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**PREPARATION, CHARACTERIZATION, ACTIVITY AND  
SELECTIVITY OF HIGHLY LOADED OXIDE PROMOTED  
RUTHENIUM CATALYSTS FOR SELECTIVE HYDROGENATION OF  
BENZENE TO CYCLOHEXENE**

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**Abstract**

The influence of promoters and precipitants of the catalyst precursor on the activity and selectivity of the hydrogenation of benzene to cyclohexene catalyzed by highly loaded oxide-promoted Ru/ZrO<sub>2</sub> catalysts, carried out in a tetraphase reactor (in the presence of an aqueous solution of ZnSO<sub>4</sub>), at 423 K and 5 MPa, was studied. The effect of hydrogen diffusion on the reaction kinetics and on the selectivity has been taken into consideration, the internal pore diffusion being actually the limiting step. Hydrogen chemisorption measurements indicate that the catalyst activity is not influenced by the Ru dispersion, but rather by weakly chemisorbed species.

*Keywords:* Benzene selective hydrogenation, cyclohexene, Ru/ZrO<sub>2</sub> catalysts, oxide promoters, weak hydrogen chemisorption

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**INTRODUCTION**

The selective hydrogenation of benzene to cyclohexene is of much interest because is connected to the synthesis of cyclohexanol, an intermediate for large-scale polyamide production. Recently, many researchers have investigated the influence of the reaction conditions on the activity and the selectivity, mainly

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employing unsupported Ru catalysts [1-6]. The best results have been obtained in a tetraphase reactor at 423 K and 5 MPa of pressure in the presence of an aqueous solution of  $\text{ZnSO}_4$  and of suspended  $\text{ZrO}_2$ . The latter inhibits the agglomeration of the Ru particles. 56% yield and 80% selectivity have been claimed [4].

The support can also be a promoter for both activity and selectivity [7, 8], as it can affect the hydrophilicity, a key factor for the catalyst selectivity, because water can displace cyclohexene from the Ru surface thus preventing further hydrogenation to cyclohexane [9-13].

In addition, it has been observed that the selectivity is influenced by the nature of the alkali used for the precipitation of the catalyst precursor [11-13].

This paper deals with the influence of different metal oxide promoters on highly loaded Ru/ $\text{ZrO}_2$  catalysts, as well as with the influence of alkali treatment on the activity and selectivity, in relation to their hydrogen chemisorption properties.

## EXPERIMENTAL

### Catalyst preparation

In a typical preparation, 80 mL of a 5% aqueous solution (or an aqueous suspension, the bases  $\text{M}(\text{OH})_2$ ,  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ , are significantly less soluble in water than the others) of the precipitant (metal hydroxide, *e.g.* NaOH) was placed into a flask to which 5 g of  $\text{Zr}(\text{OPr-}i)_4$  was quickly added at room temperature. The temperature was then raised to 353 K, the solution of the promoter and that of  $\text{RuCl}_3$  were added in sequence (Ru / promoter = 5/1, promoters:  $\text{FeCl}_3$ ,  $\text{NiCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{CrCl}_3$ ,  $\text{MnCl}_2$  and  $\text{V}_2\text{O}_5$ ). The resulting suspension was left at 353 K for 3 h and then cooled to room temperature and maintained at this temperature for 18 h. The solid was then filtered, collected in an autoclave, suspended in water and pressurized with  $\text{H}_2$  (5 MPa). The reduction was carried out for 7 h at 423 K. The reactor was then cooled to room temperature and kept overnight (16-18 h) at this temperature. The autoclave was then depressurized, opened and the catalyst was passivated in water with air for one hour. Finally, the passivated catalyst was filtered and dried under vacuum.

### Catalyst characterization

Particle size was determined by measuring the sedimentation rate, average particle diameter of 4  $\mu\text{m}$  has been observed.

Catalyst porosity and surface area has been determined by  $\text{N}_2$  adsorption and

desorption at 94 K. All catalysts present an average porosity of 0.7, average pore diameter of 7 nm and surface area in the range 170-190 m<sup>2</sup> g<sup>-1</sup> [14].

Chemisorption of hydrogen were carried by the double isotherm method at 373 K, a final pressure of 200 Torr and 30 min of equilibration time [12, 13, 15, 16]. Before the measurements, the catalyst was pretreated in order to reduce the exposed Ru atoms (reduction under H<sub>2</sub> at 673 K for 4 h and thermal treatment under vacuum at 673 K for 4 h).

The composition of the catalysts was determined by AAS analysis of the dissolved catalysts by a procedure described elsewhere [12, 13].

### Hydrogenation of benzene

The reaction was carried out in a 250 mL PTFE lined stainless steel autoclave maintained at constant pressure and temperature (typically 5 MPa and 423 K). In a typical experiment 120 mg of catalyst, 40 mL of benzene and 40 mL of aqueous 0.6 mol L<sup>-1</sup> solution of ZnSO<sub>4</sub> was loaded. The progress of the reaction was followed by GC analyses of samples of the organic phase and by measuring the hydrogen consumption [10-13].

The activity of the catalysts was calculated by fitting the experimental data with a kinetic model based on two consecutive reactions (benzene to cyclohexene and further hydrogenation to cyclohexane) and on a parallel one (direct formation of cyclohexane from benzene), as described elsewhere [11-13].

## RESULTS AND DISCUSSION

### Influence of the metals on reaction kinetics and selectivity

Entries 1-11 in Table 1 show the results obtained with Ru/M<sub>x</sub>O<sub>y</sub>/ZrO<sub>2</sub> catalysts, which are compared with those obtained with Ru/ZrO<sub>2</sub> (entry 12, [10]). The inspection of the Carberry and Wheeler-Weisz number for hydrogen suggests that kinetics is only partially affected by external diffusion limitation and that also internal diffusion has little influence even in the case of entries 6, 7 and 12 (see Table 1) [14, 15]. The comparison of the initial selectivity to cyclohexene of entries 1-11 with that of entry 12 indicates that in most cases the second metal oxide (slightly) decreases the selectivity except for entry 3. However, the catalysts promoted with Fe and precipitated with NaOH or KOH, which show a selectivity comparable to that obtained with the Ru/ZrO<sub>2</sub> catalyst give a slight increase in the maximum yield. This is because the presence of iron allows a slower decreasing of the selectivity with increasing conversion (see Fig. 1).

**Table 1**Initial rate, selectivity, yield and hydrogen diffusion parameters of Ru-M<sub>x</sub>O<sub>y</sub>/ZrO<sub>2</sub> catalysts

Entry	Catalyst <sup>a)</sup>	N <sub>Ca</sub> H <sub>2</sub>	$\eta\phi^2$ H <sub>2</sub>	r <sub>0</sub> H <sub>2</sub> <sup>b)</sup> (10 <sup>2</sup> mol L <sup>-1</sup> s <sup>-1</sup> g <sub>Ru</sub> <sup>-1</sup> )	Initial <sup>c)</sup> selectivity (%)	Maximum yield (%)
1	Ru/Ni/ZrO <sub>2</sub> -Na	0.07	0.84	18	57	26
2	Ru/Co/ZrO <sub>2</sub> -Na	0.09	1.4	19	64	35
3	Ru/Cr/ZrO <sub>2</sub> -Na	0.05	0.74	11	69	32
4	Ru/Mn/ZrO <sub>2</sub> -Na	0.10	1.5	21	67	33
5	Ru/V/ZrO <sub>2</sub> -Na	0.07	0.84	18	57	26
6	Ru/Fe/ZrO <sub>2</sub> -Na	0.11	1.8	24	68	38
7	Ru/Fe/ZrO <sub>2</sub> -K	0.10	1.6	18	68	38
8	Ru/Fe/ZrO <sub>2</sub> -Cs	0.10	1.6	24	53	23
9	Ru/Fe/ZrO <sub>2</sub> -Ca	<0.01	0.05	1.1	55	12 <sup>d)</sup>
10	Ru/Fe/ZrO <sub>2</sub> -Sr	<0.01	0.34	6.0	63	27
11	Ru/Fe/ZrO <sub>2</sub> -Ba	0.04	0.59	10	60	25
12	Ru/ZrO <sub>2</sub> -Na <sup>e)</sup>	0.11	1.8	24	69	36

<sup>a)</sup> Na, K, *etc.* indicate that the precipitant is NaOH, KOH, *etc.*

<sup>b)</sup> Initial rate is calculated by the first derivative at  $t = 0$  of the function obtained by fitting the experimental data according to [12, 13].

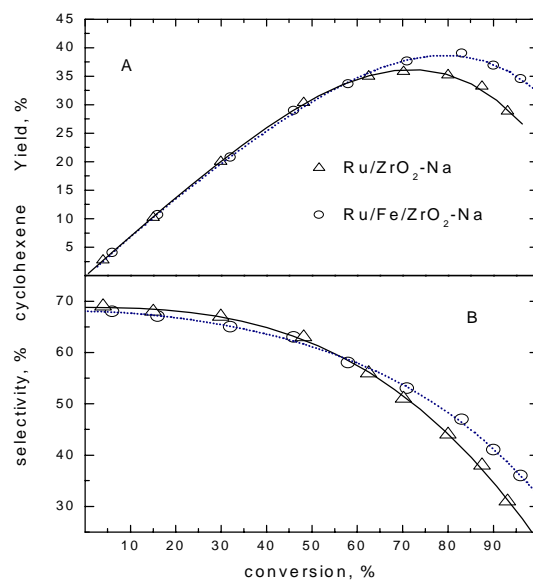
<sup>c)</sup> Initial selectivity to cyclohexene is obtained by calculating the limit for  $t \rightarrow 0$  of the function obtained by fitting the experimental data according to [12, 13].

<sup>d)</sup> Values measured at final conversion after 4 h of reaction

<sup>e)</sup> data from ref. [10]

### Relation between hydrogen chemisorption and activity

Hydrogen chemisorption obtained by the double isotherm method gives the measure of both strongly and weakly bonded hydrogen. It is accepted that the strongly chemisorbed hydrogen is a direct measure of the exposed atoms (or of the dispersion), and that the weakly adsorbed one represents highly unsaturated sites which stabilize poly-hydride moieties and the physisorbed hydrogen [17, 20, 21]. We found that hydrogen physisorption at 373 K and 180 Torr is negligible. Thus, weakly adsorbed hydrogen is an actual measure of how the surface stabilizes a hydride-like complex which could affect catalyst activity and selectivity [20, 21].



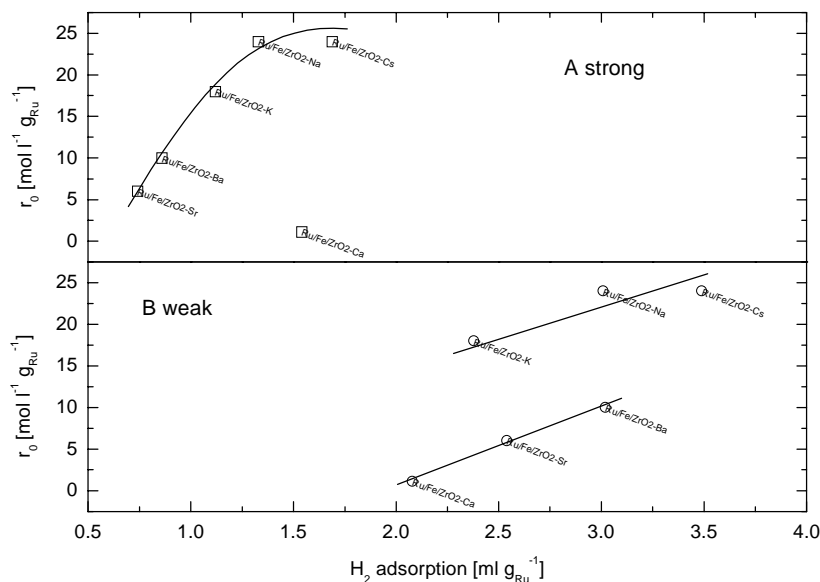
**Fig. 1.** Effect of Fe on selectivity and yield of cyclohexene vs conversion: comparison of Ru/ZrO<sub>2</sub>-Na and Ru/Fe/ZrO<sub>2</sub>-Na catalysts

**Table 2**

Hydrogen chemisorption on Ru-M<sub>x</sub>O<sub>y</sub>/ZrO<sub>2</sub> catalysts

Entry	Catalyst	Ru (%)	H <sub>2</sub> str. ads. (100 Torr mL g <sub>cat</sub> <sup>-1</sup> )	H <sub>2</sub> wk. ads. (100 Torr mL g <sub>cat</sub> <sup>-1</sup> )	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 sel. (%)	Max. yield (%)
1	Ru/Ni/ZrO <sub>2</sub> -Na	39.4	1.89	3.52	18	57	26
2	Ru/Co/ZrO <sub>2</sub> -Na	40.1	1.15	3.77	19	64	35
3	Ru/Cr/ZrO <sub>2</sub> -Na	34.5	2.02	2.22	11	69	32
4	Ru/Mn/ZrO <sub>2</sub> -Na	37.0	1.94	3.38	21	67	33
5	Ru/V/ZrO <sub>2</sub> -Na	27.8	1.36	2.28	18	57	26
6	Ru/Fe/ZrO <sub>2</sub> -Na	38.6	1.33	3.01	24	68	38
7	Ru/Fe/ZrO <sub>2</sub> -K	45.1	1.12	2.38	18	68	38
8	Ru/Fe/ZrO <sub>2</sub> -Cs	35.7	1.69	3.49	24	53	23
9	Ru/Fe/ZrO <sub>2</sub> -Ca	21.0	1.54	2.08	1.1	55	12 <sup>a)</sup>
10	Ru/Fe/ZrO <sub>2</sub> -Sr	29.5	0.74	2.54	6.0	63	27
11	Ru/Fe/ZrO <sub>2</sub> -Ba	29.9	0.86	3.02	10	60	25

<sup>a)</sup> values measured at final conversion after 4 h of reaction



**Fig. 2.** Influence of weak adsorption of hydrogen on the initial rate of reactions of Ru-Fe<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalysts

In Table 2 weak and strong hydrogen chemisorptions are reported. No direct relationship has been observed between strong chemisorbed hydrogen (or dispersion) and catalyst activity (entry 1-11), thus, it is likely that catalyst activity is a specific surface effect of each metal oxide on the active Ru particles. Entries 6-11 show the influence of the base employed for the precipitation of the Ru precursor on the support for Fe promoted catalysts. Except for entry 9 (Ru/Fe/ZrO<sub>2</sub>-Ca), catalyst activity increases with metal dispersion increasing, suggesting a specific effect of Fe<sub>2</sub>O<sub>3</sub> (see Fig. 2A). Furthermore, a trend can be established between the weakly chemisorbed hydrogen and the initial reaction rate among the same group of bases, as reported in Fig. 2B, which shows that the increase of the initial rate follows the reversible hydrogen chemisorption increasing. It is likely that weakly hydrogen adsorption occurs only on the available sites after partially covering by water, benzene, cyclohexene and cyclohexane.

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