

# Hydrogenation reactions on heterogenized Wilkinson complexes

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## Abstract

A novel clay catalyst containing a heterogenized Rh(I) triphenylphosphine complex (Rh-bentonite) has been prepared via ion exchange of a Hungarian Na<sup>+</sup>-bentonite with Wilkinson complex [RhCl(PPh<sub>3</sub>)<sub>3</sub>]. It was established that the active species [Rh(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup> was situated on the external surface of the catalyst, which was found to be efficient in the liquid-phase hydrogenation of 1-octene, cyclohexene, norbornadiene, 1,5-cyclooctadiene, phenylacetylene and cyclohexene-3-one. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

An important research area of organic catalysis is the heterogenization of metal complexes which display outstanding activities and selectivities in the homogeneous phase [1]. In order to perform hydrogenation reactions of organic compounds, various methods of heterogenization have been developed [2–4] and applied to the immobilization of transition metal complexes in clay minerals [5–7]. Immobilization may either be carried out via impregnation

(surface adsorption) or ion exchange. A possible variation of the latter is intercalation, i.e., the insertion of ionic complexes in the intracrystal space of a swelling layer lattice silicate. Although several procedures on the heterogenization of hydrogenating Wilkinson complexes have been described in the literature [2–4], the results on the use of clay minerals are rather limited. Wilkinson complexes intercalated in smectite type clay minerals have been applied for the hydrogenation of cyclohexene [8,9], benzene [10] and aldehydes [11], and for hydroformylation [12]. In order to extend the experimental results available in literature, we decided to perform the preparation and characterization of heterogenized Wilkinson complex catalysts using Na<sup>+</sup>-bentonite as the support material.

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The present study reports on the results of hydrogenation reactions on Rh-bentonite catalyst prepared by external ion exchange. The hydrogenation of 1-octene, cyclohexene, norbornadiene, 1,5-cyclooctadiene, cyclohexene-3-one and phenylacetylene have been investigated at room temperature and  $10^5$  Pa in a mixture of toluene:ethanol = 3:1 [13]. The above reactants, with the exception of 1-octene and cyclohexene, have not been studied on heterogenized metal complexes so far. Moreover, a comparison between the results of homogeneous and heterogeneous reactions can be made, as the hydrogenation of our reactants, except for cyclohexene-3-one, has already been investigated in the presence of Wilkinson complexes in the homogeneous phase [14–17]. Further, the hydrogenation activity of Rh-bentonite was compared to that of a Wilkinson complex immobilized on Cab–O–Sil by impregnation.

In the homogeneous phase, cyclohexene was the most frequently studied reactant in the presence of Wilkinson complexes [18]. The hydrogenation of 1-octene has also been thoroughly investigated [18–20]. Much less information is available for norbornadiene [16,21], 1,5-cyclooctadiene [16,22] and phenylacetylene [19,22]. In addition, considerably lower hydrogenation rates reported for the latter compounds.

## 2. Experimental

### 2.1. Materials

The reactants 1-octene, cyclohexene, norbornadiene, 1,5-cyclooctadiene, phenylacetylene and cyclohexene-3-one (Fluka, Aldrich) were distilled and GC-analyzed before use.  $\text{RhCl}(\text{PPh}_3)_3$  was purchased from Strem.

All organic solvents used were purchased from Fluka, purified by known methods before use and stored on a molecular sieve x (0.4 nm, Merck).

### 2.2. Catalysts

#### 2.2.1. Rh-bentonite

The solid support was a Hungarian bentonite from Komlóska, with the chemical composition of 61.8%  $\text{SiO}_2$ , 22.2%  $\text{Al}_2\text{O}_3$ , 4.5%  $\text{Fe}_2\text{O}_3$ , 0.2%  $\text{CaO}$ , 0.7%  $\text{MgO}$ , 3.2%  $\text{Na}_2\text{O}$ , 0.2%  $\text{K}_2\text{O}$  (loss on ignition 9.2%).

Ion exchange was carried out after removal of the water adsorbed on the bentonite support by heating the sample in a furnace at 383 K for 24 h. The Wilkinson complex was dissolved in a benzene:methanol = 7:3 solvent mixture, with a concentration of 1 g per  $100\text{ cm}^3$ . To prevent oxidation, the solution was stored under  $\text{N}_2$ . Further, a bentonite suspension of 2.5 g solid in  $100\text{ cm}^3$  of benzene:methanol = 7:3 mixture was prepared. Ion exchange was performed by adding  $5\text{ cm}^3$  of 1% Wilkinson complex to  $40\text{ cm}^3$  of the suspension at room temperature, under stirring. After 24 h, the reaction mixture was filtered, washed to chlorine free with a benzene–methanol mixture and dried.

The basal spacings of bentonite and Rh-bentonite were determined from XRD investigations effected with a Philips X-ray diffractometer operated with a Ni filter and Cu  $K\alpha$  radiation. Prior to measurement, the samples were heated at 383 K for 1 h.  $^{29}\text{Si}$  MAS NMR spectra were obtained on a Bruker AM 400 multinuclear spectrometer operated at a spinning frequency of 3.8 and 4.5 kHz by using tetramethylsilane as a reference material.

The carbon content of the samples was determined by a microanalytical method based on burning and separation by gas chromatography. The instrument used was a CHN analyser, Laboratori Pastroje, Praha. The carbon content of Rh-bentonite was 0.6%.

#### 2.2.2. $\text{RhCl}(\text{PPh}_3)_3$ supported on $\text{SiO}_2$ ( $\text{RhCl}(\text{PPh}_3)_3\text{-SiO}_2$ )

A silica-supported (BDH, Cab–O–Sil M5) Wilkinson complex was prepared by impregnation as follows: 10 mg of the Wilkinson com-

plex was dissolved in chloroform and then 1 g of Cab-O-Sil M5 was added. After stirring the mixture for 2 h, the solvent was evaporated and the solid was dried.

### 2.3. Methods

Hydrogenation in the liquid phase was performed in a conventional hydrogenation apparatus at  $10^5$  Pa [23]. The reaction was carried out at 308 K by using 0.0197 mol of reactant and  $20\text{ cm}^3$  of a toluene:ethanol = 7:3 solvent mixture. The amount of catalyst used was 60 mg of Rh-bentonite, or 60 mg of  $\text{RhCl}(\text{PPh}_3)_3\text{-SiO}_2$  or 12 mg of  $\text{RhCl}(\text{PPh}_3)_3$ . The catalyst and the solvents were placed in the reaction vessel, the system was degassed with a rotary pump ( $1.5 \times 10^3$  Pa) three times, and then filled with hydrogen. The mixture was stirred magnetically (800 rpm) and left under hydrogen for 2 h before the reactant was added with a gastight syringe. Both the temperature of the reaction mixture and the hydrogen pressure were kept constant throughout the reaction. As the reaction proceeded, the hydrogen consumption was recorded, and the composition of the reaction mixture was determined periodically by GC and GC-MS analysis.

### 2.4. Analysis and calculation

The samples of the liquid-phase hydrogenation were analyzed with a HP 5890 gas chromatograph equipped with a flame ionization detector and a 30 m DB-5 capillary column. The products were identified according to their mass spectra recorded with an HP 5890 GC with a 50-m HP-1 capillary column and an HP 5970 MSD.

## 3. Results and discussion

### 3.1. Examination of the heterogenized Wilkinson complex

The lack of  $\text{Cl}^-$  anions in Rh-bentonite suggested that ion exchange took place between

$\text{Na}^+$ -bentonite and the Wilkinson complex. The displacement of  $\text{Cl}^-$  anions from the Wilkinson complex was followed by adsorption as a cationic species  $[\text{Rh}(\text{PPh}_3)_3]^+$  in the hydration layer of bentonite. According to the carbon content of the catalyst (0.6%, as seen above), the concentration of the active species in 1 g of catalyst was  $9.26 \times 10^{-6}$  mol  $[\text{Rh}(\text{PPh}_3)_3]^+$ .

Intercalation may be excluded regarding that the basal spacing of the above sample (1.26 nm) was hardly different from that of  $\text{Na}^+$ -bentonite (1.31 nm). The same evidence was obtained from  $^{29}\text{Si}$  NMR measurements (Fig. 1). According to the literature [8], if during the ion exchange the cation is immobilized inside of the interlamellar space, a difference is expected between the two spectra. In the case of montmorillonite the peaks found at  $-150$ ,  $-99$ , and  $-50$  ppm were shifted to  $-143$ ,  $-95$ , and  $-50$  ppm after introduction of the Wilkinson complex in the interlamellar space. In the  $^{29}\text{Si}$  NMR spectra of our catalysts these shifts did not appear. It follows that under the present experimental conditions, ion exchange took place on the external surface of bentonite.

Hydrogenation reactions were studied on the Wilkinson complex heterogenized on partially ion exchanged bentonite, which has not been examined previously. The results were subsequently compared to those obtained with the Wilkinson complex in the homogeneous phase, and on a  $\text{SiO}_2$ -supported Wilkinson complex ( $(\text{RhCl}(\text{PPh}_3)_3\text{-SiO}_2)$ ).

### 3.2. Hydrogenation reactions in the liquid phase

The conversion of 1-octene investigated in the presence of the Wilkinson complex in the homogeneous phase was found to be only 3% after 15 h of reaction time (Fig. 2). The reaction was performed under the same experimental conditions as for Rh-bentonite. Considering the catalyst concentrations ( $5.6 \times 10^{-4}$  mol  $\text{dm}^{-3}$  of Wilkinson complex and  $2.5 \times 10^{-5}$  mol  $\text{dm}^{-3}$  of Rh-bentonite), the reaction rate ob-

tained for the Wilkinson complex appears to be much lower than that for Rh-bentonite. A similar observation can be made for the hydrogenation activity of  $\text{RhCl}(\text{PPh}_3)_3\text{-SiO}_2$  (Fig. 2), the concentration of which was  $2.8 \times 10^{-5} \text{ mol dm}^{-3}$ . The difference might be attributed to several reasons. For Rh-bentonite, a dispersion of 100% can be assumed, which suggests a molecular distribution of the active species. On the other hand, when the reaction is performed in the presence of the Wilkinson catalyst, complexes of dimeric structure may be the actual active species. Furthermore, the effect of an electrostatic field formed via ion exchange should also be taken into account.

The reused Rh-bentonite showed nearly the same activity in the second and third use as before.

According to the results of the hydrogenation reactions collected in Figs. 3–8, the following observations can be made: (1) The reactivity order was as follows: 1-octene > cyclohexene-3-one > 1,5-cyclooctadiene ~ cyclohexene > norbornadiene ~ phenylacetylene. (2) For the hydrogenation of dienes into olefins, the selectivity was 75–80%, i.e., hydrogenation leading to the corresponding cycloalkanes also took place. (3) The selective hydrogenation of cyclohexene-3-one into cyclohexanone was observed. (4) 1-Octene and 1,5-cyclooctadiene underwent iso-

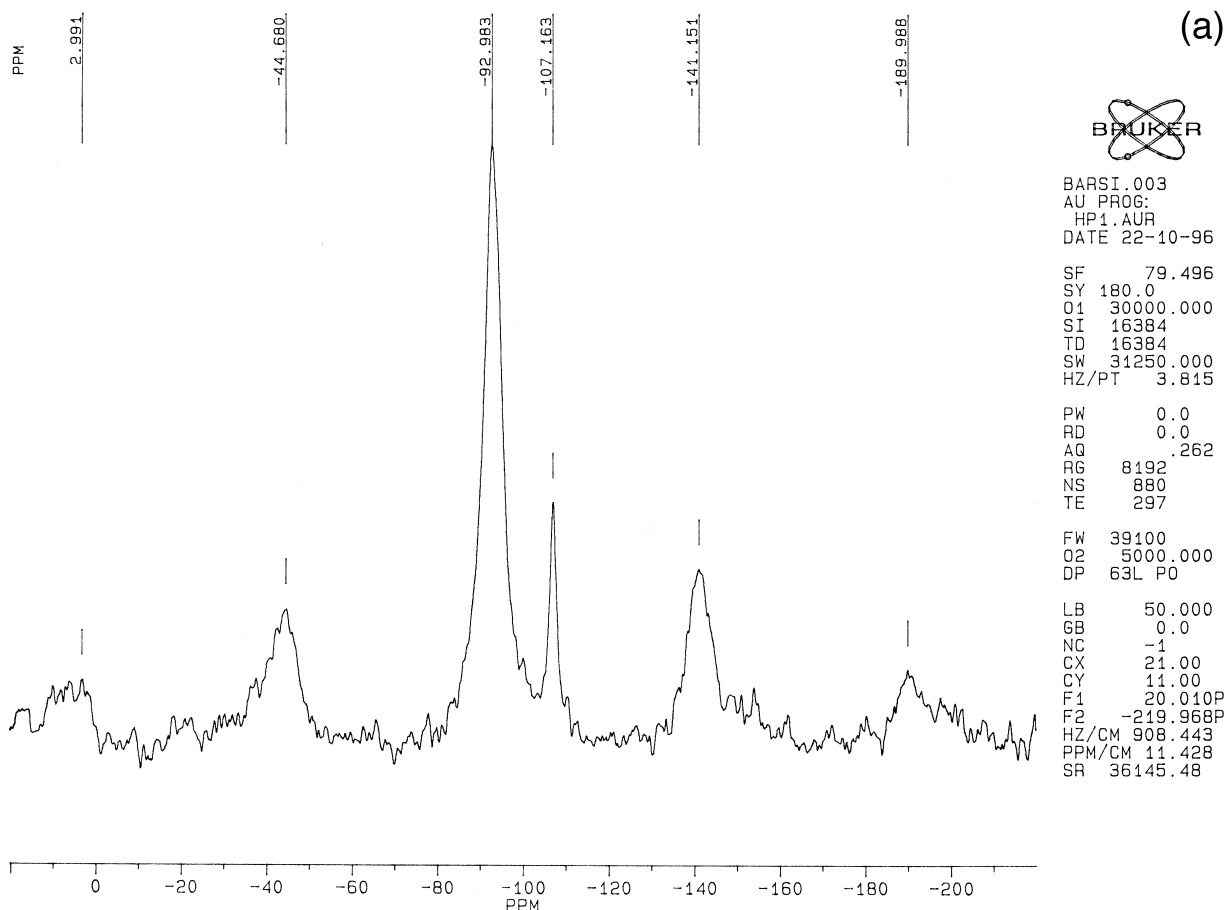


Fig. 1.  $^{29}\text{Si}$  MAS NMR spectra of  $\text{Na}^+$ -bentonite (a) and Rh-bentonite (b) (recorded with a Bruker AM 400 multinuclear spectrometer operated at a spinning frequency of 3.8).

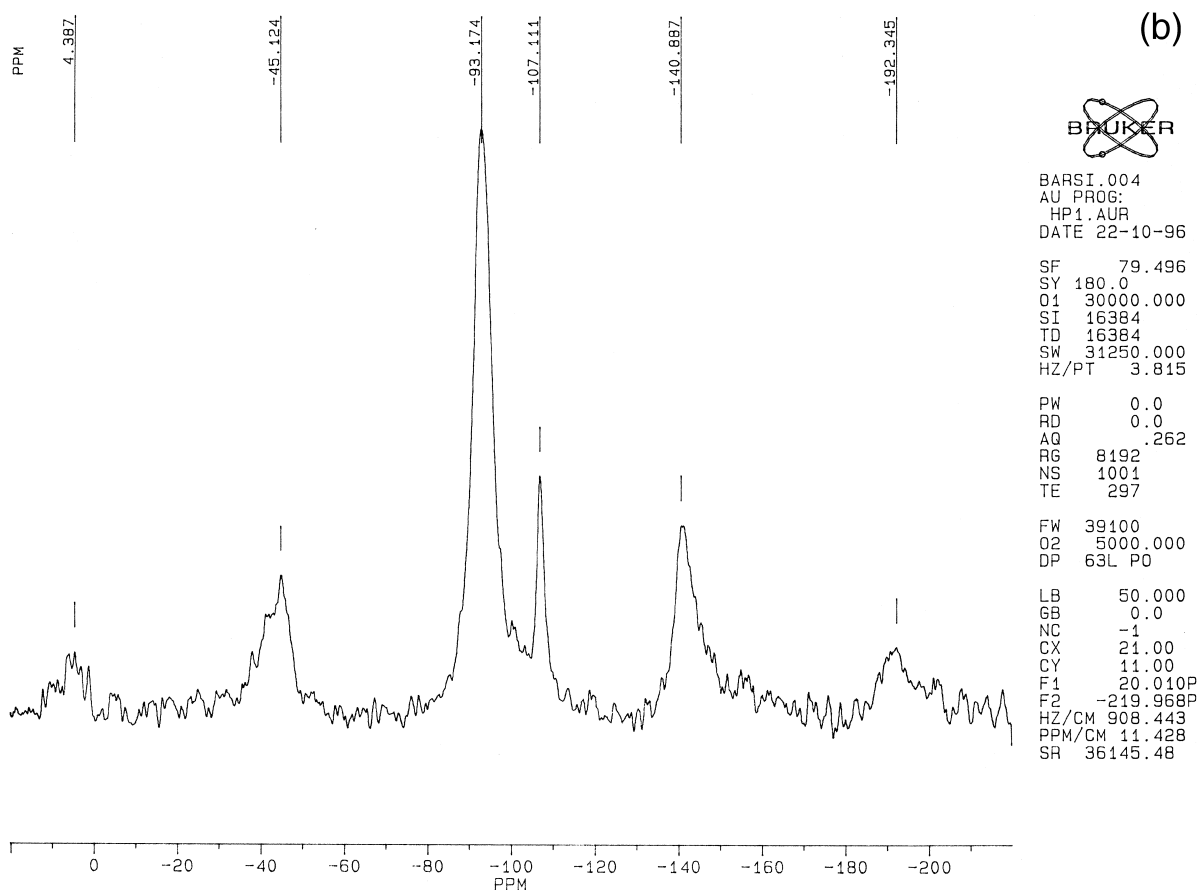


Fig. 1 (continued).

merization. (5) The selectivity of the hydrogenation of phenylacetylene into styrene was higher than 80%.

As far as the reactivity order over the Rh-bentonite is concerned, a deviation from both the Wilkinson complex and clay intercalated  $[\text{Rh}(\text{PPh}_3)_3]^+$  can be pointed out. The slow hydrogenation rate of norbornadiene and phenylacetylene as compared to olefines may be attributed to the formation of a strong bond between the former molecules and Rh, similarly as for hydrogenation in the homogeneous phase [14,16]. Namely, Jardine et al. [21] reported that the complex in the homogeneous phase selectively reduced alkynes in alkene–alkyne mixtures but, as a result of a stronger binding of the

alkyne to the metal, the catalytic activities decreased with respect to alkene hydrogenation.

The hydrogenation rates of 1-alkenes in the homogeneous phase were very close to those of cycloalkenes [14,16]. In our case, hydrogenation was accompanied by a fast isomerization reaction which may be accounted for the high hydrogenation rate of 1-octene on Rh-bentonite. The same observation was made for 1,5-cyclooctadiene. In contrast, isomerization of norbornadiene is hindered. In literature, both compounds were reported to undergo slow hydrogenation [16].

The selectivities obtained for the hydrogenation of 1-octene (Fig. 4) seem to be closer to those determined in the homogeneous phase

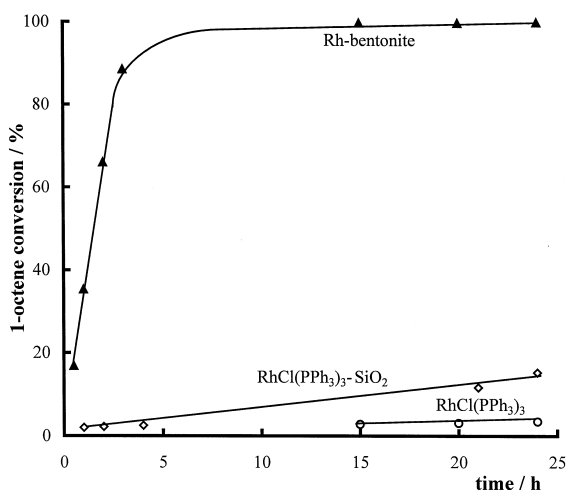


Fig. 2. Conversion of 1-octene in liquid-phase hydrogenation over  $5.6 \times 10^{-4} \text{ mol dm}^{-3} \text{ RhCl(PPh}_3)_3$ ,  $2.8 \times 10^{-5} \text{ mol dm}^{-3} \text{ RhCl(PPh}_3)_3\text{-SiO}_2$  and  $2.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ Rh-bentonite}$  ( $0.0197 \text{ mol 1-octene}$ ,  $10^5 \text{ Pa}$  hydrogen pressure, reaction at  $308 \text{ K}$  in  $20 \text{ ml}$  toluene:ethanol = 7:3 mixture).

[24] than to those reported for intercalated  $[\text{Rh(PPh}_3)_3]^+$  [6,7]. For the latter, no isomerization was found, which may be regarded as a further evidence of the presence of surface  $[\text{Rh(PPh}_3)_3]^+$  in Rh-bentonite. The difference in the specificity between the intercalated and homogeneous catalyst systems may be inter-

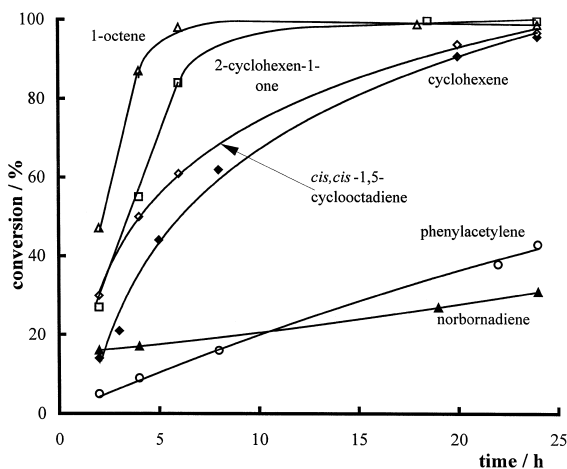


Fig. 3. Liquid-phase hydrogenation of cyclohexene, 1-octene, phenylacetylene, norbornadiene, *cis,cis*-1,5-cyclooctadiene and 2-cyclohexene-1-one over Rh-bentonite (60 mg catalyst, 0.0197 mol substrate,  $10^5 \text{ Pa}$  hydrogen pressure, reaction at  $308 \text{ K}$  in  $20 \text{ ml}$  toluene:ethanol = 7:3 mixture).

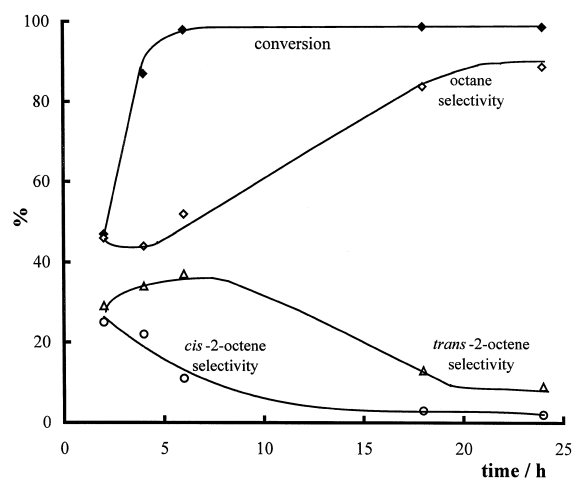


Fig. 4. Conversion and product selectivity in 1-octene liquid-phase hydrogenation over Rh-bentonite (60 mg catalyst, 0.0197 mol 1-octene,  $10^5 \text{ Pa}$  hydrogen pressure, reaction at  $308 \text{ K}$  in  $20 \text{ ml}$  toluene:ethanol = 7:3 mixture).

preted in terms of an equilibrium, previously proposed by Schrock and Osborn [25], between the catalytically active dihydride and monohydride rhodium complexes:  $\text{RhH}_2\text{L}_n^+ \rightleftharpoons \text{RhHL}_n + \text{H}^+$ . The dihydride is a good terminal olefin hydrogenation catalyst, but a poor isomerization catalyst, whereas the monohydride is both a good hydrogenation and isomerization catalyst.

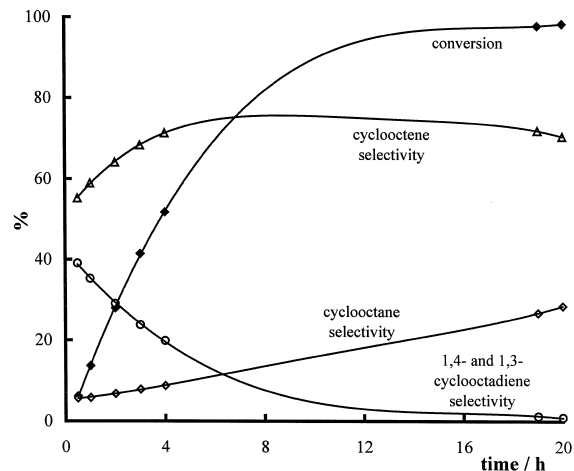


Fig. 5. Conversion and product selectivity in *cis,cis*-1,5-cyclooctadiene liquid-phase hydrogenation over Rh-bentonite (60 mg catalyst, 0.0197 mol *cis,cis*-1,5-cyclooctadiene,  $10^5 \text{ Pa}$  hydrogen pressure, reaction at  $308 \text{ K}$  in  $20 \text{ ml}$  toluene:ethanol = 7:3 mixture).

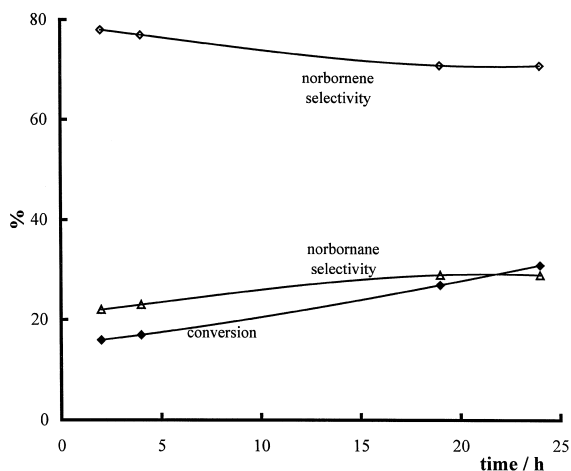


Fig. 6. Conversion and product selectivity in norbornadiene liquid-phase hydrogenation over Rh-bentonite (60 mg catalyst, 0.0197 mol norbornadiene,  $10^5$  Pa hydrogen pressure, reaction at 308 K in 20 ml toluene:ethanol = 7:3 mixture).

The hydrogen uptake of cyclohexene-3-one was found to be remarkably fast and resulted in the formation of cyclohexanone with an outstanding selectivity. No reference data could be found in literature for the reaction of cyclohexene-3-one on the Wilkinson complex, but a 100% selectivity of cyclohexanone was published on a Pt–Sn phosphine complex at 363 K and  $3.4 \times 10^6$  Pa [16]. For the hydrogenation of

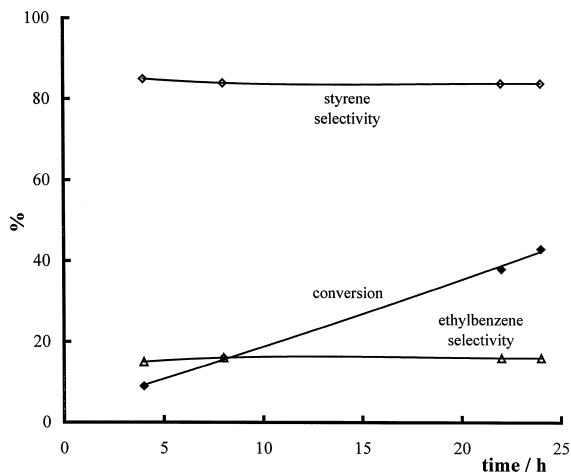


Fig. 7. Conversion and product selectivity in phenylacetylene liquid-phase hydrogenation over Rh-bentonite (60 mg catalyst, 0.0197 mol phenylacetylene,  $10^5$  Pa hydrogen pressure, reaction at 308 K in 20 ml toluene:ethanol = 7:3 mixture).

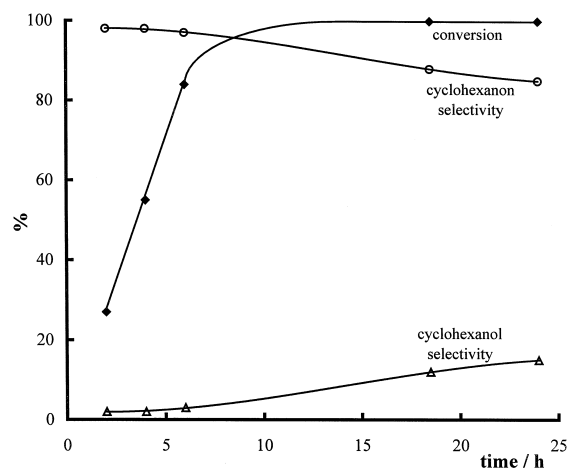


Fig. 8. Conversion and product selectivity in 2-cyclohexene-1-one liquid-phase hydrogenation over Rh-bentonite (60 mg catalyst, 0.0197 mol 2-cyclohexene-1-one,  $10^5$  Pa hydrogen pressure, reaction at 308 K in 20 ml toluene:ethanol = 7:3 mixture).

phenylacetylene, a lower selectivity of styrene was observed than that for intercalated  $[\text{Rh}(\text{PPh}_3)_3]^+$  [6]. At the same time, the selectivity of 80% obtained for styrene is quite impressive, as mostly the formation of ethylbenzene was reported under homogeneous conditions [19,22].

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