 | RhCl ₃ ·3H ₂ O/TPPTS | 15,000 | 96 | 100 | 86,800 |
| 4/3 | RhCl ₃ ·3H ₂ O/TPPTS | 24,000 | 48 | 100 | 136,700 |
| 4/4 | RhCl ₃ ·3H ₂ O/TPPTS | 30,000 | 38 | 100 | 135,700 |
| 4/5 | RhCl ₃ ·3H ₂ O/TPPTS | 36,000 | 30 | 100 | 128,200 |
| 4/6 | RhCl ₃ ·3H ₂ O/TPPTS | 60,000 | 5 | 100 | 38,800 |

^a Reaction conditions: T = 130 °C; except entry 4/2, T = 120 °C; P_{H2} = 80 bar; except entry 4/1, P_{H2} = 30 bar; t = 5 min; except entries 4/1 and 4/2, t = 10 min; 2.63 mg (0.01 mmol) RhCl₃·3H₂O; 18.5 mg (0.03 mmol) TPPTS (P/Rh molar ratio = 3); except entries 4/3, 4/4 and 4/6, 24.6 mg (0.04 mmol) TPPTS (P/Rh molar ratio = 4); 10 ml deaerated distilled demineralized water; except entries 4/3 and 4/4, 3 ml of water and entries 4/5 and 4/6, 5 ml of water; pH of the aqueous catalyst phase after the reaction = 2.8–3.5; stirring rate = 670 rpm.

^b Defined as mole of hydrogenated C=C units of benzene per mole of Rh per hour.

3.1.3. Effect of pH

Table 5 presents the activity and selectivity exhibited Rh/TPPTS catalytic complexes in the hydrogenation of benzene to cyclohexane in aqueous/organic two-phase systems as a function of the pH value of the aqueous catalyst phase. The highest catalytic activity (TOF = 52,900 h⁻¹) with quantitative selectivity to cyclohexane was obtained under acidic conditions i.e., at a pH value of 3.5 (Table 5, entry 5/1). The catalytic activity decreases with increasing pH values of the aqueous catalyst phase to give under neutral conditions i.e., at pH 7.0 adjusted by a NaH₂PO₄/NaOH-buffer a TOF of 42,400 h⁻¹ (entry 5/2) and under basic conditions at pH 12.0 a lower catalytic activity of TOF = 39,500 h⁻¹ with quantitative selectivities to cyclohexane (entry 5/3). This pH effect observed in the biphasic hydrogenation of benzene that at increasing pH values the TOF's decrease (entries 5/1–5/3) suggests a homogeneous nature for the Rh/TPPTS catalyst in aqueous media under acidic conditions. The pH effect is an evaluation method to decide for the presence of a water-soluble homogeneous catalyst or for heterogeneous catalytic metal nanoparticles in aqueous/organic two-phase systems. Daguinet and Dyson [16] developed this pH evaluation method as a screen to help to assess for the homogeneous nature of water-soluble single metal catalytic complexes versus heterogeneous metal nanoparticles in aqueous/organic two-phase systems. No black rhodium metal aggregates were observed in the biphasic hydrogenation reactions of benzene under acidic conditions, which indicates that the Rh/TPPTS catalyst remains intact without decomposition after the reaction in the aqueous layer which is a clear solution. In sharp contrast, at pH = 7.0 and 12.0 (entries 5/2 and 5/3) black rhodium metal aggregates were observed from a visual inspection after the reaction indicating the presence of hetero-

ogeneous catalysts under neutral and basic conditions. The TOF's obtained with black rhodium metal aggregates at pH of 7.0 and 12.0 (entries 5/2 and 5/3) are in a similar order as those obtained with related ruthenium catalytic nanoparticles [6c].

3.1.4. Micellar Rh/TPPTS-catalyzed hydrogenation of benzene to cyclohexane

The presence of the non-ionic surfactants polyoxyethylene(23)lauryl ether (Brij-35) and polyoxyethylene(4)lauryl ether (Brij-30) (Fig. 1) has a remarkable effect on the Rh/TPPTS-catalyzed hydrogenation activity to reduce benzene to cyclohexane in aqueous/organic two-phase systems, which is shown in Table 6. When the non-ionic surfactant Brij-35, which possesses a hydrophilic-lipophilic balance (HLB) value of 16.9 [17], was added at a molar ratio of Brij-35/TPPTS = 1, a higher catalytic activity (TOF = 186,600 h⁻¹) was obtained in the Rh/TPPTS-catalyzed hydrogenation of benzene (entry 6/2) compared to the activity (TOF = 136,700 h⁻¹) observed in the absence of surfactants in neat aqueous/benzene two-phase systems under the same conditions (entry 6/1). At a molar ratio of Brij-35/TPPTS = 2, the catalytic activity was further increased to TOF = 195,400 h⁻¹ (entry 6/3). However, with the Brij-30 surfactant, which has a lower HLB value of 9.7 [17] even higher catalytic activities were achieved in the Rh/TPPTS-catalyzed hydrogenation of benzene to cyclohexane to give at molar ratios of Brij-30/TPPTS = 1 and 2 rates of TOF = 197,400 h⁻¹ and 204,400 h⁻¹, respectively, (entries 6/5 and 6/6) compared to the activities obtained with Rh/TPPTS/Brij-35 systems (entries 6/2 and 6/3) and also in the absence of surfactants (TOF = 135,700 h⁻¹) under the same conditions in neat aqueous/organic two-phase systems (entry 6/4). To our knowledge, these are the highest catalytic activities

Table 5
Effect of the pH value on the hydrogenation of benzene catalyzed by Rh/TPPTS complexes in aqueous/organic two-phase systems.^a

| Entry | Catalyst precursor | C=C units/Rh molar ratio | pH value | Conversion (mol%) | Selectivity cyclohexane (mol%) | TOF ^b (h ⁻¹) |
|-------|--------------------------------------------|--------------------------|-------------------|-------------------|--------------------------------|-------------------------------------|
| 5/1 | RhCl ₃ ·3H ₂ O/TPPTS | 24,000 | 3.5 ^c | 88 | 100 | 52,900 |
| 5/2 | RhCl ₃ ·3H ₂ O/TPPTS | 24,000 | 7.0 ^d | 87 | 100 | 42,400 |
| 5/3 | RhCl ₃ ·3H ₂ O/TPPTS | 24,000 | 12.0 ^e | 83 | 100 | 39,500 |

^a Reaction conditions: *T* = 120° C; *P*_{H₂} = 50 bar; *t* = 10 min; 2.63 mg (0.01 mmol) RhCl₃·3H₂O; 49.8 mg (0.08 mmol) TPPTS (*P*/Rh molar ratio = 8); 10 ml deaerated distilled demineralized water; [Rh] = 100 ppm; 6.25 g ≈ 7.1 ml (80 mmol) benzene, *V*_{H₂O}/*V*_{benzene} (ml/ml) = 1.4; stirring rate = 670 rpm.

^b Defined as mole of hydrogenated C=C units of benzene per mole of Rh per hour.

^c No buffer was added.

^d 110.4 mg (0.8 mmol) NaH₂PO₄·H₂O, pH adjusted with 5% aqueous NaOH. Formation of rhodium black.

^e Adjusted with 5% aqueous NaOH. Formation of massive rhodium black.

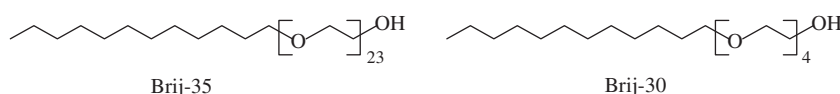


Fig. 1. Structures of the non-ionic surfactants polyoxyethylene(23)lauryl ether (Brij-35) and polyoxyethylene(4)lauryl ether (Brij-30).

Table 6
Effect of the presence and nature of added surfactants in the biphasic hydrogenation of benzene catalyzed by Rh/TPPTS complexes.^a

| Entry | Catalyst precursor | C=C/Rh molar ratio | Surfactant | Surf./L molar ratio | <i>V</i> _{H₂O} / <i>V</i> _{benzene} (ml/ml) | H ₂ O (ml) | Benzene (ml) | Conv. (mol%) | Select. C ₆ H ₁₂ (mol%) | TOF ^b (h ⁻¹) |
|-------|--------------------------------------------|--------------------|------------|---------------------|--------------------------------------------------------------------------|-----------------------|--------------|--------------|-----------------------------------------------|-------------------------------------|
| 6/1 | RhCl ₃ ·3H ₂ O/TPPTS | 24,000 | – | – | 0.4 | 3 | 7.1 | 48 | 100 | 136,700 |
| 6/2 | RhCl ₃ ·3H ₂ O/TPPTS | 24,000 | Brij-35 | 1 | 0.4 | 3 | 7.1 | 65 | 100 | 186,600 |
| 6/3 | RhCl ₃ ·3H ₂ O/TPPTS | 24,000 | Brij-35 | 2 | 0.4 | 3 | 7.1 | 68 | 100 | 195,400 |
| 6/4 | RhCl ₃ ·3H ₂ O/TPPTS | 30,000 | – | – | 0.3 | 3 | 8.9 | 38 | 100 | 135,700 |
| 6/5 | RhCl ₃ ·3H ₂ O/TPPTS | 30,000 | Brij-30 | 1 | 0.3 | 3 | 8.9 | 55 | 100 | 197,400 |
| 6/6 | RhCl ₃ ·3H ₂ O/TPPTS | 30,000 | Brij-30 | 2 | 0.3 | 3 | 8.9 | 57 | 100 | 204,400 |

^a Reaction conditions: *T* = 130° C; *P*_{H₂} = 80 bar; *t* = 5 min; 2.63 mg (0.01 mmol) RhCl₃·3H₂O; 24.6 mg (0.04 mmol) TPPTS (*P*/Rh molar ratio = 4); [Rh] = 340 ppm; pH of the aqueous catalyst phase after the reaction = 2.8–3.5; stirring rate = 670 rpm.

^b Defined as mole of hydrogenated C=C units of benzene per mole of Rh per hour.

exhibited so far by water-soluble transition metal TPPTS complexes in aqueous/organic two-phase systems.

The higher catalytic activity of Rh/TPPTS complexes in the hydrogenation of benzene to cyclohexane in the presence of non-ionic Brij surfactants could probably be explained due to interactions between the length of the apolar saturated hydrocarbon chain and the polar polyoxyethylene moiety of the Brij surfactant and the length and nature of the six-membered aromatic ring of benzene starting material, which are in a critical relationship for the dependence of the position of rhodium in the polarity gradient between the Stern layer and the core of the micelle for obtaining maximum catalytic hydrogenation activity when micellar catalysis is operative. However, it should be mentioned that the cloud point temperatures of Brij-35 (approximately 100 °C) and of Brij-30 (2–7 °C) [18] were exceeded at the hydrogenation reaction temperature of 130 °C; and therefore, it is highly probable that under the reaction conditions the Brij surfactants only act as solvents for benzene in the biphasic catalytic hydrogenation reaction.

A higher catalytic activity (TOF = 195,400 h⁻¹) was obtained at a C=C units/Rh molar ratio of 24,000 (Table 7 entry 7/1) in the Rh/TPPTS-catalyzed hydrogenation of benzene in the presence of Brij-35 surfactant compared to the activity of TOF = 187,500 h⁻¹ achieved at a higher C=C units/Rh molar ratio of 30,000 (entry 7/2). In contrast, with Brij-30 surfactant, the highest catalytic activity (TOF = 204,400 h⁻¹) was achieved at the molar ratio of C=C units/Rh = 30,000 (entry 7/4), whereas at lower and higher C=C units/Rh molar ratios of 27,000 and 33,000 the catalytic activity decreases to give TOF values of 193,800 h⁻¹ and 195,100 h⁻¹, respectively (entries 7/3 and 7/5).

3.1.5. Recycling of the Rh/TPPTS catalyst

In order to prove the stability of industrially applied Rh/TPPTS catalytic complexes, a recycling experiment with a consecutive run was carried out in the hydrogenation of benzene in aqueous/organic two-phase systems (Table 8, entries 8/1 and 8/2). The biphasic hydrogenation of benzene catalyzed by Rh/TPPTS complexes was performed at 120 °C under 60 bar dihydrogen partial pressure, a molar ratio of C=C units/Rh = 15,000 and of TPPTS/Rh = 4 at a rhodium concentration of 100 ppm in water and a vol-

ume ratio of aqueous/benzene phase of 2.2 within 10 min reaction time to give a TOF value of 75,100 h⁻¹ with quantitative selectivity toward cyclohexane (entry 8/1). The bottom aqueous catalyst phase of the biphasic reaction as described in entry 8/1 was easily separated from the upper organic layer by decantation, which was then recycled; and after addition of a fresh portion of benzene starting material, the biphasic hydrogenation reaction was performed again under the same conditions to give a TOF = 75,600 h⁻¹ and quantitative selectivity to cyclohexane (entry 8/2). No black rhodium metal aggregates were observed from a visual inspection in both hydrogenation reactions of benzene as described in entries 8/1 and 8/2. Rh/TPPTS complexes are robust catalytic systems and stable toward sulfur-containing compounds, which were present in concentrations of 4 ppm in the benzene starting material used in this work. The high stability of Rh/TPPTS catalyst against sulfur-containing compounds contrasts with the low stability of heterogeneous nickel catalysts applied industrially in hydrogenation processes of benzene to cyclohexane. A further recycling experiment with five consecutive runs is given in the following section.

3.2. The nature of Rh/TPPTS catalyst in the biphasic benzene hydrogenation

The Rh/TPPTS catalyst used in this work was prepared in situ after dissolution under argon of RhCl₃·3H₂O with TPPTS in H₂O and immediate subjection of the mixture to a hydrogen atmosphere under the chosen hydrogenation reaction conditions. Although the catalyst was added as a rhodium(III) salt, the actual catalyst is a rhodium(I) TPPTS complex, *i.e.*, RhCl(TPPTS)₃, formed in situ from RhCl₃·3H₂O under hydrogenation conditions with TPPTS in aqueous media and the immediate subjection of the catalyst precursor aqueous mixture namely the RhCl₃·3H₂O/TPPTS/H₂O mixture to hydrogen atmosphere gives priority to hydrogen to act as a reducing agent to rhodium(III) salt and not to the water-soluble phosphine TPPTS, which acts only as a ligand [19,20].

The absence of an induction period in the Rh/TPPTS-catalyzed biphasic benzene hydrogenation suggests for a homogeneous nature of the Rh/TPPTS catalytic complex. To verify whether the benzene hydrogenation reaction proceeds homogeneously by Rh/

Table 7
Effect of the C=C units/Rh molar ratio in the presence of non-ionic Brij surfactants on the biphasic hydrogenation of benzene catalyzed by Rh/TPPTS complexes.^a

| Entry | Catalyst precursor | C=C/Rh molar ratio | Surfactant | V _{H₂O} /V _{benzene} (ml/ml) | H ₂ O (ml) | Benzene (ml) | Conv. (mol%) | Select. C ₆ H ₁₂ (mol%) | TOF ^b (h ⁻¹) |
|-------|--------------------------------------------|--------------------|------------|-----------------------------------------------------------|-----------------------|--------------|--------------|-----------------------------------------------|-------------------------------------|
| 7/1 | RhCl ₃ ·3H ₂ O/TPPTS | 24,000 | Brij-35 | 0.4 | 3 | 7.1 | 68 | 100 | 195,400 |
| 7/2 | RhCl ₃ ·3H ₂ O/TPPTS | 30,000 | Brij-35 | 0.3 | 3 | 8.9 | 52 | 100 | 187,500 |
| 7/3 | RhCl ₃ ·3H ₂ O/TPPTS | 27,000 | Brij-30 | 0.4 | 3 | 8.0 | 60 | 100 | 193,800 |
| 7/4 | RhCl ₃ ·3H ₂ O/TPPTS | 30,000 | Brij-30 | 0.3 | 3 | 8.9 | 57 | 100 | 204,400 |
| 7/5 | RhCl ₃ ·3H ₂ O/TPPTS | 33,000 | Brij-30 | 0.3 | 3 | 9.8 | 49 | 100 | 195,100 |

^a Reaction conditions: T = 130 °C; P_{H₂} = 80 bar; t = 5 min; 2.63 mg (0.01 mmol) RhCl₃·3H₂O; 24.6 mg (0.04 mmol) TPPTS (P/Rh molar ratio = 4); Brij/TPPTS molar ratio = 2; [Rh] = 340 ppm; pH of the aqueous catalyst phase after the reaction = 2.8–3.5; stirring rate = 670 rpm.

^b Defined as mole of hydrogenated C=C units of benzene per mole of Rh per hour.

Table 8
Recycling of the Rh/TPPTS catalyst in the hydrogenation of benzene in aqueous/organic two-phase systems.^a

| Entry | Catalyst precursor | C=C/Rh molar ratio | T (°C) | P _{H₂} (bar) | t (min) | V _{H₂O} /V _{benzene} (ml/ml) | H ₂ O (ml) | Benzene (ml) | Conv. (mol%) | Select. C ₆ H ₁₂ (mol%) | TOF ^b (h ⁻¹) |
|------------------|--------------------------------------------|--------------------|--------|----------------------------------|---------|-----------------------------------------------------------|-----------------------|--------------|--------------|-----------------------------------------------|-------------------------------------|
| 8/1 | RhCl ₃ ·3H ₂ O/TPPTS | 15,000 | 120 | 60 | 10 | 2.2 | 10 | 4.5 | 83 | 100 | 75,100 |
| 8/2 ^c | Recycled catalyst | 15,000 | 120 | 60 | 10 | 2.2 | 10 | 4.5 | 84 | 100 | 75,600 |

^a Reaction conditions: 2.63 mg (0.01 mmol) RhCl₃·3H₂O; 24.6 mg (0.04 mmol) TPPTS (P/Rh molar ratio = 4); pH of the aqueous catalyst phase after the reaction = 2.6–3.0; [Rh] = 100 ppm; 3.90 g ≈ 4.46 ml (50 mmol) benzene; stirring rate = 670 rpm.

^b Defined as mole of hydrogenated C=C units of benzene per mole of Rh per hour.

^c The aqueous catalyst layer (10 ml) of entry 8/1, after separation of the upper organic phase, was re-used after addition of a new portion of 3.90 g ≈ 4.46 ml (50 mmol) benzene.

TPPTS complexes in water dynamic light scattering measurements on an aqueous Rh/TPPTS catalyst solution, which was recycled five times after six consecutive biphasic benzene hydrogenation runs suggested that the reaction is most likely catalyzed by single metal homogeneous Rh/TPPTS complexes and not by heterogeneous rhodium metal nanoparticles.

In the first run, the Rh/TPPTS catalyst was prepared in situ after dissolution of 2.63 mg (0.01 mmol) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with 49.8 mg (0.08 mmol) TPPTS (P/Rh molar ratio = 8) in 10 ml of deaerated distilled demineralized water. Addition of 3.90 g \approx 4.46 ml (50 mmol) benzene results a two-phase system where the $\text{C}=\text{C}$ units/Rh molar ratio was 15,000 and the volume ratio of the aqueous to the benzene phase 2.2. The concentration of rhodium in the aqueous catalyst phase was 100 ppm. The temperature for the hydrogenation reaction was 120 °C, the hydrogen partial pressure 60 bar and the reaction time 10 min. After the reaction, the Rh/TPPTS catalyst was easily recovered by a simple phase separation of the aqueous phase from the upper organic layer, and the aqueous phase containing the catalyst was re-used 5 times under the same hydrogenation reaction conditions after addition, each time, of a new portion of 3.90 g \approx 4.46 ml (50 mmol) benzene. The pH value of the aqueous catalyst solution was 3.5. The catalytic activity remained high ($\text{TOF} = 72,100 \text{ h}^{-1}$) with quantitative selectivity to cyclohexane in all consecutive biphasic benzene hydrogenation runs. Dynamic light scattering measurements on the aqueous Rh/TPPTS catalyst solution obtained after the 5th recycle benzene hydrogenation experiment suggested that the Rh/TPPTS catalyst is of a homogeneous nature in aqueous media without formation of any heterogeneous rhodium catalytic nanoparticles.

Furthermore, an alternative explanation regarding the nature of the catalytic active species namely the formation of catalytic active Rh(0) nanoparticles by reducing $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ with hydrogen could be excluded in those experiments where no surfactants as stabilizing protective dispersants were added and TPPTS acts as an electrolyte [21] without possessing any surfactant properties.

Another explanation regarding stabilization of catalytic active Rh(0) nanoparticles by TPPTS-oxide [22] could also be excluded because the TPPTS ligand we prepared (vide supra) and applied in the biphasic benzene hydrogenation reactions is free of TPPTS-oxide, which is also not produced during the in situ synthesis of the $\text{RhCl}(\text{TPPTS})_3$ catalytic complex due to the immediate subjection of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}/\text{H}_2\text{O}$ mixture to hydrogen atmosphere and further could also be excluded because we observed no induction period which contrasts with induction periods observed in hydrogenation reactions catalyzed by rhodium nanoparticles stabilized by TPPTS-oxide where the induction period is necessary in order to be produced enough TPPTS-oxide [22].

Moreover, the pH effect we observed in the biphasic hydrogenation of benzene (vide supra) suggests a homogeneous nature for the Rh/TPPTS catalyst in aqueous media under acidic conditions.

It should be mentioned that also a homogeneous nature of in situ prepared Ru/TPPTS catalysts was found in PCS experiments of aqueous phase catalytic hydrogenation reaction mixtures of fructose [23] and in TEM-EDX measurements on aqueous phase catalytic hydrogenation reaction mixtures of fractions of fast pyrolysis oil [24].

Furthermore, in situ prepared $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{TPPTS}$ catalysts and pre-formed homogeneous $\text{RhCl}(\text{TPPTS})_3$ catalytic complexes gave the same catalytic activity in the hydrogenation of polybutadiene-1,4-*block*-poly(ethylene oxide) in aqueous media [19].

4. Conclusions

The work presented in this paper demonstrated again the high potential of efficient green aqueous phase organometallic catalysis

through a new application. We have demonstrated that the Rh/TPPTS-catalyzed hydrogenation of a difficult to reduce substrate namely benzene proceeds with exceptionally high catalytic activities ($\text{TOF} > 204,000 \text{ h}^{-1}$) to yield quantitatively cyclohexane in aqueous/organic two-phase systems. This is the highest catalytic activity exhibited so far by transition metal TPPTS complexes and contrasts with the general perception that industrially applied Rh/TPPTS catalysts normally exhibit low rates in aqueous/organic biphasic media. Optimum results were obtained at a low volume ratio of the aqueous/benzene phase of 0.4 which is a great advantage of this biphasic reaction due to substantial savings in reactor volume. Another great advantage is the large heat capacity of water, which makes it an excellent medium to perform more safe and selective strongly exothermic reactions such as the benzene hydrogenation reaction, which is especially important in large-scale industrial processes. Furthermore, the influence of several operating parameters such as temperature, TPPTS/Rh molar ratio, hydrogen partial pressure, $\text{C}=\text{C}$ units/Rh molar ratio as well as the pH effect and the presence of non-ionic Brij surfactants on the catalytic activity and selectivity to cyclohexane were investigated. The industrially applied Rh/TPPTS catalysts which are stable toward sulfur-containing compounds were easily recovered in active form from organic reaction product by a simple phase separation and recycling experiments showed that both the catalytic activity and selectivity to cyclohexane remained high in five consecutive runs. Dynamic light scattering studies on a five times recycled aqueous Rh/TPPTS catalyst solution, the absence of an induction period and the pH effect observed in biphasic benzene hydrogenation reactions suggest for a homogeneous nature of Rh/TPPTS catalytic complexes in aqueous media without formation of any heterogeneous rhodium catalytic nanoparticles. This efficient biphasic catalytic benzene hydrogenation reaction may yield new industrial process for the production of cyclohexane where the green and safe aqueous medium provides the means for quantitative recovery of the catalytic complex by a simple phase separation. Hence, we are currently investigating the scope of this useful arenehydrogenation reaction in green aqueous/organic two-phase systems.

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