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Catalysis Today 2359 (2001) 1–7

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# Selective hydrogenation of benzene to cyclohexene catalyzed by Ru supported catalysts

## Influence of the alkali promoters on kinetics, selectivity and yield

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### Abstract

The selective hydrogenation of benzene to cyclohexene in the presence of Ru supported catalysts has been investigated 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  $\text{ZnSO}_4$  ( $0.6 \text{ mol l}^{-1}$ ). A study of the influence of the transport phenomena on the reactivity of the catalyst has been carried out. But no correlation between Carberry and Wheeler–Weisz numbers and the selectivity of the catalysts has been found. The main features of the catalysts are the strong dependence between the catalysts preparation procedure and their activity and selectivity. The best results have been observed with Ru/ $\text{ZrO}_2$  catalysts. The influence of the bases employed in the precipitation of the catalysts precursor has also been investigated. KOH is the most effective, yield of 41% and initial selectivity of 80% of cyclohexene has been observed. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydrogenation; Ru catalyst; Alkali promoters

### 1. Introduction

The benzene selective hydrogenation to cyclohexene is connected with the synthesis of cyclohexanol for large-scale polyamide production. Recently, many researchers investigated the influence of the reaction conditions on the selectivity of the reaction employing mainly unsupported Ru catalyst [1]. The best results, reported in an Asahi Patent, were obtained in a tetraphase reactor at 150°C and 50 atm of pressure in the presence of an aqueous solution of  $\text{ZnSO}_4$  and of  $\text{ZrO}_2$ , the latter inhibits the agglomeration of the Ru particles. Yield of 56% and the selectivity of 80% are claimed.

In a previous paper we studied the influences of alkaline hydroxides as promoters in the preparation of some unsupported Ru catalysts [2]. The alkaline treatment enhances both activity and selectivity, probably because the alkali hydroxide on the Ru surface increases the hydrophilicity of the catalyst granule and may act as electronic promoter [3].

More recently, differently loaded supported Ru catalysts have been compared. The main result was that the low loaded Ru catalysts have high activity (almost 10 times that of the unsupported catalysts) but poor selectivity to cyclohexene [4]. Ru catalysts with higher loads are almost as active as the low loaded ones, with selectivity to cyclohexene even higher than those of the unsupported catalysts. Here we discuss the influence of the support and of the alkaline promoter on the reactivity of highly loaded Ru catalysts.

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### Nomenclature

[A]	moles of cyclohexane/initial moles of benzene (%)
[B]	moles of benzene/initial moles of benzene (%)
$c_{\text{H}_2}^*$	equilibrium concentration of hydrogen
$d_p$	catalyst particles diameter (m)
$D_{\text{H}_2, \text{eff}}$	effective diffusivity of hydrogen
[E]	moles of cyclohexene/initial moles of benzene (%)
$k_{\text{ls}}$	mass transfer coefficient of hydrogen at external liquid/solid interface ( $\text{m s}^{-1}$ )
$r_0$	initial rate of hydrogen consumption ( $\text{mol s}^{-1} \text{g}^{-1}$ )
$w$	catalyst weight (mg)

#### Greek symbols

$\eta\phi^2$	Wheeler–Weisz group
$\rho_{\text{av}}$	granule average density

## 2. Experimental

### 2.1. Hydrogenation reaction

The reaction was carried out in 250 ml stainless steel autoclave (AISI 316). Reagents and products were contained in a baffled PTFE beaker. Efficient stirring was achieved due to a self-aspirating turbine, which allowed an agitation rate up to 2000 rpm. Temperature and pressure were maintained constant (423 K and 5 MPa). The reaction was carried out in a tetraphase system (gas/liquid/liquid/solid), composed of two liquid phases, an organic one (benzene) and an aqueous  $\text{ZnSO}_4$  solution ( $0.6 \text{ mol l}^{-1}$ ). The kinetics was followed by sampling the organic phase and measuring the hydrogen consumption. The detailed hydrogenation procedure is described in a previous paper [2].

### 2.2. Catalyst preparation

#### 2.2.1. Preparation of 50% Ru supported catalyst

The highly loaded supported Ru catalysts (50% of theoretical ruthenium) have been prepared employ-

ing different supports, obtained by precipitation of metal chloride or alcoxide with different alkali hydroxides. In particular, the influence of Ti, Zr, Fe oxide and mixtures of them has been studied. The effect of the different alkali hydroxide has also been investigated.

In a typical preparation, 80 ml of a 5% solution (or a suspension) of the precipitant (metal hydroxide, e.g. NaOH) was placed into a 250-ml flask and the calculated amount of the support precursor was quickly added at room temperature. Some catalysts have been obtained carrying out the precipitation of the support in the presence of also a polyketone polymer. The temperature was then raised to 353 K and the Ru precursor ( $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ) was added. The resulting mixture was left at 353 K for 3 h and then cooled to room temperature and maintained at this temperature for 18 h. The calculated Ru percentage of each catalyst was 50% and the actual concentration of Ru as measured by AAS. The catalyst precursor was then reduced as follows.

#### 2.2.2. Catalyst reduction

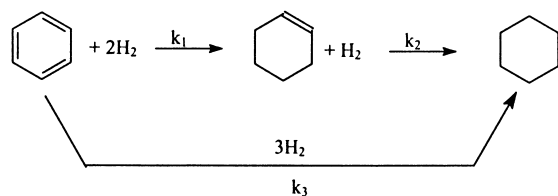
The reduction was carried out for 7 h at 423 K, 5 MPa of hydrogen pressure. The reactor was cooled to room temperature and kept overnight (16–18 h) at this temperature. After this the autoclave was depressurized, opened and the catalyst was passivated with air saturated water for 1 h. Finally the passivated catalyst was filtered off and vacuum dried.

### 2.3. Catalysts characterization

Particle size determination was carried out by measuring the sedimentation rate employing a Micromeritics Sedigraph 5000 D in the region between 0.4 and  $63 \mu\text{m}$ . The results are in good agreement with SEM measurements.

Catalyst porosity has been determined by  $\text{N}_2$  adsorption and desorption at 94 K. Total pore volume has been evaluated at relative pressure of  $p/p_0 = 0.94$  using an automatic adsorption unit (Micromeritics ASAP 2010C) [5].

Chemisorption of hydrogen were carried at the temperature of 373 K with the double isotherm method and 30 min of equilibration time (Micromeritics ASAP 2010C) [6,7].



Scheme 1. Reaction model proposed for benzene selective hydrogenation.

### 3. Results and discussion

#### 3.1. Estimation of the kinetic parameters

In order to fit the experimental concentration profile of the species involved in the reaction, we propose the model as shown in Scheme 1.

The model is based on two consecutive reactions and on a parallel one (the direct formation of cyclohexane from benzene). Such a model has been proposed because of the presence of cyclohexane detected even at a conversion below 1%. Moreover, cyclohexadiene as an intermediate has never been detected. In order to describe reaction kinetics affected by diffusion limitation, it is useful to employ simultaneous power law kinetic equations:

$$-\frac{d[B]}{dt} = k_1[B]^l + k_3[B]^m \quad (1)$$

$$-\frac{d[E]}{dt} = -k_1[B]^l + k_2[E]^n \quad (2)$$

$$-\frac{d[A]}{dt} = k_3[B]^m + k_2[E]^n \quad (3)$$

The optimization of the parameters  $k_1$ ,  $k_2$ ,  $k_3$ ,  $l$ ,  $m$ ,  $n$  of the simultaneous equations has been carried out by searching the minimum of the sum of the square differences between the experimental and the calculated values. A detailed description of the computing procedure was described elsewhere [3].

In order to estimate the importance of the diffusion resistance (external liquid/solid and internal), the Carberry number and the Wheeler–Weisz group were taken into consideration. The numbers are defined as follows [8–10]:

$$Ca = \frac{r_0}{[k_{1s} c_{H_2}^* (6w/d_p \rho_{av})]} \quad (4)$$

$$\eta\phi^2 = \left[ \frac{d_p^2}{c_{H_2}^* 4D_{H_2,eff.}} \right] \rho_{av} r_0 \quad (5)$$

Evaluation of  $k_{1s}$ ,  $D_{H_2,eff.}$ , and  $c_{H_2}^*$  has been reported in previous papers [2,3]. Particle size distribution gives in each case an average diameter of  $d_p = 4 \mu\text{m}$ . N<sub>2</sub> adsorption shows porosity of 0.7 for all the catalysts. These features are probably due to the particular synthesis conditions: fast hydrolysis in alkaline solutions and high Ru loading explain the homogeneity of the sample.

#### 3.2. Selectivity and yield of the supported catalysts

Table 1 reports the reactivity of different supported catalysts. The first interesting difference between these catalysts and the unsupported ones (Ru–Na) is the higher activity of the former due to the higher liquid/solid contact area of the supported catalysts. The influence of the external liquid/solid diffusion on the reaction kinetics is almost similar for all the catalysts as suggested by the inspection of the Carberry number for hydrogen [2]. It has been pointed out that external diffusion reduces the concentration of hydrogen on the catalyst surface, increasing the hydrophilicity of the catalyst [11]. This is strictly related to the selectivity to cyclohexene because benzene is seven times more soluble than cyclohexene in water [8]. Moreover water displaces cyclohexene from Ru surface further increasing the selectivity [8,11]. It is likely that internal diffusion is less effective in avoiding external surface hydride formation, which makes the surface hydrophobic. However, this is not the only key factor to explain the selectivity to cyclohexene, because high initial selectivity can be achieved also with catalyst in which diffusion limitation is not so important.

It is interesting to observe that supported catalysts show reaction order for benzene to cyclohexene near to zero. The reaction rate is poorly influenced by the decrease of benzene concentration. In the case of unsupported catalysts, a reaction order higher than 1 was found [3].

As a matter of fact, selectivity of the catalyst seems mainly influenced by the nature of the support, and by its interaction with the metal. The most hydrophilic oxides give the best results (see experiences 2–4). The poorest selectivity is observed

Table 1

No.	Catalyst	Ru (%)	Order B → Ce, $l^a$	Order B → Ca, $m^b$	Order Ce → Ca, $n$	Ca H <sub>2</sub>	$\eta\phi^2$ H <sub>2</sub>	$r_0$ H <sub>2</sub> ( $\times 10^2$ mol $l^{-1} s^{-1} g_{Ru}^{-1}$ )	Initial selection (%)	Maximum yield (%)
1	Ru–Na <sup>c</sup>	77	1.5	0.76	1.2	0.12	3.2	9.2	62	28
2	50% Ru/Yb <sub>2</sub> O <sub>3</sub>	43.7	0.35	0.66	0.72	0.09	1.6	20.9	70	30.1
3	50% Ru/ZrO <sub>2</sub>	37.9	0.01	1.0	1.0	0.1	1.8	24.1	69	36
4	50% Ru/Fe <sub>2</sub> O <sub>3</sub>	48.5	0.00	0.52	0.49	0.005	0.1	1.28	73	25.9 <sup>d</sup>
5	50% Ru/ZrO <sub>2</sub> –TiO <sub>2</sub>	32.8	0.01	0.83	1.06	0.15	2.7	36.7	42	18
6	50% Ru/TiO <sub>2</sub>	31.8	0.01	0.51	0.51	0.13	2.1	30.6	48	26
7	50% Ru/polyketone	40.1	0.10	0.87	1.02	0.2	3.4	45.4	46.1	9.5
8	50% Ru/ZrO <sub>2</sub> /polyketone	41.2	0.10	0.85	1.02	0.17	3.1	41.7	30.8	9.8

<sup>a</sup> B, benzene; Ce, cyclohexene.

<sup>b</sup> Ca, cyclohexane.

<sup>c</sup> Data from Ref. [2].

<sup>d</sup> After 1 h of reactions.

with polyketone as support, because low yield and selectivity are achieved. Probably, the hydrophobic nature of the polymer favors surrounding of catalyst particles with benzene, with fast non-selective hydrogenation to cyclohexane as a consequence. Even though the kinetics of Ru/Fe<sub>2</sub>O<sub>3</sub> catalyst is not diffusion limited, the highest initial selectivity has been observed. Moreover, support hydrophilicity does not completely explain such kinetic behavior because these oxides have similar wetting enthalpy (0.5–0.6 J m<sup>-2</sup>), but different selectivity has been observed [12]. Thus, it is likely that metal–support interactions influence the reactivity of Ru supported oxide catalysts.

### 3.2.1. Hydrogen chemisorption on supported catalysts

It is well known that hydrogen chemisorption kinetics on Ru is a rather slow process and needs about 30 min at 373 K to reach the equilibrium. Moreover, at this temperature no bulk hydride is formed [13]. The double isotherm method gives the measure of both strongly and weakly bonded hydrogen on Ru surface. However neither of the two types of bonded hydrogen allows to know the nature of the catalyst active sites and only an approximate idea can be given. It is accepted that the strongly chemisorbed hydrogen is a direct measure of the exposed atoms, and that the weakly adsorbed one represents highly unsaturated sites which stabilize polyhydride moiety plus the physisorbed part [5,6,13,14]. As a matter of fact, hydrogen physisorption at 373 K and 180 Torr is negligible. Weak ad-

sorbed hydrogen is thus an actual measure of how the surface stabilizes a hydride-like complex which could affect catalyst reactivity. Further, important considerations must be given about catalyst pretreatment. Indeed, in order to avoid that chemisorbed substances or unreduced metal particles which impair the results of the measurements, high temperature pretreatment is needed (673 K) [7,13]. However, these treatments give rise to many problems. Surface reconstruction and redistribution of the metal particles are unavoidable. Strong metal–support interactions (SMSIs) may also occur [15].

Table 2 reports the results of hydrogen chemisorption on Ru/oxides catalysts. TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> containing catalysts give very low values of strongly adsorbed hydrogen. It is likely that such values are due to SMSI for M/TiO<sub>2</sub> hydrogenation catalysts [15]. On the contrary, the Fe<sub>2</sub>O<sub>3</sub> containing catalyst shows low values of strongly adsorbed hydrogen and low values of initial hydrogenation rate. The different activity (low rate, high selectivity) and the very low hydrogen adsorption capability can be due to the interactions of Fe<sub>2</sub>O<sub>3</sub> with Ru metal which lowers the hydrogen adsorption at the surface, increasing the selectivity to cyclohexene but depressing the hydrogenation activity.

### 3.3. Influence of the base on Ru/ZrO<sub>2</sub> catalysts

In Table 3 the influence of the base employed in the precipitation has been investigated. Since the reaction order for benzene to cyclohexene is near to zero, the

Table 2

Catalyst	Ru (%)	H <sub>2</sub> strong adsorbed (ml g <sub>cat</sub> <sup>-1</sup> )	H <sub>2</sub> weak adsorbed (ml g <sub>cat</sub> <sup>-1</sup> )	Metal dispersion, Ru <sub>s</sub> /Ru <sub>tot</sub> (%)	r <sub>0</sub> H <sub>2</sub> (×10 <sup>2</sup> mol l <sup>-1</sup> s <sup>-1</sup> g <sub>Ru</sub> <sup>-1</sup> )	Initial selection (%)	Maximum yield (%)
50% Ru/Yb <sub>2</sub> O <sub>3</sub>	43.7	2.88	2.74	5.88	20.9	70	30.1
50% Ru/ZrO <sub>2</sub>	37.9	1.97	2.98	4.56	24.1	69	36
50% Ru/Fe <sub>2</sub> O <sub>3</sub>	48.5	0.092	0.35	0.17	1.28	73	25.9 <sup>a</sup>
50% Ru/TiO <sub>2</sub>	31.8	0.37	0.76	1.04	30.6	48	26
50% Ru/ZrO <sub>2</sub> -TiO <sub>2</sub>	32.8	0.87	2.85	2.37	36.7	42	18

<sup>a</sup> After 1 h of reactions.

Table 3

Catalyst	Ru (%)	Ca H <sub>2</sub>	ηφ <sup>2</sup> H <sub>2</sub>	Order B → E, l	Order B → A, m	Order E → A, n	r <sub>0</sub> H <sub>2</sub> (×10 <sup>2</sup> mol l <sup>-1</sup> s <sup>-1</sup> g <sub>Ru</sub> <sup>-1</sup> )	Initial selection (%)	Maximum yield (%)
<i>Promoter: IA group metal hydroxide</i>									
Ru/ZrO <sub>2</sub> -Na	37.9	0.1	1.8	0.0	1.0	1.0	24.1	69	36
Ru/ZrO <sub>2</sub> -K	45.1	0.09	1.5	0.20	1.2	1.2	17.9	75	41
Ru/ZrO <sub>2</sub> -Cs	35.7	0.1	1.8	0.1	0.91	0.9	23.4	63	32
<i>Promoter: IIA metal hydroxide</i>									
Ru/ZrO <sub>2</sub> -Ca	21	0.003	0.041	0.33	0.71	0.71	1.2	74	8.5 <sup>a</sup>
Ru/ZrO <sub>2</sub> -Sr	29.5	0.06	0.879	0.33	0.81	0.81	13.2	70	37
Ru/ZrO <sub>2</sub> -Ba	29.9	0.04	0.691	0.1	1.0	0.98	10.1	64	27

<sup>a</sup> After 2.5 h of reactions.

Table 4

Catalyst	Ru (%)	H <sub>2</sub> strong (ml g <sub>Ru</sub> <sup>-1</sup> )	H <sub>2</sub> weak (ml g <sub>Ru</sub> <sup>-1</sup> )	Ru dispersion, Ru <sub>s</sub> /Ru <sub>tot</sub> (%)	r <sub>0</sub> H <sub>2</sub> (×10 <sup>2</sup> mol l <sup>-1</sup> s <sup>-1</sup> g <sub>Ru</sub> <sup>-1</sup> )	Initial selection (%)	Maximum yield (%)
<i>Promoter: IA group metal hydroxide</i>							
Ru/ZrO <sub>2</sub> -Na	37.9	1.97	2.98	4.6	24.1	69	36
Ru/ZrO <sub>2</sub> -K	45.1	1.36	2.12	2.6	17.9	75	41
Ru/ZrO <sub>2</sub> -Cs	35.7	0.94	2.57	1.9	23.4	63	32
<i>Promoter: IIA metal hydroxide</i>							
Ru/ZrO <sub>2</sub> -Ca	21	1.38	1.87	5.7	1.2	74	8.5 <sup>a</sup>
Ru/ZrO <sub>2</sub> -Sr	29.5	2.68	3.95	6.0	13.2	70	37
Ru/ZrO <sub>2</sub> -Ba	29.9	1.69	4.07	3.7	10.1	64	27

<sup>a</sup> After 2.5 h of reactions.

decrease of benzene concentration poorly influences the reaction rate.

It is likely that because of the fast precipitation of the catalyst precursor, part of metal hydroxide is incorporated into the precipitated particles thus modifying their microstructure. As reported in a previous paper for unsupported Ru catalysts, the base influences the Ru surface reactivity (Table 4).

In a similar way alkaline hydroxide influenced the activity of a Ru/ZrO<sub>2</sub> catalyst. The most effective one is the Ru/ZrO<sub>2</sub>-K, which gives the best results (75% of initial selectivity and 41% of cyclohexene yield). Also in the case of unsupported catalysts, KOH gave the higher yield and selectivity to cyclohexene [2,3]. Thus the base acts as a promoter or modifier.

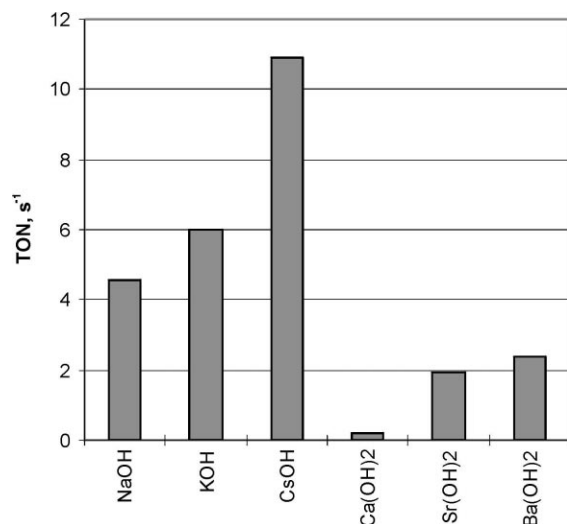


Fig. 1. Influence of the base on TON. Run conditions:  $T = 423$  K,  $P = 5$  MPa, reaction volume = 80 ml, benzene = 40 ml, aqueous  $\text{ZnSO}_4$  ( $0.6 \text{ mol l}^{-1}$ ) = 40 ml, catalyst  $\text{Ru/ZrO}_2\text{-M} = 120$  mg.

The Carberry and Wheeler–Weisz numbers of catalysts prepared employing a IA metal hydroxide as precipitant have similar behavior, but different selectivity and yield have been found. This is a further evidence that the base acts as a modifier–promoter.

Catalysts prepared employing a IIA metal hydroxide as precipitant are less active than those prepared employing IA bases; however, they show comparable selectivity to cyclohexene. Moreover, diffusion limitation is less important in particular for  $\text{Ru/ZrO}_2\text{-Ca}$  that is negligible at all.

The influence of poisoning on catalyst selectivity and reactivity has not been studied even though the catalysts used three times show analogous reactivity with respect to the fresh ones.

### 3.3.1. Influence of the base on hydrogen chemisorption

As already observed, metal dispersion is not strictly related to catalyst activity. This is due to the specific surface activity of each catalyst. However, it is noteworthy that turnover numbers increase with increasing molecular weight of the hydroxide into the same group (see Fig. 1). This can be related to the different promotional effect of each base on the Ru hydroxide precursor or on the metal itself. Similar trends have been found for unsupported catalyst [2].

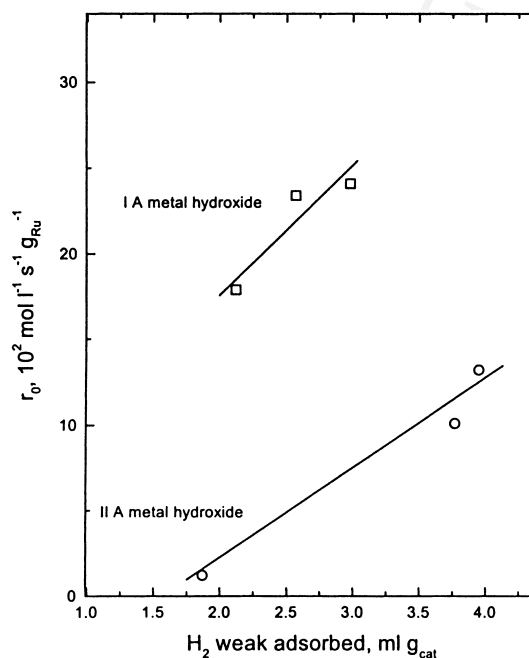


Fig. 2. Relation between weak chemisorbed hydrogen and catalyst activity. Run conditions:  $T = 423$  K,  $P = 5$  MPa, reaction volume = 80 ml, benzene = 40 ml, aqueous  $\text{ZnSO}_4$  ( $0.6 \text{ mol l}^{-1}$ ) = 40 ml, catalyst  $\text{Ru/ZrO}_2\text{-M} = 120$  mg.

Another interesting feature is the correlation observed between the weakly chemisorbed hydrogen and the initial reaction rate. Among the same group of bases, as the amount of reversible hydrogen increases, the initial rates increase too, as shown in Fig. 2. It is likely that during the hydrogenation process, the activation of hydrogen occurs only in the available sites partially covered by water, benzene, cyclohexene and cyclohexane, which give weak adsorption.

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