

Hydrogenation of benzene to cyclohexene over polymer-supported ruthenium catalysts

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Abstract

Partial liquid-phase hydrogenation of benzene to cyclohexene over ruthenium catalysts supported on charcoal and anionic cross-linked polymers is described. The influence of the polarity of polymeric supports, nature of the solvent and the presence of zinc additives on the performance of the catalyst in a glass-lined reactor at 100–110°C and a pressure of 1.5 MPa have been studied. It has been found that at 42–47% conversion of benzene, the selectivity to cyclohexene, observed in water with Ru catalysts supported on a strongly hydrophilic microporous resin, is higher than that displayed by Ru supported on charcoal. The effect of water on the performance of the catalyst is probably a result of formation of a suitable environment around Ru particles and of a good accessibility of metal particles dispersed within the hydrophilic polymer support.

Keywords: Hydrogenation; Benzene; Cyclohexene; Liquid phase; Ruthenium; Polymeric support; Supported catalysts

1. Introduction

Partial hydrogenation of benzene to cyclohexene is a subject of great interest, from both theoretical and practical aspects, as cyclohexene is a very attractive industrial chemical for the synthesis of organic compounds [1]. In spite of the fact that cyclohexene is an intermediate product of the hydrogenation of benzene, maximizing the yield of cyclohexene is very difficult, owing to the kinetically favoured hydrogenation of cyclohexene to cyclohexane. This is

valid for the majority of metals used as hydrogenation catalysts, e.g. Ni, Pd, Pt, Ru [2]. In order to increase the yield of cyclohexene, it is necessary to affect the metal morphology or to arrange conditions for the transport of reactants and products to and from the surface of the catalyst to specifically favour the rapid desorption of cyclohexene from the surface of the catalyst.

Dini et al. [3] applied a polymer-supported platinum catalyst prepared from Nylon-3 and polyacrylonitrile. A selectivity of 78.6% was achieved under hydrogenation of benzene at 160°C in the vapour phase using polyacryloni-

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trile treated with acetone solution of $\text{PtCl}_2(\epsilon\text{-caprolactam})_2$. A limitation of the process described is a low conversion, less than 1%, under which such good selectivity was achieved. Galvagno et al. [4] hydrogenated benzene in the vapour phase, using palladium, platinum and rhodium supported on Nylon, under atmospheric pressure and at a temperature of 150°C . These authors obtained the best results with rhodium; selectivity was more than 30% at a conversion of about 5%. A good selectivity, higher than 60%, at an acceptable conversion of about 40%, can be achieved according to Japanese patents of Nahagara and Kohishi [5,6]. The principle of this process is a control of cyclohexene mass transport through water solution of zinc salt and changing of Ru particles from hydrophobic to hydrophilic character. Some quantitative aspects of this process are available in the papers of Struijk et al. [7,8].

In order to utilize mass transport control for the improvement of the selectivity in a water-containing complex reaction system we evaluated the ability of microporous hydrophilic resins to act as convenient support of ruthenium crystallites. Recently [9,10] we have reported on the synthesis and full characterization of new anionic microporous resins, which were utilized as supports for palladium and tested for the hydrogenation of *p*-nitrotoluene to *p*-toluidine. In this paper, we refer to anionic resins supported ruthenium catalysts, as a potential alternative for the hydrogenation of benzene to cyclohexene.

2. Experimental

2.1. Catalysts

Powdered Ru catalysts were prepared by the procedure given by Struijk et al. [7]. Metallic Ru catalyst deposited on charcoal (5 wt.% of metal) was prepared by impregnation of charcoal (particle size 0.1–0.315 mm, surface area $1265\text{ m}^2\text{ g}^{-1}$) with ruthenium chloride followed

by reduction with formaldehyde [11]. Ru supported on anionic polymers was prepared by an ion exchange of the sodium or potassium form with $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ and the subsequent reduction by sodium borohydride in ethanol as described for palladium catalysts in [9] and [10]. The following catalysts were prepared:

1. S4NR4; 4 wt.% of Ru, styrene–divinylbenzene sulfonated resin S4 (commercially denoted as KS 0409 [12]) 4 mol.% crosslinked, 5 mmol/g of sulfonic groups, particles 0.315–0.8 mm.
2. S8NR4; 4 wt.% of Ru, styrene–divinylbenzene sulfonated resin S8 (commercially denoted as KS 0807 [12]) 8 mol.% crosslinked, 5 mmol/g of sulfonic groups, particles 0.16–0.315 mm.
3. P4NR4; 4 wt.% of Ru, dimethylacrylamide–styrene sodium sulphionate–methylene bis(acrylamide) resin [9], 4 mol.% of crosslinker, 1.7 mmol/g of sulphonic group, P4N, particles 0.05–0.2 mm.
4. P4NR8; 8 wt.% of Ru, support as for P4NR4.
5. M4KR4; 4 wt.% of Ru, dimethylacrylamide–potassium 1-methacryloyl ethylene 2-sulphonate–methylene bis(acrylamide) resin [10], 4% of crosslinker, 1.8 mmol/g of sulphonic groups, M4K, particles 0.05–0.2 mm.
6. M4KR8; 8 wt.% of Ru, support as for M4KR4.

2.2. Apparatus

Catalytic experiments were carried out in a 50 cm^3 glass-lined stainless steel reactor connected with a flexible metal capillary to the apparatus for measuring the hydrogen consumption at constant pressure. The reactor was filled with reactants, catalyst and hydrogen, heated in a thermostated oil bath and vigorously agitated using a vibrator (frequency about 6 Hz).

2.3. Analysis

The reaction mixture was extracted three times by diethyl ether and products were ana-

lyzed with a Hewlett Packard 5890 gas chromatograph using the capillary column HP 20 M (Carbowax 20 M, length 30 m, inner diameter 0.53 mm, 1.33 μm film thickness) and a flame ionization detector.

3. Results and discussion

The distribution of ruthenium inside a catalyst particle was checked through X-ray microprobe analysis. The uniform distribution of the metal was found for all catalysts, an example is given in Fig. 1.

Results from the hydrogenation of benzene (Table 1, Fig. 2) show that at a 42–47% conversion of benzene, the selectivity with respect to cyclohexene formation is significantly influenced by the nature of the support. The highest selectivity achieved with Ru catalysts supported on M4K microporous resin can be explained on the basis of hydrophilicity and accessibility of the interior space of the resin. The particles of

the well swollen hydrophilic polymer act as small water droplets (vide infra), so that cyclohexene should be easily expelled from the catalyst particle just after its formation owing to its very low water solubility [7].

The type of the polymer also affects the accessibility of metal crystallites. The M4K resin has slightly lower swellability than the P4N resin but the reaction time with the M4K based catalyst for ca. 50% conversion is approximately half in comparison with P4N based catalyst. This behaviour can be caused by a different hindrance of ethylene sulphonic and phenylene sulphonic groups against diffusional transport of reactants and products. We suppose that ethylene sulphonic groups enable formation of better accessible space, which is indicated by the higher hydrogenation rate and consequently by the higher selectivity to cyclohexene. A relationship between accessibility and selectivity is fairly illustrated also for sulphonated styrene–divinylbenzene resin whose swellability is low, i.e. active ruthenium particles are less accessible

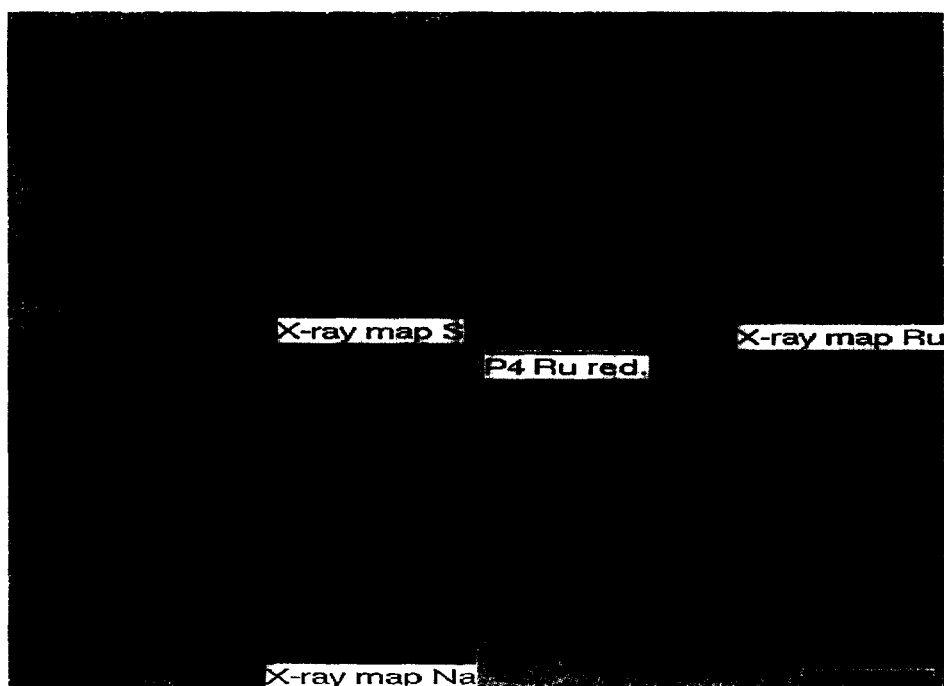


Fig. 1. SEM and XRM maps of sulphur, sodium and ruthenium in the P4NR4 catalyst.

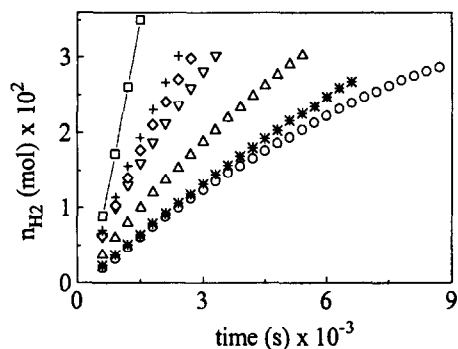


Fig. 2. Hydrogen consumption (n_{H_2}) vs. time (t). Symbols as given in Table 1.

and both the reaction rate and selectivity are lower in comparison with P4N and M4K based catalysts (Fig. 3).

Powdered ruthenium and especially Ru/C catalysts under comparable conditions are significantly less selective (Table 1). If a polymer supported catalyst is not swollen as in the case of the experiments without water, metal crystallites are poorly accessible and reaction rate is very low (Table 1). Also, in this experiment the effect of the resin hydrophilicity supports the good selectivity to cyclohexene.

Table 1
Effect of catalyst on the conversion and the selectivity of benzene hydrogenation

Catalyst	Reaction time (min)	Conversion (%)	Selectivity (%)	Symbols in Fig. 2
Ru powder	103	37.8	1.8	*
5%Ru/C	33	55.3	0.5	□
5%Ru/C ^a	8	51.2	< 0.3	-
S4NR4 (4%Ru)	145	43.1	3.0	○
S8NR4 (4%Ru)	147	44.6	4.4	○
P4NR4 (4%Ru)	89	45.4	5.6	△
P4NR4 ^a	360	4.3	9.3	-
P4NR8 (8%Ru)	49	45.3	5.4	▽
M4KR4 (4%Ru)	47	47.2	8.1	◇
M4KR8 (8%Ru)	37	42.3	7.0	+

Conditions: 100°C, 1.5 MPa, 2 ml benzene, 0.75 ml water, 2 mg Ru in the catalyst.

^a 110°C, without water.

Table 2
Effect of zinc salts on both conversion and selectivity of hydrogenation of benzene at 110°C and 1.5 MPa of total pressure. 2ml benzene, 0.75 ml water, 2 mg of Ru in the catalyst

Catalyst	Zn salt	Zn/Ru (g/g)	Reaction time (min)	Conversion (%)	Selectivity (%)	Symbols in Fig. 4
Ru powder ^a	-	0	300	35.5	0.8	
Ru powder ^a	acetate	1.25	585	4.9	2.0	
Ru powder	acetate	1.25	473	10.3	5.6	
	-	0	33	55.3	0.5	
	sulphate	1.32	190	43.5	< 0.3	
Ru/C ^b	sulphate	4.0	165	42.6	< 0.3	
	acetate	1.32	360	8.8	< 0.3	
	acetate	4.0	345	11.2	0.8	
P4NR4	-	0	80	42.2	6.5	△
P4NR4	sulphate	0.006	240	40.9	7.7	□
P4NR4	sulphate	0.5	450	23.6	8.2	◇
P4NR4	sulphate	4	420 ^b	16.4	11.5	*
P4NR4	acetate	0.006	270	43.4	8.7	+
P4NR4	acetate	1.32	480	3.8	17.4	○

^a At 50°C.

^b At 100°C.

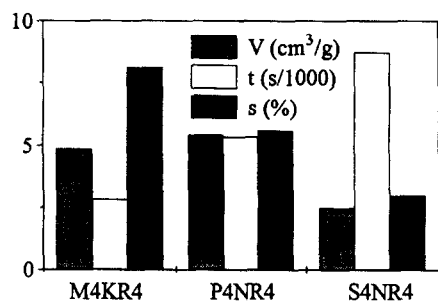


Fig. 3. Swellability (V), reaction time (t_r) and selectivity (s) for various ruthenium catalysts.

From the literature it is known [8] that zinc additives positively influence the selectivity of benzene hydrogenation to cyclohexene but strongly decrease the reaction rate. The primary function of the added salt is believed to be in making the ruthenium crystallites more hydrophilic. Its action strongly depends on its adsorbability. Results summarized in Table 2 demonstrate that zinc compounds improve the selectivity to cyclohexene and that zinc acetate is more effective than sulphate for ruthenium catalysts supported on anionic resins. On the contrary, no influence on the Ru/C catalyst is observed. As shown in Fig. 4, the presence of zinc salts, in agreement with literature data [8], significantly decreases the rate of hydrogenation.

The obtained results suggest that a higher selectivity to cyclohexene during hydrogenation of benzene over ruthenium catalysts supported

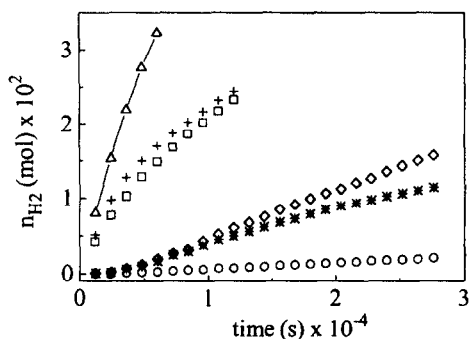


Fig. 4. Hydrogen consumption (n_{H_2}) vs. time (t) in the runs with P4NR4 catalysts without modifiers and with modifiers. Symbols as given in Table 2.

on anionic resins is promoted by a marked hydrophilicity of the ruthenium microenvironment, which is one of the predominant factors influencing the selectivity of this reaction. As is also known from the literature [7], another factor is temperature, which raises the selectivity considerably. In this connection, further work is in progress in these laboratories.

4. Conclusions

Experimental results of liquid-phase hydrogenation of benzene catalyzed by resins-supported ruthenium particles, in water show that the hydrophilicity of ruthenium particle surroundings is a very important factor influencing the selectivity of cyclohexene formation. The best results were obtained with the Ru catalyst supported on a highly hydrophilic support, i.e. potassium methacryloyl ethylene sulphonate resin. Under comparable conditions (100°C and 1.5 MPa of total pressure) this catalyst possesses higher selectivity than Ru/C catalysts. The resin supported catalysts are also more sensitive to zinc additives, which positively influence the selectivity to cyclohexene. However, this effect is accompanied by a strong decrease of the rate of hydrogenation and is dependent on the counter anion in the zinc compound. Another important factor influencing the catalyst activity is the swellability of the resin, i.e. a factor decisive for the accessibility of Ru particles to reactants.

References

- [1] A.K. Varshney, M.A. Siddigui and M.H. Mehta, *J. Sci. Ind. Res.* 48 (1989) 524.
- [2] A.W. Sleight and U. Chowdhry, in E.L. Bruce (Ed.), *Applied Industrial Catalysis*, Vol. 2, Academic Press, New York, 1983.
- [3] P. Dini, S. Dones, S. Montelatici and N. Giordano, *J. Catal.*, 30 (1973) 1.
- [4] D. Galvagno, A. Donato, G. Neri, D. Pietropaolo and P. Staiti, *React. Kinet. Catal. Lett.*, 37 (1988) 443.

- [5] H. Nahagara and M. Kohishi, Jpn. Pat. 6 281 332 (1986) to Asahi Chem. Ind.
- [6] H. Nahagara and M. Kohishi, Eur. Pat. 220 525 (1986) to Asahi Chem. Ind.
- [7] J. Struijk, M. d'Angremond, W.J.M. Lucas-de Regt and J.J.F. Scholten, Appl. Catal. A, 83 (1992) 263.
- [8] J. Struijk, R. Moene, T. van der Kamp and J.J.F. Scholten, Appl. Catal. A, 89 (1992) 77.
- [9] M. Kralik, M. Hronec, S. Lora, G. Palma, M. Zecca, A. Biffis and B. Corain, J. Mol. Catal. A, 97 (1995) 145.
- [10] M. Kralik, M. Hronec, V. Jorik, S. Lora, G. Palma, M. Zecca, A. Biffis and B. Corain, J. Mol. Catal. A, 101 (1995) 143.
- [11] M. Hronec, Z. Cvengrosova and J. Kizlink, J. Mol. Catal., 83, (1993) 75.
- [12] Ostion ionexes, Commercial Technical Report 81/21, Spolchemie, Czechoslovakia, 1977