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# SUPPORTED Ru CATALYSTS: A STUDY OF THE INFLUENCE OF SUPPORTS, PROMOTERS AND PREPARATIVE VARIABLES ON THE CATALYTIC ACTIVITY AND SELECTIVITY

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**Abstract**

The influence of some preparative variables, of the metal loading and of the support on the activity of Ru catalysts for the selective hydrogenation of benzene to cyclohexene has been studied. The reaction has been carried out in a tetraphase reactor (in the presence of an aqueous solution of $ZnSO_4$) at 423 K and 5 MPa pressure. The effect of hydrogen diffusion on the reaction kinetics and on cyclohexene selectivity was studied. The hydrophilicity of the support was related to the observed selectivity. Hydrogen chemisorption indicates that the catalyst activity is not influenced by the Ru dispersion, but mainly by the weakly chemisorbed species on the catalyst surface.

*Keywords:* Benzene selective hydrogenation, Ru catalyst preparations, Ru chemisorption

## INTRODUCTION

In recent years, many researchers have investigated the influence of reaction conditions on the selectivity of benzene selective hydrogenation to cyclohexene [1-6]. The best results are reported in Asahi patents, where the reaction is carried out in a tetraphase reactor at 150°C and 50 atm in the presence of $ZrO_2$ and an aqueous solution of $ZnSO_4$ [1]. The process has been recently developed into a large scale plant [7]. In spite of the importance of the reaction, few studies have appeared in the literature up to now [3-10].

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In a previous paper we reported the influence of alkali hydroxides in the preparation of unsupported Ru catalysts. The alkali treatment enhances both the activity and the selectivity of the catalysts [11-13].

This paper deals with the influence of several preparative variables on the activity of supported Ru catalysts in the hydrogenation of benzene to cyclohexene.

## EXPERIMENTAL

### Catalyst preparation

Catalysts were prepared following three different techniques.

*Precipitation*

To the desired amount of a support dispersed in water, an aqueous solution of $RuCl_3$ (40 g $L^{-1}$ of Ru) was added under vigorous stirring. After one hour the precipitant, typically NaOH, was added and the mixture was heated at 353 K for 3 h. The slurry was then cooled, kept overnight (16-18 h) and filtered.

*Chemical mixing*

To a hydroalcoholic solution of TEOS (tetraethoxysilane) and $RuCl_3 \cdot nH_2O$, 36% aqueous HCl was added to the final concentration of $10^{-3}$ mol $L^{-1}$. This mixture was refluxed for 10 min and then allowed to stand at room temperature for 30 days to ensure gelation and ageing. Finally the solid was ground in an agate mortar and dried at 393 K and $10^{-2}$ Torr.

*Hydrolysis-precipitation*

A desired amount of support precursor [$Ti(OPr)_4$, $TiCl_4$, $Zr(OPr)_4$, $ZrOCl_2$, $FeCl_3 \cdot 6H_2O$, $YbCl_3 \cdot 8H_2O$] was quickly added to a 5% aqueous NaOH solution under vigorous stirring. Then, a solution of $RuCl_3$ was quickly added. The resulting system was heated for 3 h at 353 K, cooled, kept overnight and filtered.

Reduction of the catalyst was carried out in an autoclave at 5 MPa hydrogen pressure at 423 K for 7 h and passivated with air-saturated water for 1 h.

## Characterization of the catalyst

The determination of Ru content was carried out using an atomic absorption spectrometer (Perkin Elmer) employing an air-acetylene flame after catalyst dissolution in aqueous solvent.

The measurements of hydrogen chemisorption were carried out in an automatic chemisorption unit (Micromeritics ASAP 2010C) using the double isotherm method at 373 K and with 30 min of equilibration time [14-16].

## Hydrogenation

The reaction was carried out in a 250 mL PTFE lined stainless steel autoclave maintained at constant pressure (typically 5 MPa). The progress of the reaction was followed by sampling the organic phase (GC analysis) and measuring the hydrogen consumption [11]. In a typical experiment 120 mg of catalyst, 40 mL of benzene and 40 mL of 0.6 mol $L^{-1}$ aqueous solution of $ZnSO_4$ was loaded.

The kinetic model is based on two consecutive reactions and on a parallel one (direct formation of cyclohexane from benzene) [12]. Simultaneous power law kinetic equations have been employed to fit experimental data. The optimization procedure of the parameters (kinetic constants and apparent reaction order) was described elsewhere [12]. Such a model takes into account only the species detected by GC in the organic phase, it can be useful to compare the reactivity of different catalysts, but that does not give any information on the reaction mechanism. Inspection of the Carberry number (Ca) of the Wheeler-Weisz group ($\eta\phi^2$) allows to investigate the influence of external and internal diffusion [11-13]. If Ca < 0.05 and $\eta\phi^2$ < 0.1, external and internal diffusion may be neglected [17-19].

## RESULTS AND DISCUSSION

### Low loaded Ru catalysts

Two series of supported catalysts have been prepared employing different supports in order to study the influence on the catalytic activity. The results are reported in Table 1.

It has been reported that the catalyst becomes more hydrophobic when hydrogen is chemisorbed [21]. Under diffusion controlled conditions the catalyst is preferentially surrounded by water. Since cyclohexene is seven times

less soluble than benzene in water, the hydrogenation of cyclohexene is slower and higher selectivity is achieved.

**Table 1**

Activity and selectivity of low-loaded supported Ru catalysts

| Catalyst | $C_a$ $H_2$ | $\eta\phi^2$ $H_2$ | $R_0, H_2{}^\#$ (mol L$^{-1}$ s$^{-1}$ $g_{Ru}{}^{-1}$) $10^2$ | Sel. (%) | Yield (%) | React. time (min) |
|---|---|---|---|---|---|---|
| | | | **1% Ru catalyst** | | | |
| Ru/BaSO$_4$ | <0.01 | 0.11 | 75.3 | 16 | 5 | 90 |
| Ru/MgO | <0.01 | <0.01 | 0.1$^\S$ | 13.4 | 0.3 | 105 |
| Ru/SiO$_2$ | 0.011 | 0.20 | 138 | 6.9 | 2.1 | 65 |
| 1%Ru/polyketone | 0.012 | 0.22 | 150 | 5.4 | 2.8 | 35 |
| 1%Ru/Ni Raney | <0.01 | 0.15 | 1.0 | 4.0 | 1.39 | 134 |
| Ni Raney | <0.01 | 0.18 | 1.2 | 2.9 | 0.54 | 60 |
| | | | **5% Ru catalyst** | | | |
| 5%Ru/TiO$_2$ | 0.053 | 0.96 | 128 | 19.8 | 13.4 | 41 |
| 5%Ru/ZrO$_2$ | 0.048 | 0.86 | 115 | 20.1 | 11 | 45 |
| 5%Ru/Al$_2$O$_3$ | 0.019 | 0.34 | 45 | 21.4 | 9 | 60 |

[#] Measured from hydrogen consumption.

[§] Very slow reaction rate evaluated from 2.3% conversion after 105 min.

Run conditions: T = 423 K, P = 5 MPa, reaction volume 80 mL, benzene 40 mL, aqueous ZnSO$_4$ 0.6 mol L$^{-1}$ 40 mL, catalyst 120 mg

In the first series of catalysts, diffusion of hydrogen does not influence the hydrogenation kinetics (see Table 1, the Carberry and Wheeler-Weisz numbers). Therefore, the active role of the support is shown by significant differences in catalysts activity and selectivity.

The hydrophilicity of solids can be evaluated by the heat of immersion in water. Thus their different behavior can be related to the reactivity of the corresponding catalyst [20]. Heats of immersion of BaSO$_4$ and MgO in water (0.5-0.6 J m$^{-2}$) are about three times higher than that of SiO$_2$ (0.16 J m$^{-2}$) [20]. This can explain the higher selectivity observed for 1%Ru/BaSO$_4$ and

1%Ru/MgO catalysts. The very low activity of the latter can be explained in terms of Ru metal particle coverage caused by dissolution and precipitation of $Mg(OH)_2$ during MgO hydration [22, 23]. $SiO_2$ and polyketone show similar behaviors both in selectivity and activity, probably due to the low hydrophilicity of the supports. Poor selectivity is obtained also with Ni-Raney and Ru/Ni-Raney systems.

The activity of 5 % Ru catalysts is comparable to that of the 1% Ru catalysts, but selectivity is significantly higher. In the second series of catalysts, the inspection of the Carberry and Wheeler-Weisz parameters indicates that intraparticle diffusion may influence the kinetics (Carberry number *ca* 0.05). However, the main feature in these catalysts is the supports which, obtained by an alkaline hydrolysis of $ZrOCl_2$ or $TiCl_4$, are amorphous highly hydrophilic $TiO_2$ or $ZrO_2$ (heat of immersion *ca*. 0.5 J m$^{-2}$).

### Table 2

Kinetics of highly loaded Ru catalysts

| | Catalyst | Ru (%) | order B → Ce l | order B → Ch m | order Ce → Ch n | Ca $H_2$ | $\eta\phi^2$ $H_2$ | $r_0$ $H_2$ $10^2$ (mol L$^{-1}$ s$^{-1}$ g$_{Ru}$-1) | Initial select (%) | Max. yield (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Ru-Na[§] | 77 | 1.5 | 0.76 | 1.2 | 0.12 | 3.2 | 9.2 | 62 | 28 |
| 2 | 50%Ru/TiO$_2$ | 31.8 | 0.01 | 0.51 | 0.51 | 0.13 | 2.1 | 30.6 | 48 | 26 |
| 3 | 50%Ru/ZrO$_2$-TiO$_2$ | 32.8 | 0.01 | 0.83 | 1.06 | 0.15 | 2.7 | 36.7 | 42 | 18 |
| 4 | 50%Ru/ Yb$_2$O$_3$ | 43.7 | 0.35 | 0.66 | 0.72 | 0.09 | 1.6 | 20.9 | 70 | 30.1 |
| 5 | 50%Ru/ZrO$_2$ | 37.9 | 0.01 | 1.0 | 1.0 | 0.1 | 1.8 | 24.1 | 69 | 36 |
| 6 | 50%Ru/Fe$_2$O$_3$ | 48.5 | 0.00 | 0.52 | 0.49 | 0.005 | 0.1 | 1.28 | 73 | 25.9* |
| 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$_2$/polyketone | 41.2 | 0.10 | 0.85 | 1.02 | 0.17 | 3.1 | 41.7 | 30.8 | 9.8 |
| 9 | Ni-Raney | / | / | / | / | 0.01 | 0.18 | 1.2* | 2.9 | 0.54 |
| 10 | 50%Ru/Ni-Raney | 41.8 | / | / | / | 0.021 | 0.38 | 1.2* | 36.4 | 2.0 |

B = benzene, Ce = cyclohexene, Ch = cyclohexane

[§] Data from ref. [11]

* After 1 h reaction.

Run conditions: those of Table 1

The comparison between the two series of catalysts (at 1% and 5% of Ru) confirms the importance of diffusion limitation of hydrogen on the selectivity of the process. In addition, it suggests that the support may play an important role

on the control of the selectivity and activity. Ru loading slightly influences the activity (see Table 1). The performances of the catalysts are also compared to those of a commercial 5% $Ru/Al_2O_3$ catalyst (Engelhard ESCAT 44).

## High loaded Ru catalysts

Some results of a kinetic analysis of high loaded Ru catalysts are summarized in Table 2. Higher catalyst selectivity and activity than with unsupported ones is observed (compare entry 1 with 3 and 4). This can be due to the combined effect of highly hydrophilic supports (heat of immersion in water about 0.5 J m$^{-2}$) with high metal loading, which cause hydrogen diffusion limitation, allowing higher selectivity to cyclohexene.

The reaction order for benzene to cyclohexene is close to 0 (except entry 4, which is 0.35), thus the reaction rate (benzene to cyclohexene) is not influenced by the degree of conversion. On the other hand, the unsupported catalyst (entry 1) shows that the reaction order is *ca*. 1.5 so that the higher the conversion the lower the rate (benzene to cyclohexene). In each case, the rates (benzene to cyclohexane and cyclohexene to cyclohexane) are influenced by the reaction progress (see Table 3, entries 1-8).

**Table 3**

Chemisorption measurements of highly loaded Ru catalysts

| Catalyst | Ru (%) | H$_2$ str. ads. (mL g$_{cat}^{-1}$) | H$_2$ wk. ads. (mL g$_{cat}^{-1}$) | Metal dispersion Rus/Rutot (%) | r$_0$ H$_2$ 10$^2$ (mol L$^{-1}$ (s$^{-1}$ g$_{Ru}^{-1}$) | Initial select. (%) | Max. yield (%) |
|---|---|---|---|---|---|---|---|
| 50%Ru/TiO$_2$ | 31.8 | 0.37 | 0.76 | 1.04 | 30.6 | 48 | 26 |
| 50%Ru/ZrO$_2$-TiO$_2$ | 32.8 | 0.87 | 2.85 | 2.37 | 36.7 | 42 | 18 |
| 50%Ru/Yb$_2$O$_3$ | 43.7 | 2.88 | 2.74 | 5.88 | 20.9 | 70 | 30.1 |
| 50%Ru/ZrO$_2$ | 37.9 | 1.97 | 2.98 | 4.56 | 24.1 | 69 | 36 |
| 50%Ru/Fe$_2$O$_3$ | 48.5 | 0.092 | 0.35 | 0.17 | 1.28 | 73 | 25.9* |

*After 1 h reaction
Run conditions: those of Table 1

All the rates are limited by the rate of hydrogen diffusion (except entry 6) which explains the higher selectivity observed with high Ru loaded catalysts with respect to the low loaded ones. It is noticeable that the $Ru/Fe_2O_3$ catalyst is

not affected by hydrogen diffusion limitation; however it gives the highest initial selectivity to cyclohexene. This can be ascribed not only to the high hydrophilicity (0.53 J m$^{-2}$) of the support but also to an electronic promotion of the Fe$_2$O$_3$ on Ru particles.

Best results have been obtained with the Ru/ZrO$_2$ catalyst (entry 5), which gives high hydrogenation rate and high selectivity.

The catalyst prepared with a mixed support TiO$_2$-ZrO$_2$ is less selective with respect to the ones prepared with only TiO$_2$ or ZrO$_2$. As already observed with 1% Ru catalysts neither polymer (entries 7 and 8) nor Ni Raney are suitable support for this reaction since they give very poor yield in cyclohexene. This is probably due to the higher affinity of these supports for the organic phase.
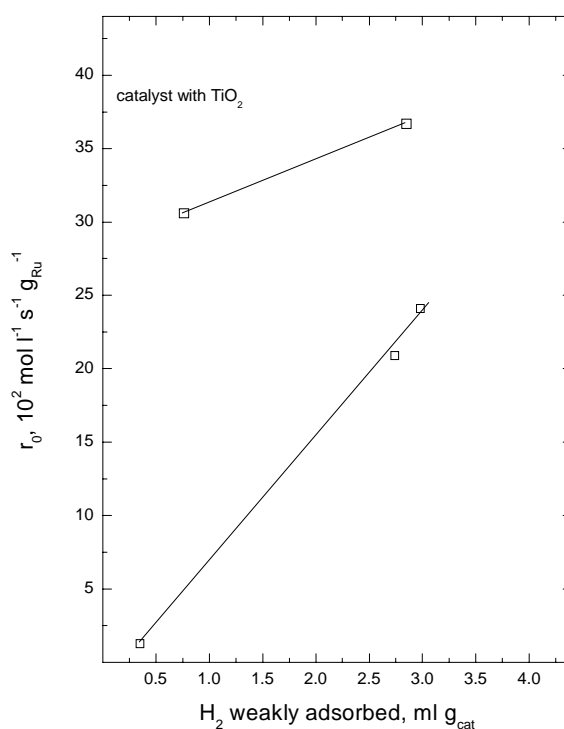


**Fig. 1.** Relation between weakly chemisorbed hydrogen and catalyst activity. Run conditions: T = 423 K, P = 5 MPa, reaction volume 80 mL, benzene 40 mL, aqueous ZnSO$_4$ 0.6 mol L$^{-1}$ 40 mL, catalyst 120 mg

Table 3 shows the results of hydrogen chemisorption on some high loaded Ru catalysts. SMSI, which occurs during the pretreatment for chemisorption measurement, probably explains the low dispersion values of Ru/TiO$_2$ against the high activity of the catalyst. It is noteworthy that Ru/Fe$_2$O$_3$ gives both lower hydrogen adsorption and initial reaction rate. However, the simple explanation in terms of low metallic dispersion does not take into account the high selectivity of the catalyst, which can be ascribed to a promotional effect of the support.

No comparison can be made with TiO$_2$ containing catalysts, because the influence of SMSI decreases hydrogen chemisorption. However, no relationship has been observed between metal dispersion and catalyst activity and selectivity. On the other hand, the existence of a direct correlation between the amount of weakly adsorbed hydrogen and the reaction rate can be observed (see Fig. 1). This behavior can be ascribed to the activation of hydrogen on a covered metal surface in which only sites giving weak adsorption are available.

## CONCLUSIONS

Physically limited kinetics influence catalyst selectivity because the granule hydrophilicity is lowered by the formation of surface hydrides, giving less selective hydrogenation. However, catalysts prepared with highly hydrophilic supports give very different behavior unrelated to the extent of the physical limitation. These features indicate that specific Ru-support interactions exist. Moreover, the rate of hydrogenation is not related to the metal dispersion but rather to weakly adsorbed hydrogen.

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