Selective hydrogenation of benzene to cyclohexene using a Ru catalyst suspended in an aqueous solution in a mechanically agitated tetraphase reactor: a study of the influence of the catalyst preparation on the hydrogenation kinetics of benzene and of cyclohexene

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Abstract

The reactivity of Ru based catalysts in the benzene selective hydrogenation to cyclohexene has been studied. The reaction has been carried out in a tetraphase slurry reactor at 423 K, at 5 MPa of pressure, in the presence of two liquid phases: benzene and an aqueous solution of $0.6 \, mol \, l^{-1}$ $ZnSO_4$. A detailed kinetic measurement has been carried out in order to study the influence of the preparation procedure and of the treatments on the catalyst activity and selectivity. Moreover, a comparison of benzene and cyclohexene hydrogenation kinetics is presented in order to evaluate, which are the influence of the treatments carried out on the unreduced catalyst on the activity, selectivity and yield to cyclohexene. The kinetics of benzene hydrogenation indicates that the catalyst activity is influenced by the time, during which it remains in the mixture of precipitation for its preparation. The longer the time, the lower the activity is. Selectivity and yield remain practically unaffected after 18 h of permanence in the mixture of precipitation. Treatment of the unreduced catalyst with water depresses both activity and selectivity, while treatment with $1 \, mol \, l^{-1}$ NaOH gives the best results. On the contrary, in the hydrogenation of cyclohexene, the NaOH treated catalyst is three times less active than the catalyst treated with water. These results are in agreement with the higher selectivity achieved using NaOH treated catalysts. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Benzene selective hydrogenation; Ru catalysts; Hydrogenation kinetics

1. Introduction

Cyclohexene is an important intermediate for many chemicals. Of particular industrial relevance is the cyclohexanol production via cyclohexene hydration [1]. The importance of cyclohexanol is related to the production of the polyamides. For example Nylon 66 is produced by polymerization of adipic acid with hexamethylendiamine. The first step of the production of both monomers is the oxidation of cyclohexane, produced in turn via benzene by hydrogenation. The main limit is the low selectivity of the oxidation step. The new route, via selective hydrogenation of benzene to cyclohexene, followed by hydration of the latter, allows to avoid the poorly selective cycloexane oxidation step. Cyclohexene hydration occurs in high yield, thus, the critical step of the process is the selective hy-

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Nomenclature

[A]	cyclohexane moles fraction (%)
[B]	benzene moles fraction (%)
[E]	cyclohexene moles fraction (%)
M	number of differential equations
N	number of experiments
q_{1-q}	least square estimators
SR	square residual sum
t_i	time of sampling
X_{if}	derivative matrix
Y_{ij}	matrix of the experimental values
∇_q	nabla operator of q coordinate

drogenation of benzene to cyclohexene. Recently, several authors have studied the selective hydrogenation of benzene to cyclohexene, mainly employing ruthenium based catalysts, which give the best results [2–5].

In the benzene hydrogenation, cyclohexene was detected for the first time in 1957 by Anderson, employing a Ni film as catalyst [6]. Ru based catalysts were employed by Hartog and Zwietering [7]. The reaction was carried out in the presence of an aliphatic alcohol with Ru-black as catalyst. The yield of cyclohexene was as low as 2.2%.

From an industrial point of view, the first encouraging result was obtained by Drinkard, who found that a much higher selectivity can be achieved when the hydrogenation is carried out in the presence of water. By employing a tetraphase reactor at 130–180°C and 70 atm of pressure, in the presence of an aqueous solution in which a Ru precursor was precipitated by an alkaline hydroxide, the yield to cyclohexene was 30% [3]. The basic idea of Drinkard has been developed by others, who studied new catalytic systems [3,4,7]. The effect of promoters and co-catalysts has been investigated. The results are reported in particular in the patent literature [1–5,8].

In 1988, Nagahara and co-workers [8] reported the synthesis o a particularly efficient catalyst composed of a Ru-black promoted with ZnO. The reaction was carried out in a tetraphase reactor at 150°C and 50 atm of pressure in the presence of a solution of $ZnSO_4$ and of suspended ZrO_2, to avoid catalyst agglomeration. The yield of 56% and the selectivity of 80% was believed to be high enough to develop an industrial process.
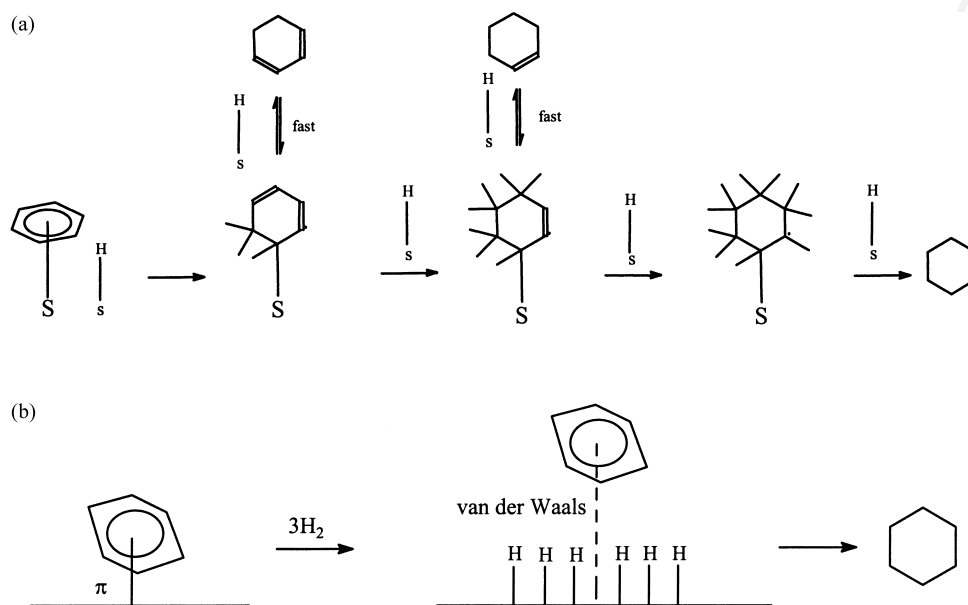
The selective of benzene in a tetraphase reactor in the presence of Ru-black and an aqueous solution was extensively studied by Odembrand et al. in early 1980s [9,10]. They investigated the effect of the composition of the water solution on yield and selectivity, which are significantly influenced by the diffusion of the reagents.

Recently, Scholten and co-workers studied the effect of the reaction variables employing an unsupported Ru catalyst without any promoter, in the presence of an aqueous solution of $ZnSO_4$. These authors pointed out that the role of the aqueous solution is strictly connected with the diffusion limitation of hydrogen to the catalytic surface, which lowers the hydrogen availability on the catalyst surface. Catalyst hydrophilicity is clearly related to catalyst selectivity to cyclohexene. As a matter of fact if the organic phase surrounds the catalyst, cyclohexene is not detected because the hydrogenation proceeds to cyclohexane. The hydrophilicity of the granules is strongly influenced by the presence of hydrogen, as the adsorption enthalpy of water on Ru particles in the presence of hydrogen is half the value when no hydrogen is present [11]. On the basis of such evidences, the authors proposed that part of the granules could be covered with the organic phase with consequent lowering of the selectivity to cyclohexene [12,13].

Many authors have reported the importance of the promoters on the catalyst activity [11,14–16]. In particular, the reactivity of catalyst surface is strongly influenced by the presence of alkali. Waghray and Blackmond reported that Ru/SiO_2 K_2O promoted catalysts selectively hydrogenate the 3-methyl-2-butenal to the 3-methyl-2-buten-1-ol. In these cases the base reduces the selectivity toward the hydrogenation of the carbon-carbon double bond [17,18].

Many authors have extensively studied the benzene hydrogenation kinetics to cyclohexane [19–21]. They mainly, employed gas phase reactors with several metals as catalysts. One of the most interesting mechanisms of benzene hydrogenation has been proposed from Prasad et al. in the early 1980s [22]. The main features of the model are the contemporary presence of two reaction routes:

1. A planar π complex of benzene undergoes a step hydrogenation via linear σ-bonded benzene (S sites type) in the presence of two hydrides bonded in different catalyst sites (S sites type) (Scheme 1a).

(a)

(b)

Scheme 1.

2. A planar π complex of benzene is displaced in one step by six hydrides with a formation of a van der Waals adduct followed by complete hydrogenation to cyclohexane (Scheme 1b).

These mechanisms are operative at the same time and the prevalence of one is related to the molar ratio of benzene. At low molar ratio of benzene, the first mechanism is predominant, at higher benzene pressure, the second becomes more important. These findings can provide an explanation on the role of the water when the hydrogenation is carried out with the catalyst suspended in a benzene water medium. When the catalyst is wetted by water, because of the low solubility of benzene in water, the step mechanism is predominant. Moreover, water competes with cyclohexene on surface adsorption, thus, disfavoring its hydrogenation to cyclohexane.

In a previous paper [23], it was observed that the catalysts activity was mainly due to their surface reactivity and not only to the diffusion limitation of the reagents at the interfaces. In the present study, the influence of the treatments on the unreduced catalyst on the rate, the selectivity and the yield of benzene selective hydrogenation to cyclohexene is presented.

2. Experimental

2.1. Materials

The following chemicals were employed without any purification: hydrogen, nitrogen and helium research grade (purity>99.999% SIAD); benzene 'analyzed reagent' (purity>99%, tiophene<1 ppm Baker); cyclohexene (purity>99% Acros); cyclohexane RPE (purity>99% Carlo Erba); $RuCl_3 \cdot n H_2O$ (Ru 41% Alfa); sodium hydroxide (purity>96% BDH).

2.2. Hydrogenation reactions

The reaction was carried out in a 250 ml stainless steel autoclave (AISI 316). Reagents and product were contained in a baffled PTFE beaker fitted to the autoclave wall (no volume is outside the beaker). Efficient stirring was provided by a magnedrive self-aspirating turbine, which allows agitation rate up to 2000 rpm. Temperature control was obtained by a circulation oil bath (Haake mod. F3) equipped with a Pt-100 thermoresistance, which automatically controlled the internal temperature of the reactor within
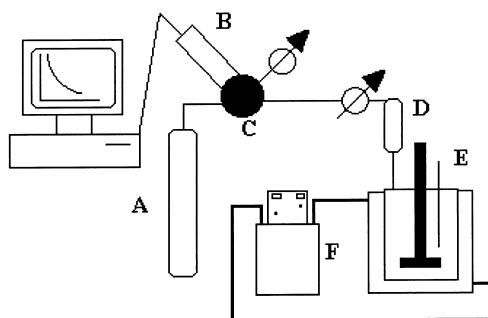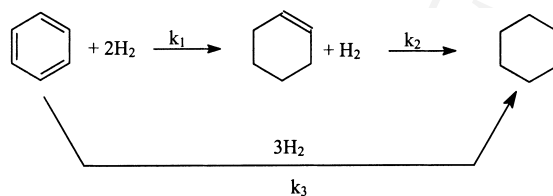
Fig. 1.

0.5 K (in slow reactions). An auxiliary autoclave allowed the injection of benzene to the autoclave to start the reaction at the desired pressure. The pressure of the autoclave was maintained constant by a membrane regulator within 50 kPa. The hydrogen consumption was evaluated by measuring the pressure drop in a vessel of known volume (1120 ml) which was recorded by a PC. The progress of the reaction was monitored also by sampling the organic phase through a capillary of 0.2 mm of inner diameter. During the sampling, the agitation was interrupted in order to stop the reaction. The hydrogenation equipment is shown schematically in Fig. 1.

Reaction samples were analyzed by a gascromatograph (HP mod. 5890 II series) equipped with a 530 μm E.D. and 30 m long FFAP column employing nitrogen as carrier 7.5 ml min^{-1}. Temperature analysis was 308 K for 1.5 min, heating 15 K min^{-1} to 353 K.

The experimental procedure can be summarized as follows:

- the catalyst was charged into the reactor (typically 90 mg);
- forty milliliters of $ZnSO_4$ solution (0.6 mol l^{-1}) was introduced into the beaker;
- the reactor was closed, purged with hydrogen and pressurized at 3 MPa;
- forty milliliters of benzene or cyclohexene was charged into the auxiliary autoclave purged with hydrogen and pressurized at 5 MPa;
- the reactor was heated at 423 K for 2 h with a stirring rate of 800 rpm in order to reactivate the catalyst;
- the substrate was injected into the reactor and the pressure was regulated at 5 MPa

Scheme 2. Reaction model proposed for benzene selective hydrogenation.

- before starting the reaction, it was necessary to wait for 5 min without agitation in order to stabilize the temperature;
- periodically the stirrer was stopped and the organic phase was sampled; during this operation the reaction time was not computed.

2.3. Catalyst preparation

2.3.1. Unreduced catalysts preparation

A suitable amount of $RuCl_3$ was dissolved in water to obtain a 4 g l^{-1} solution. A 30% NaOH aqueous solution was quickly added to the Ru solution under vigorous stirring, until the final concentration of the precipitant was 22.4 g l^{-1}. The resulting slurry was heated at 353 K for 3 h, cooled and left to stand for the desired time (0–72 h, typically 18 h). Then the unreduced catalyst was filtered, washed with 60 ml of water and treated as follows:

- no treatment (catalyst Ru-18 of Table 1, unreduced catalyst);
- treatment with H_2O for 3 h at 353 K, cooling to room temperature and overnight digestion (catalyst Ru-H_2O of Table 1, unreduced catalyst);
- treatment with 1 mol l^{-1} NaOH for 3 h at 353 K, cooling to room temperature and overnight digestion (catalyst Ru-NaOH of Table 1, unreduced catalyst);

Table 1

Parameter errors, correlation between the parameters and mean square residuals of cyclohexene hydrogenation kinetics[a]

Catalyst	q (ce–ca)	Error q	k (ce–ca)	Error (k)	σ	Correlation $(q–k)$
Ru-H_2O	2.0	0.065	0.00043	0.00012	2.6	0.998
Ru-18	0.84	0.037	0.043	0.0066	1.5	0.999
Ru-NaOH	1.0	0.054	0.011	0.0024	0.48	0.997

[a] Run conditions: T=423 K, P=5 MPa, reaction volume 80 ml (40 ml cyclohexene, 40 ml water solution 0.6 mol l^{-1} $ZnSO_4$), catalyst loading 90 mg and agitation rate 1500 rpm.
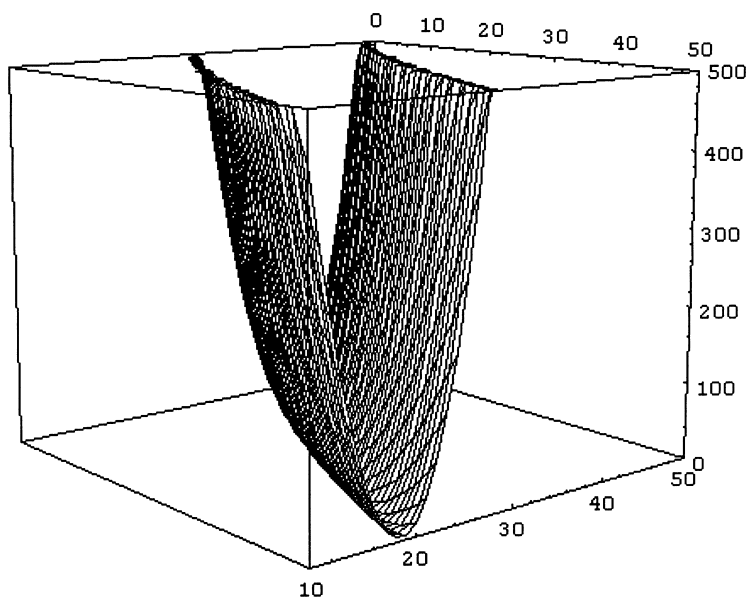
Fig. 2.

- prereduction with N_2H_4 10% for 1 h at 353 K cooling to room temperature and washed with distilled water until neutrality (catalyst Ru-Na-N_2H_4 of Table 1, prereduced catalyst);
- prereduction with HOOCH 10% for 1 h at 353 K, cooling to room temperature and washed with distilled water until neutrality (catalyst Ru-Na-HOOCH of Table 1, prereduced catalyst).

2.3.2. Catalyst reduction

An unreduced or a prereduced catalyst was placed into the reaction beaker together with 60 ml of water, the slurry is practically in neutral conditions, except that obtained with NaOH treated catalyst (pH>12). Then the reactor was purged with hydrogen, pressurized with 3.5 MPa and heated at 423 K under stirring (700 rpm). The reduction was carried out for 7 h at 423 K. The reactor was then cooled down at room temperature. The suspension was allowed to stand overnight (18 h). The autoclave was then depressurized, opened and the catalyst was passivated by treating it with distilled water saturated with air for 1 h. Finally, the passivated catalyst was filtered off, vacuum dried, and used thereof.

2.4. Non-linear regression analysis

The program used to calculate the least square estimate of the kinetics parameters, was built in *Mathematica*. In order to take into account the complexity of the model, which consists in a simultaneous power law differential equation (see later), the square residual is defined by Eq. (1), in which the functions f_j are the kinetic model (*M* equations), t_i and Y_{ij} are the experimental values (time and concentrations respectively), and $q_1, q_2, \ldots, q_p$ are the kinetic parameters (the least square estimators). The numerical solution of the differential equation was carried out by an internal routine of *Mathematica* which calculates the numerical solution of differential equations at any desired precision [24].

$$SR = \sum_{i=1}^{N} \sum_{j=1}^{M} [Y_{ij} - f_j(t_i, q_1, q_2, \ldots, q_p)^2] \qquad (1)$$

The minimization of the square residual sum was achieved by a modified simplex method [25]. The convergence to a minimum was verified by reducing the step of two order of magnitude and obtaining a constant values of the square residuals sum.
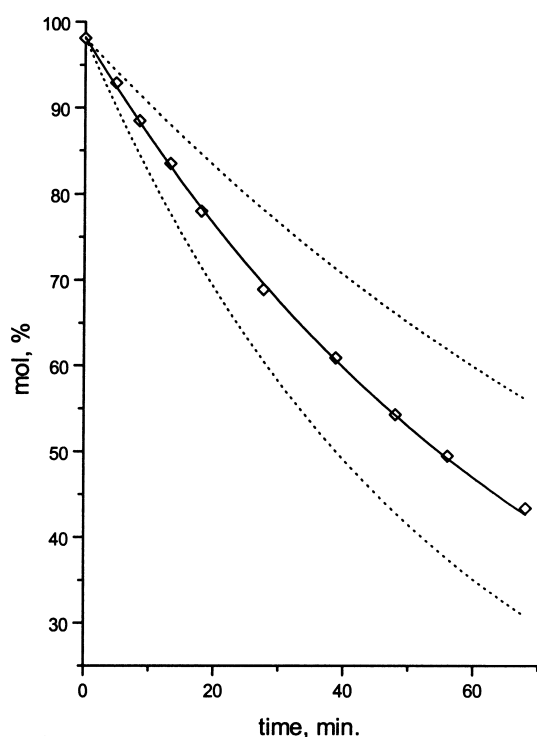
Fig. 3.

Table 2
Correlation matrix of the kinetic parameters estimation for benzene hydrogenation employing Ru-NaOH catalyst[a]

	k_1	k_2	k_3	n	m	l
k_1	1					
k_2	0.286	1				
k_3	−0.959	−0.128	1			
n	−0.999	−0.243	0.962	1		
m	0.929	0.0114	−0.992	−0.938	1	
l	−0.219	−0.997	0.0579	0.175	0.0584	1

[a] Run conditions: T=423 K, P=5 MPa, reaction volume 80 ml (40 ml benzene, 40 ml water solution and $0.6 \, \text{mol} \, 1^{-1}$ $ZnSO_4$), catalyst loading 90 mg and agitation rate 1500 rpm.

3. Results and discussion

3.1. Comparison of the hydrogenation kinetics of benzene and cyclohexene

The hydrogenation kinetics of both benzene and cyclohexene catalyzed by the following catalyst: Ru-18, Ru-H_2O and Ru-NaOH is discussed here.

3.1.1. Evaluation of the kinetic parameters
As other authors pointed out, the diffusion of the reagents at the interfaces, strongly affects catalyst selectivity [10–13]. In order to compare the reactivity of many catalysts, it is necessary to determine for each one, the extent of the physical limitation at the interfaces. As previously reported, the reaction kinetics is affected by diffusion limitation at liquid/solid and into the pores of the catalyst [23]. The effect of such a limitation on both the yield and selectivity of the partial hydrogenation of benzene to cyclohexene has been presented in a previous work [23]. The extent of the influence of the liquid/solid diffusion and of the internal one has been evaluated respectively by the Carberry and Wheeler–Weisz numbers. No correlation has been observed between these parameters and the selectivity and the yield of the reaction [23]. Thus, the different activity of the catalysts can be mainly due to the differences in the intrinsic catalyst activity.

The regression of the time varying concentrations of the reacting species allows the evaluation of the kinetic parameters (i.e. kinetic constant and reaction order) both in benzene and cyclohexene hydrogenation.

The errors and the parameters correlation matrix has been evaluated using a first order approximation of the square residual hypersurface in the convergence point [26]. As a matter of fact, the derivative matrix of the least square estimator $(q_1, q_2, \ldots, q_p)$ has been numerically evaluated with the central difference formula. The constancy of the derivative value was achieved with a third order truncation error term [25].

The rectangular matrix of the least square estimator derivatives was defined as follows:

$$\boldsymbol{X}_{if} = -\nabla_q \sum_{j=1}^{M} [\boldsymbol{Y}_{ij} - f_j(t_i, q_1, q_2, \ldots q_p)] \qquad (2)$$

The $\boldsymbol{X}_{if}$ matrix contains the first order approximation of the parameter error information. Then, following the procedure proposed by Bates and Watts, the calculation of the error and of the correlation matrix has carried out [26].

Table 3
Parameters and parameter errors for benzene hydrogenation[a]

Catalist	l ord. (bz–ce)	Error (l)	m ord. (bz–ca)	Error (m)	n ord. (ce–ca)	Error (n)	k_1 ord. (bz–ce)	Error (k_1)	k_2 ord. (ce–ca)	Error (k_2)	k_3 ord. (bz–ca)	Error (k_3)
Ru-H_2O	0.70	0.49	0.73	0.58	1.6	0.71	0.052	0.12	0.0046	0.011	0.040	0.11
Ru-18	0.7	3.0	0.72	2.7	1.6	1.2	0.054	0.59	0.0048	0.027	0.038	0.48
Ru-NaOH	1.5	0.15	0.76	0.087	1.2	0.63	0.0018	0.0012	0.0053	0.011	0.034	0.014

[a] Run conditions: $T=423$ K, $P=5$ MPa, reaction volume 80 ml (40 ml benzene, 40 ml water solution and $0.6\,\mathrm{mol\,l^{-1}}$ $ZnSO_4$), catalyst loading 90 mg and agitation rate 1500 rpm.

From these data, initial overall activity and initial cyclohexene selectivity together with the maximum yield to cyclohexene are calculated which are a useful tool to compare the reactivity of the catalysts.

The reaction model is the same proposed in the previous paper [23] and it is reported in Scheme 2.

The model is based on two consecutive reactions and on a parallel one (the direct formation of the cyclohexane from benzene). Such a model has been proposed because the presence of cyclohexane has been detected even at a conversion below 1%. Moreover, cyclohexadiene as intermediate has never been observed.

In order to describe reaction, kinetics affected by diffusion limitation at the interface, it is useful to employ simultaneous power low kinetic equations:

$$-\frac{d[B]}{dt} = k_1[B]^l + k_3[B]^m \tag{3}$$

$$-\frac{d[E]}{dt} = -k_1[B]^l + k_2[E]^n \tag{4}$$

$$\frac{d[A]}{dt} = k_3[B]^m + k_2[E]^n \tag{5}$$

In order to compare the kinetics of benzene hydrogenation with the cyclohexene hydrogenation kinetics, a power law equation has been employed to describe the hydrogenation of cyclohexene. Thus, the kinetic law is:

$$-\frac{d[E]}{dt} = k[E]^q \tag{6}$$

The optimization of the parameters (k_1, k_2, k_3, l, m, n of the simultaneous equations and the parameters k and q of the kinetic equation of the cyclohexene hydrogenation) has been carried out by searching the minimum of the square residual (SR function).

The procedure employed for searching the minimum of the SR surface is out the scope of the present paper, thus, only the main results of the analysis are reported.

Fig. 2 represents the sum of the square differences between calculated and experimental values of the
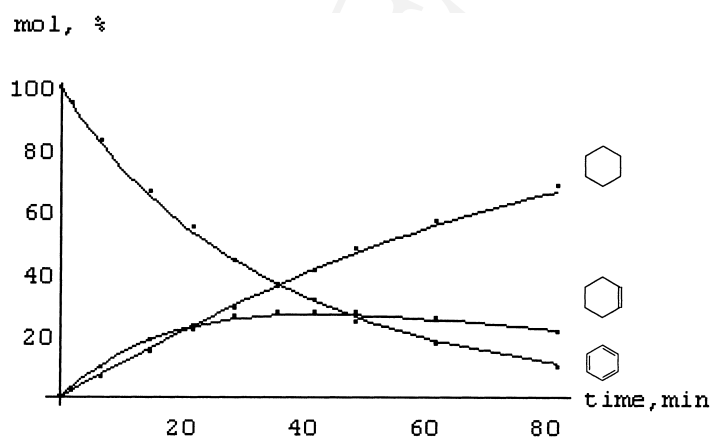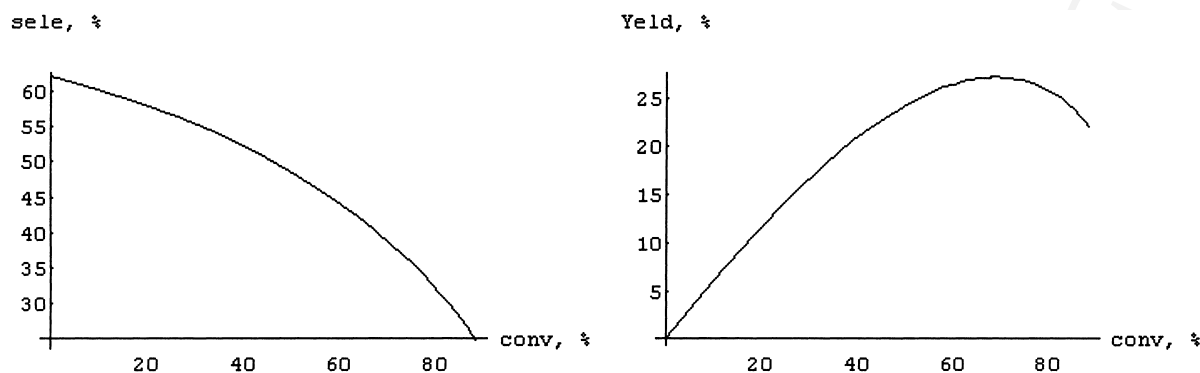

Fig. 4.

sele, %

Yeld, %

Fig. 5.

kinetics of cyclohexene hydrogenation to cyclohexane, in the presence of the Ru-NaOH catalyst. The sharp valley represents the values of q and k that minimize the SR function.

A similar shape of the SR surface indicates high correlation between the equation parameters (q and k), as confirmed from calculated first order mutual correlation indexes which are close to 1 (see Table 1). This means that an infinity of estimators couples minimize the surface giving also, high parameter errors and consequently a large 95% confidence band (see Fig. 3).

This treatment, however, gives an indication of the interval of q and k where the SR function is mini-

mized, which allows only an indicative estimation of the parameters but a good measure of yield and selectivity over the whole reaction time. Thus, initial reaction rate, selectivity and maximum yield can be evaluated.

In a similar way, the optimization of the kinetic parameters of benzene hydrogenation (Eqs. (3)–(5)) has been carried out searching minims of the SR function and the results are exposed, for example, in Tables 2 and 3. Table 2 shows clearly that these parameters are highly correlated, which suggests that only an indicative reaction order and kinetic constant can be evaluated.
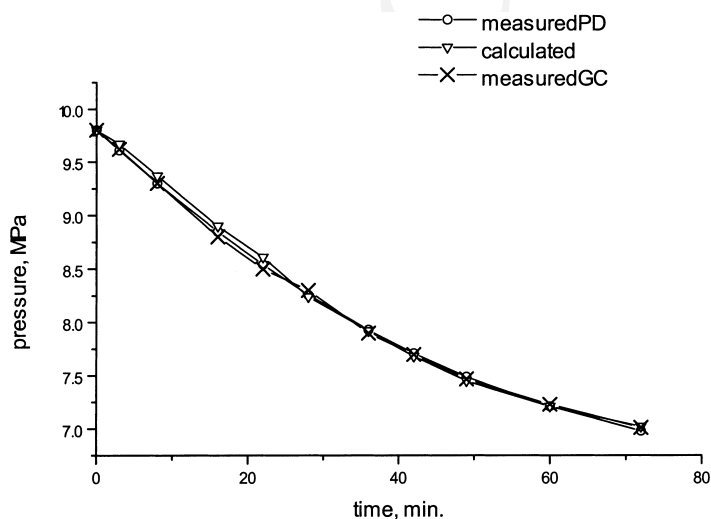
Fig. 6.

Table 4
Benzene hydrogenation catalyzed by Ru Catalysts[a]

	Catalyst	Ru (%)	Treatment	r_0, $H_2 \times 10^2$ (mol l^{-1} s^{-1} g_{Ru}^{-1})	Initial select (%)	Maximum yield (%)
1	Ru-Na-N$_2$H$_2$	84	10% N$_2$H$_2$, 353 K, 3 h	0.37	4.3[c]	2.9[c]
2	Ru-Na-HCOOH	86	10% HCOOH, 353 K, 3 h	0.58	4.3[d]	1.4[d]
3	Ru-0	81	0 h digestion[b]	9.2	48	18
4	Ru-72	78	72 h digestion[b]	6.1	51	22
5	Ru-H$_2$O	80	18 h digestion[b] water 353 K, 3 h	7.8	51	22
6	Ru-18	79	18 h digestion[b]	7.9	54	23
7	Ru-NaOH	77	18 h digestion[b], 1 mol l^{-1} NaOH 353 K, 3 h	9.2	62	28

[a] Run conditions: T=423 K, P=5 MPa, reaction volume 80 ml (40 ml benzene, 40 ml water solution and 0.6 mol l^{-1} ZnSO$_4$), catalyst loading 90 mg and agitation rate 1500 rpm.

[b] Digestion of the precipitated precursor in the precipitation environment.

[c] At 32.8% of conversion.

[d] At 68.2% of conversion.

Table 3 reports the non-linear regression analysis results of the benzene hydrogenation kinetics. The calculated errors are really large, this is mainly due to the large number of parameters employed in the model, which causes an increase of the variance and of the error values [26].

Even though, the large error and the strong correlation, the estimation of the kinetic parameters allows the calculation of the reaction profile, which in turn allows the evaluation of the reagents concentration over the whole reaction time. The results of these calculations are then employed to compare the hydrogenation kinetics measured in the presence of the Ru catalysts.

An example of the data fitting is reported in Fig. 4.

The calculated profile of the yield and selectivity plotted in function of the conversion is represented in Fig. 5.

3.1.2. Mass balance

The mass balance has been checked from the comparison of the experimental pressure drops into the hydrogen vessel reservoir, the chromatographic analysis of the sampled organic phase and the calculated pressure drops from the kinetic parameters. Fig. 6 shows an example of the mass balance result for benzene hydrogenation. The good agreement indicates that co-products are not formed in significant amount, and the fitting procedure is a reliable method to compare catalyst activity on the hydrogenation kinetic.

3.2. Influence of the catalyst treatment on yield and selectivity

The comparison of the catalysts performances has been done by the initial rate of hydrogenation, the initial cyclohexene selectivity (both calculated by the limit of zero conversion) and by the maximum cyclohexene yield (obtained by putting the yield first, derivative respect to conversion equal to zero). These are calculated by the kinetic parameters obtained from non-linear regression analysis, described in the previous chapter.
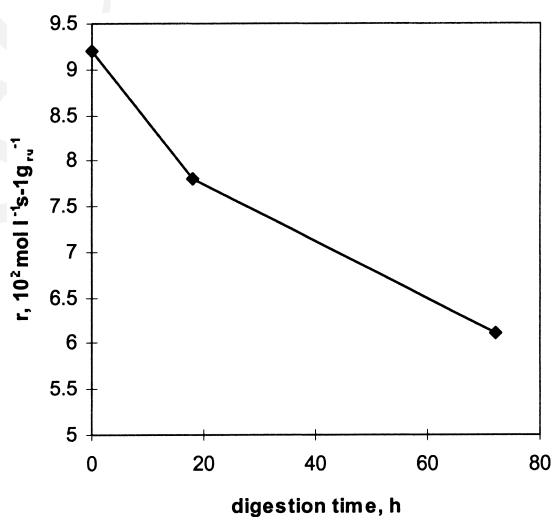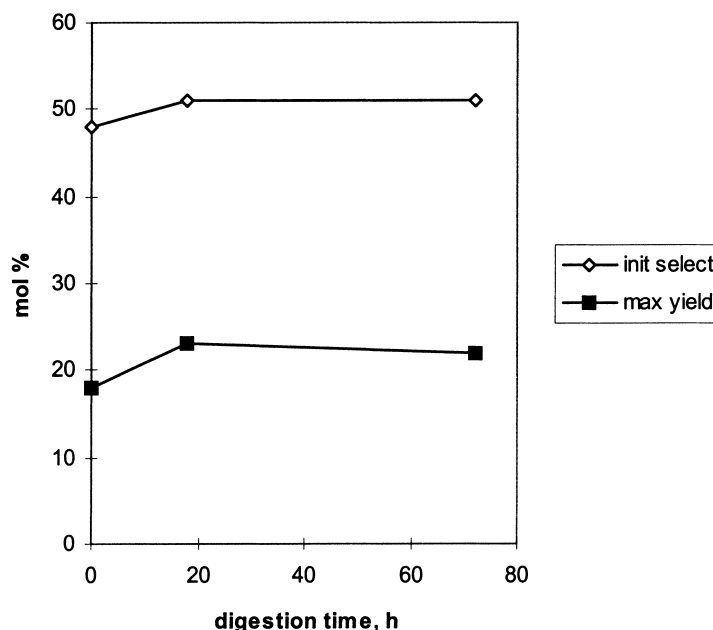

Fig. 7.

Fig. 8.

In Table 4, the effects of the treatments on the selectivity and on the activity are summarized. When the unreduced catalyst is treated with N_2H_2 or with HCOOH, the activity is strongly depressed (entries 1 and 2). Moreover, both selectivity and yield to cyclohexene are very poor. On the contrary, treatment with $1 \, mol \, l^{-1}$ NaOH improves both the activity and selectivity, which indicates that the treatment with a base plays an important role (entry 7). Another preparation parameter which influences both activity and selectivity, is the digestion time of the unreduced catalyst in the precipitation medium, as the longer the time is, the lower the reaction initial rate is, as shown in Fig. 7.

Thus, the base influences the activity of the catalyst. This can be ascribed to three different causes:

- a saturation effect of the active sites, by adsorption of NaOH;
- an increasing of the average particles diameter;
- an increasing of the crystallite size.

Even though the reaction rate decreases with the increasing of the digestion time of the precipitated precursor in NaOH, both initial selectivity and maximum yield increase to a plateau after 20 h (see Fig. 8).

3.2.1. Comparison between the hydrogenation kinetics of benzene and cyclohexene catalyzed by Ru-H_2O, Ru-18 and Ru-NaOH

In a previous work, it was found that the nature of the base employed in the precipitation step, strongly influences the activity and the selectivity of a catalyst.

Table 5
Results of the benzene selective hydrogenation catalyzed by Ru catalysts[a]

Catalist	Ru (%)	Initial select (%)	Maximum yield (%)	Conv. Maximum yield (%)	r_0, $H_2 \times 10^2$ ($mol \, l^{-1} \, s^{-1} \, g_{Ru}^{-1}$)
Ru-H_2O	80	51	22	72	7.8
Ru-18	79	54	23	68	7.9
Ru-NaOH	77	62	28	69	9.2

[a] Run conditions: T=423 K, P=5 MPa, reaction volume 80 ml (40 ml benzene, 40 ml water solution and $0.6 \, mol \, l^{-1}$ $ZnSO_4$), catalyst loading 90 mg and agitation rate 1500 rpm.

Table 6
Comparison between the cyclohexene hydrogenation kinetics[a]

Catalist	Initial rate of cyclohexene hydrogenation in benzene $r0$, $H2 \times 10^2$ (mol l^{-1} s^{-1} g_{Ru}^{-1})	Reaction order	Initial rate of cyclohexene hydrogenation $r0$, $H2 \times 10^2$ (mol l^{-1} s^{-1} g_{Ru}^{-1})	Reaction order
Ru-H$_2$O	4.4	2.0	4.9	1.6
Ru-18	4.3	0.84	3.5	1.6
Ru-NaOH	0.98	1.0	1.4	1.2

[a] Run conditions: $T=423$ K, $P=5$ MPa, reaction volume 80 ml (40 ml benzene, 40 ml water solution and 0.6 mol l^{-1} ZnSO$_4$), catalyst loading 90 mg and agitation rate 1500 rpm.

In order to establish, which is the catalyst preparation step that influences most the catalyst activity and selectivity, the effect some washing treatment on the unreduced Ru catalyst has been studied. The comparison of the hydrogenation kinetics of benzene and cyclohexene allows to state, what is the role of the base on catalyst activity and selectivity. A batch of unreduced catalyst prepared by precipitation of RuCl$_3$ solution with NaOH (the catalyst Ru-18) has been treated as follows:

- treatment with H$_2$O for 3 h at 353 K, cooling and over night digestion;
- treatment with 1 mol l^{-1} NaOH for 3 h at 353 K, cooling and over night digestion.

Table 5 reports the initial hydrogen consumption, initial selectivity and maximum yield. These results clearly indicate that, when the unreduced catalyst is

washed with H$_2$O, neither the initial hydrogenation rate of benzene nor the selectivity to cyclohexene are influenced significantly. On the contrary, when the unreduced catalyst is treated with 1 mol l^{-1} NaOH, the initial hydrogenation rate, selectivity and maximum yield increase. Thus, the base can play an important role on the catalyst activity. Moreover, the catalyst Ru-NaOH causes a shift of the reaction order of the cyclohexene hydrogenation from 1.5–2 to ca. 1 (see Table 5). This is a further evidence that the treatment with NaOH strongly modifies the reactivity of the catalyst, probably due to a different surface reactivity.

Also in the case of cyclohexene hydrogenation, the cyclohexene reaction order decrease from 2 to 1. However, it should be noted that the rate of cyclohexene hydrogenation is strongly depressed whenever the
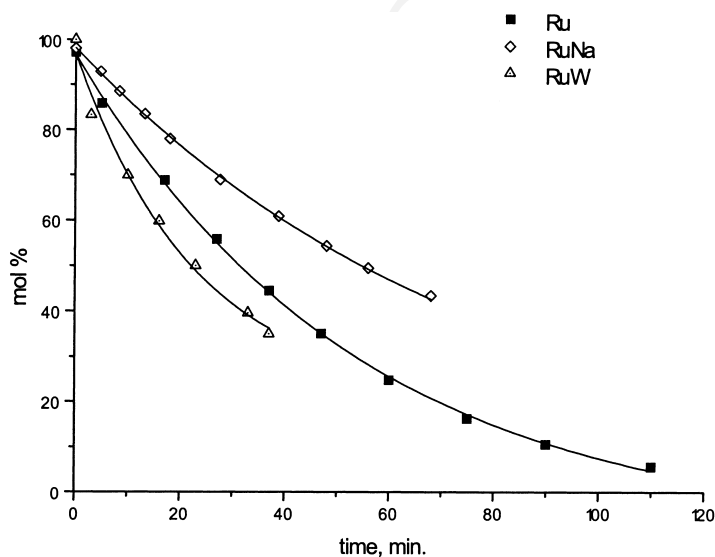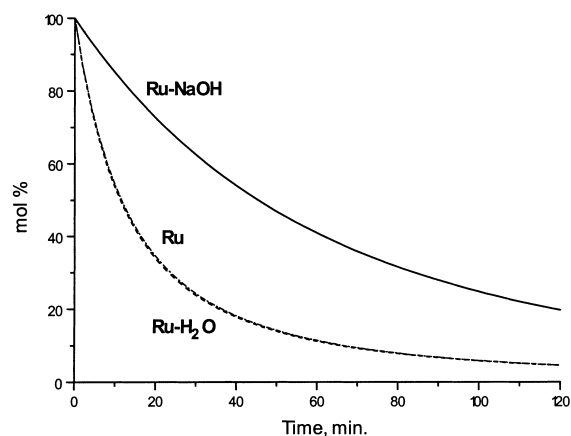

Fig. 9.

Fig. 10.

unreduced catalyst is treated with NaOH, as reported in Table 6. This is observed both in cyclohexene hydrogenation and by calculating the initial cyclohexene hydrogenation rate with the kinetic constants obtained by the hydrogenation kinetics of benzene.

Fig. 9 shows the fittings of the cyclohexene hydrogenation kinetics using the three differently treated catalysts.

Fig. 10 shows the simulation of the cyclohexene consumption obtained from the parameters, calculated from the hydrogenation of benzene. The comparison of Figs. 9 and 10 indicates a clear influence of the NaOH treatments on the Ru-NaOH catalyst. It can be noted that the cyclohexene hydrogenation rate is strongly lowered in the presence of the NaOH treated catalyst.

These results, suggest that the catalyst activity and selectivity are influenced by the interaction of the metallic Ru surface with the NaOH during the catalyst preparation. A reasonable explanation of these facts can be enhancement of the surface hydrophilicity due to the NaOH treatment. As reported in other papers, the presence of the $0.6\,mol\,l^{-1}$ $ZnSO_4$ solution enhances the hydrophilicity of the catalyst particles which become more hydrophobic in the presence of hydrogen [13]. As a matter of fact, the reaction carried out in the presence of pure water is very fast but poorly selective [12]. The lower hydrophilicity of the particle favors the contact of the catalyst directly with the organic phase and consequently a fast hydrogenation to cyclohexane occurs. However, this does not explain the differences in cyclohexene hydrogenation rate.

The catalyst performance enhancement caused by the NaOH treatment can be due also to the electronic promotion of the catalyst surface. Both the hypotheses (enhancement of the hydrophilicity and electronic promotion) are consistent and may be related the differences in the cyclohexene hydrogenation rate.

4. Conclusions

In the present paper, it has been studied the selective hydrogenation of benzene to cyclohexene in a tetraphase slurry reactor at 423 K and 5 MPa of pressure in the presence of an aqueous solution of $0.6\,mol\,l^{-1}$ $ZnSO_4$, using Ru based catalysts. The effect of some catalyst preparation parameters on their reactivity has been investigated. In order to make possible the comparison of the activity of each catalyst, a power law kinetic model has been employed, both for benzene as well as for cyclohexene hydrogenation. The technique of optimization has been extensively described in order to validate the calculated values obtained from the data fittings. In particular the influence of the NaOH, employed in the preparation of the unsupported catalyst, as a promoter has been studied. As a matter of fact, the treatment with NaOH enhances the selectivity to cyclohexene. The kinetic measurements show that benzene hydrogenation rate is promoted when the catalyst is treated with NaOH, on the contrary, it is three times less active in cyclohexene hydrogenation. Moreover, the reaction order respect to cyclohexene is lowered (from 1.5–2 to ca. 1) when the catalyst treated with NaOH is employed. These results have been explained by supposing that the base enhance the hydrophilicity of the catalyst and also it has an electronic promotion effect on the surface of the catalyst.

References

[1] U.S. Pat. 4,661,639 to Asahi chem. Co. (1985).
[2] O. Mitsuie Y. Fukuoka, U.S. Pat. 4,678,861 to Asahi chem. Co. (1987).
[3] W.L. Drinkart, NL Pat. 7,205,832 to Dupont de Nemours, 1972.
[4] M.M. Johnson, G.P. Nowack, U.S. Pat. 3,793,383 to Philips Petroleum, 1974.

[5] H. Ichicashi, Eur. Pat. 214530 to Sumitomo Chem. Co. (1987).

[6] J.R. Anderson, Aust. J. Chem. 1 (1957) 210.

[7] F. Hartog, P. Zwietering, J. Catal. 2 (1963) 79.

[8] H. Nagahara, M. Konishi, U.S.Patent 4,734,536 to Asahi chem. Co. (1988).

[9] C.U.I. Odembrand, S.T. Lundin, J. Chem. Technol. Biotechnol. 30 (1980) 677.

[10] C.U.I. Odembrand, S.T. Lundin, J. Chem. Technol. Biotechnol. 31 (1981) 660.

[11] J.A. Don, J.J.F. Scholten, Appl. Catal. 41 (1981) 146.

[12] J. Struijk, M. d'Agremont, W.J.M. Lucas-de Regt, J.J.F. Scholten, Appl. Catal. A 83 (1992) 263.

[13] J. Struijk, M.R. Moene, T. Van der Kamp, J.J.F. Scholten, Appl. Catal. A 89 (1992) 77.

[14] I.W. Bassi, F. Garbassi, G. Vlaic, A. Marzi, G.R. Tauszik, G. Cocco, S. Galvagno, G. Parravano, J. Catal. 64 (1980) 405.

[15] S. Galvagno, A.G. Shastri, J. Schwank, J. Catal. 100 (1986) 446.

[16] B. Coq, E. Crabb, M. Warawdekar, G.C. Bond, J.C. Slaa, L. Mercadante, S. Galvagno, M.C. Sanchez Sierra, J. Mol. Catal. 92 (1994) 107.

[17] A. Waghray, D.G. Blackmond, J. Phys. Chem. 97 (1993) 6002.

[18] A. Waghray, D.G. Blackmond, Catalysis of Organic Reactions, p. 295.

[19] P. Chou, A. Vannice, J. Catal. 107 (1987) 129.

[20] S.D. Lin, A. Vannice, J. Catal. 143 (1993) 539.

[21] S.D. Lin, A. Vannice, J. Catal. 143 (1993) 554.

[22] K.H.V. Prasad, K.B.S. Prasad, M.M. Mallikarjunan, R. Vaidyeswaran, J. Catal. 84 (1983) 65.

[23] L. Ronchin, L. Toniolo, Catal. Today 48 (1999) 255.

[24] M.L. Abell, J.P. Braselton, The Mathematica Handbook, Academic Press, New York, 1992.

[25] J.H. Mathews, Numerical Methods for Computer Science, Engineering and Mathematics, Prentice-Hall, NJ, 1987.

[26] D.M. Bates, D.G. Watts, Non linear Regression Analysis and its Applications, Wiley New York, 1988.