Catalysis Today 149 (2010) 321–325

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Influence of the support nature and morphology on the performance of ruthenium catalysts for partial hydrogenation of benzene in liquid phase

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ARTICLE INFO

Article history:
Received 8 March 2009
Received in revised form 1 July 2009
Accepted 27 July 2009
Available online 7 November 2009

Keywords:
Ruthenium catalysts
Benzene
Cyclohexene
Alumina and niobia

ABSTRACT

This paper is aimed at studying the influence of the support nature and morphology on the performance of ruthenium catalysts for partial hydrogenation of benzene in liquid phase. Therefore, Al_2O_3 and Nb_2O_5 supports were employed with different values of particle diameter and superficial specific area. The catalysts were prepared through incipient impregnation from an aqueous solution of the $RuCl_3{\cdot}xH_2O$ precursor. After impregnation, the solids underwent a reduction treatment under H_2 flow at the temperature of 573 K. The solids were characterized through the techniques of particle size distribution, XRD, BET, SEM + EDX and TPR. The catalytic performances were evaluated within the hydrogenation of benzene in liquid phase, conducted at 373 K under constant pressure of 5.0 MPa of H_2. For the conditions employed, the results show that the support nature practically exerts no influence upon the selectivity of the intermediate product to the benzene → cyclohexene → cyclohexane reaction. However, the increase in the particle diameter or in the superficial specific area of the support decreases the yield of cyclohexene.

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1. Introduction

The partial hydrogenation of benzene is a chemical reaction that raises both scientific and industrial interest. Owing to the serious current restrictions on the presence of toxic aromatic compounds in oil-derived fuels, such reaction stands for a promising alternative treatment with no significant loss to octane rating [1,2]. Moreover, the cyclohexene obtained can be used to synthesize several compounds, mainly in nylon production [3].

All the metals classically employed as hydrogenation catalysts are able to hydrogenate the benzene, but the ruthenium based catalysts have led to the most significant yields concerning the intermediate product of the benzene → cyclohexene → cyclohexane reaction [4]. The nature of precursor ruthenium salts can also influence catalytic activity and selectivity. Chlorine precursors generate more selective catalysts in comparison to non-chlorine precursors [5].

Meanwhile, in order to obtain greater yields through Ru catalysts in this reaction, the presence of water in the reaction medium is required. Therefore, the catalyst must bear a hydrophilous character in itself or be forced by adding promoters to the reaction medium [6].

Recently, ruthenium catalysts supported in Al_2O_3 (220 m^2/g) and Nb_2O_5 (15 m^2/g) were studied, aiming at the partial hydrogenation of benzene in liquid phase [7]. The authors concluded that the greatest cyclohexene selectivities were observed with Ru/Nb_2O_5 catalysts. However, the largest difference between values in the superficial specific areas of these employed supports may have influenced the performance of the catalysts under study.

In such context, this paper is aimed at studying the influence of the nature and morphology of Al_2O_3 and Nb_2O_5 supports on the performance of ruthenium catalysts for partial hydrogenation of benzene in liquid phase. Thus, catalysts of Ru/Al_2O_3 and Ru/Nb_2O_5 were prepared from their respective supports with different particle sizes and specific surface areas. The conditions employed for the preparation of catalysts and the conditions used for the catalytic tests (amount of catalyst, reaction temperature, pressure of H_2, the rate of agitation, adding water to the reaction medium, etc.), were based on results in several previous studies in our laboratory [6,8–10]. Therefore, it is expected to contribute to a better understanding of the effects of physical and chemical characteristics of Ru catalysts on the selectivity of intermediate product in the benzene hydrogenation.

2. Experimental

2.1. Catalysts preparation

Ru/Al_2O_3 and Ru/Nb_2O_5 catalysts were prepared through incipient impregnation from an aqueous solution of ruthenium III chloride hydrate ($RuCl_3.xH_2O$) by Aldrich Chemical Co., so that a

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0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.07.113

5% mass fraction of the active metal is obtained. The alumina employed as catalysts support was supplied by Degussa (higher specific areas) and by Alfa Aesar Co. (very small specific area). Before impregnation took place, the Degussa alumina was classified through the use of strainers in order to obtain the particle size ranges required for the study. On its turn, the Nb_2O_5 in use was obtained from a niobium pentoxide hydrate (niobic acid) with a 160 m^2/g specific area supplied by "Companhia Brasileira de Metalurgia e Mineração" (CBMM), a Brazilian Mining & Steelwork Company. The Nb_2O_5 provided underwent calcination at two different temperature ranges (673 K and 923 K) in order to obtain the specific areas as required for the study.

After impregnation, the resulting material was left at rest for 12 h at room temperature. Next, the solid was dried in a drying chamber for 24 h at 358 K. Then, the material underwent heat treatment for direct reduction at 573 K under a H_2 flow equal to 40 mL/min and at a heating rate of 10 K/min, from room temperature to 573 K, remaining at this temperature for 180 min. The catalysts underwent direct reduction because previous studies demonstrated that this treatment may lead to higher yields of cyclohexene [8].

2.2. Catalysts characterization

The characterization of solids was performed to provide a better understanding of the catalytical behaviors observed. The following techniques were used: granulometric analysis, X-ray diffraction (XRD), determination of superficial specific area (BET method), energy dispersive X-ray (EDX) and temperature programmed reduction (TPR).

The granulometric analyses of the supports were performed through wet-way dispersion in a Malvern Mastersizer (analyzer of the size of particles through laser diffraction) with a detection range of 0.05–900 μm.

The XRD was employed to identify the solid phases and performed in Rigaky Miniflex equipment with a cobalt X-ray tube supplied with a 635 V operational voltage, 2.00°/min scanning speed, angular values (2θ) of 3–90 and continuous scanning.

The superficial specific area of the supports and catalysts was determined by N_2 adsorption. The solid was previously vacuum-dried at 473 K, and the N_2 adsorption was performed at the temperature of liquid nitrogen (77 K) in a Micrometrics Tristar model equipment. The adjustment of experimental points was performed by employing the classic BET model.

The scanning electron microscopy with microprobe for the spectrometric of Energy Dispersive X-ray analysis (SEM + EDX) was used aiming at quantifying the main elements found in the catalysts as well as to observing their morphology. The analyses were performed at Leica equipment, model LEO 440i. The initial stage consisted of metalizing the catalyst to form a thin layer of gold atoms on it with a 92-Å film thickness. The analyses were performed by employing a 3 MA current for 180 s.

The TPR was performed so that Ru reducibility could be studied by employing a conventional experimental apparatus. The reduction profiles were obtained by using a 50 mg mass from the solid, which was linearly heated at a rate of 10 K min^{-1}, from 298 K to 573 K, under a flow of 40 mL/min of a 2% H_2/N_2 mixture.

2.3. Catalytic tests

The catalytic tests in the benzene hydrogenation reaction were performed in a Parr reactor of the slurry type with the presence of water in the reaction medium. The reactions were conducted at the hydrogen pressure of 5 MPa and at the temperature of 373 K, employing a catalyst mass of 200 mg and a stirring rate of 1000 rpm.

Before starting the reaction, the catalyst was activated *in situ* at the temperature of 373 K for 45 min. Reaction medium samples were collected during the reaction and analyzed through gas chromatography. For that purpose, a TRACE GC 2000 chromatographer by Thermo Finnigan was used. It was equipped with a flame ionization detector and a CG 151-40 capillary column with a polydimethyl-siloxane FI-53 phase (diameter of 0.25 mm and 25 m of length).

The results generated from the benzene hydrogenation reaction allowed determining the yield of cyclohexene (R) during the reaction, i.e., owing to the conversion of benzene (X). The following equations were employed for the respective calculations:

$$R = \frac{\Delta(C_6H_{10})}{(C_6H_6)^0} \tag{1}$$

and

$$X = \frac{\Delta(C_6H_6)}{(C_6H_6)^0}; \tag{2}$$

where $(C_6H_6)^0$ corresponds to the initial molar concentration of benzene and Δ (i) to the variation of molar concentration concerning the compound *i*.

3. Results and discussion

3.1. Study of catalysts morphology

The values of the average particle diameters for each support used in the study are presented in Table 1.

The results presented in Table 1 show four values for the experimental average particle diameter, which stand for about 7 ± 2 μm for the so-called dpP_P (very small particle diameter); 20 ± 5 μm for dpP (small particle diameter); 56 ± 1 μm for dpM (intermediate particle diameter), and 110 ± 1 μm for dpG (large particle diameter).

When comparing the values of the nominal and experimental average particle diameters, one is able to notice that the experimental for dpP_P, dpP and dpG remained within the range of respective nominal values informed by the suppliers. On the other hand, the experimental values for dpM were lightly above the nominal range.

The X-ray diffractograms obtained for the supports revealed that the alumina acquired from Alfa Aesar (Al_2O_3-dpP_PSpP support) is at α-Al_2O_3 phase, whose structure is rhombohedral. The alumina in such phase is known for it low specific area according to the results presented later. Degussa's alumina from the SpM (intermediate specific area) series, on its hand, is at the δ-Al_2O_3 phase, whose structure is tetragonal and known for having an intermediate specific area. For Degussa's alumina from the SpG (large specific area) series, the diffractogram obtained did not lead to a precise identification of the solid phase, which can be due to the high amorphous character of the material as observed in the diffractogram (wide, not so intense bands). However, this alumina is probably bound to evolve to the γ-Al_2O_3 phase owing to the high specific area obtained for this solid. On the other hand, the niobic acid diffractograms showed that the niobia calcinated at 673 K is found at a hexagonal structure, whereas the one calcinated at 923 K presents an orthorhombic structure.

The values obtained through the BET method for the superficial specific areas of the employed supports and the prepared catalysts are presented in Table 2.

The results presented in Table 2 show three values for the specific area, which remain around 16 ± 4 m^2/g for SpP (small

Table 1
Nominal and experimental values of the average particle diameter (dp) for the supports.

Support	Nominal dp (μm)	Experimental dp (μm)
Al_2O_3-dpP$_P$SpP	1	4
Al_2O_3-dpPSpM	dp < 37	24
Al_2O_3-dpMSpM	37 < dp < 43	57
Al_2O_3-dpGSpM	dp > 43	110
Al_2O_3-dpPSpG	dp < 37	15
Al_2O_3-dpMSpG	37 < dp < 43	56
Al_2O_3-dpGSpG	dp > 43	111
Nb_2O_5-dpP$_P$SpP	dp < 37	9
Nb_2O_5-dpP$_P$SpM	dp < 37	9

dp: average particle diameter; Sp: superficial specific area; Pp: very small; P: small; M: intermediate; G: large; nominal: supplier's value.

Table 2
Superficial specific area (Sp) of supports and catalysts.

Support	Sp (m^2/g)	Catalyst	Sp (m^2/g)
Al_2O_3-dpP$_P$SpP	12	Ru/Al_2O_3-dpP$_P$SpP	15
Al_2O_3-dpPSpM	80	Ru/Al_2O_3-dpPSpM	90
Al_2O_3-dpMSpM	90	Ru/Al_2O_3-dpMSpM	95
Al_2O_3-dpGSpM	90	Ru/Al_2O_3-dpGSpM	100
Al_2O_3-dpPSpG	200	Ru/Al_2O_3-dpPSpG	150
Al_2O_3-dpMSpG	205	Ru/Al_2O_3-dpMSpG	200
Al_2O_3-dpGSpG	220	Ru/Al_2O_3-dpGSpG	170
Nb_2O_5-dpP$_P$SpP	20	Ru/Nb_2O_5-dpP$_P$SpP	25
Nb_2O_5-dpP$_P$SpM	75	Ru/Nb_2O_5-dpP$_P$SpM	65

dp: average particle diameter; Sp: superficial specific area; Pp: very small; P: small; M: intermediate; G: large.

specific area); 84 ± 9 m^2/g for SpM (intermediate specific area) and 208 ± 12 m^2/g for SpG (large specific area).

The small values of the specific areas obtained for the prepared Nb_2O_5 supports show that the calcination heat treatments decreased the specific area of the niobic acid hydrate supplied by CBMM (160 m^2/g), obtaining the specific area values necessaries for the present study.

For most prepared catalysts, the values obtained for the specific areas are very close to the ones of the respective supports. Such phenomenon was observed in previous studies performed with catalysts containing a mass fraction of 5% ruthenium supported on Al_2O_3, TiO_2, La_2O_3 or CeO_2 [9,10].

Table 3
Chemical composition of non-reduced Ru/Al_2O_3 solids.

Catalyst	Mass fraction (%)			
	Ru	Cl	Al	O
Ru/Al_2O_3-dpP$_P$SpP	5.1	2.9	40	52
Ru/Al_2O_3-dpPSpM	3.9	3.1	41	52

3.2. Catalysts composition

The results obtained by EDX for some prepared Ru/Al_2O_3 catalysts are presented in Table 3.

Although the analytical method by EDX is considered to be semi-quantitative, the results presented in Table 3 indicate that the content of active metal in the catalysts is close to the nominal value of 5% in Ru mass, which was established for this study. The presence of chlorine is also found in the analyzed catalysts in very similar quantities, which shows the effectiveness of the performed preparations.

3.3. Study of the active phase formation

The TPR profiles obtained for non-reduced Ru/Al_2O_3 catalysts are presented in Fig. 1.

Fig. 1.I gathers the profiles of non-reduced Ru/Al_2O_3 catalysts with a small average particle diameter in order to assess the influence of the specific area on ruthenium reduction, which is present in the solid as $RuCl_3$ precursor. The TPR profile of the solid Ru/Al_2O_3-dpP$_P$SpP (Fig. 1.I.a) presents a main consumption peak of H_2, whose maximum is approximately at 441 K, with a slight shoulder around 385 K. Similarly, the profiles of catalysts Ru/Al_2O_3-dpPSpM (Fig. 1.I.b) and Ru/Al_2O_3-dpPSpG (Fig. 1.I.c) present a main consumption peak of H_2, whose maximum is at 410 K in both cases. These results reveal that the reduction of precursor $RuCl_3$ is more difficult on the solid with the smallest specific area (Ru/Al_2O_3-dpP$_P$SpP). Such phenomenon could occur due to a smaller dispersion of precursor $RuCl_3$ over the surface of the support with the smallest area, thus making its reduction by H_2 more difficult.

Fig. 1.II shows the profiles of non-reduced Ru/Al_2O_3 catalysts with a large specific area in order to evaluate the influence of the average particle diameter on ruthenium reduction. The profile of solid Ru/Al_2O_3-dpPSpG (Fig. 1.II.a) presents a unique H_2 consumption peak, whose maximum is approximately at 410 K. The profiles of catalysts Ru/Al_2O_3-dpMSpG (Fig. 1.II.b) and Ru/Al_2O_3-dpGSpM

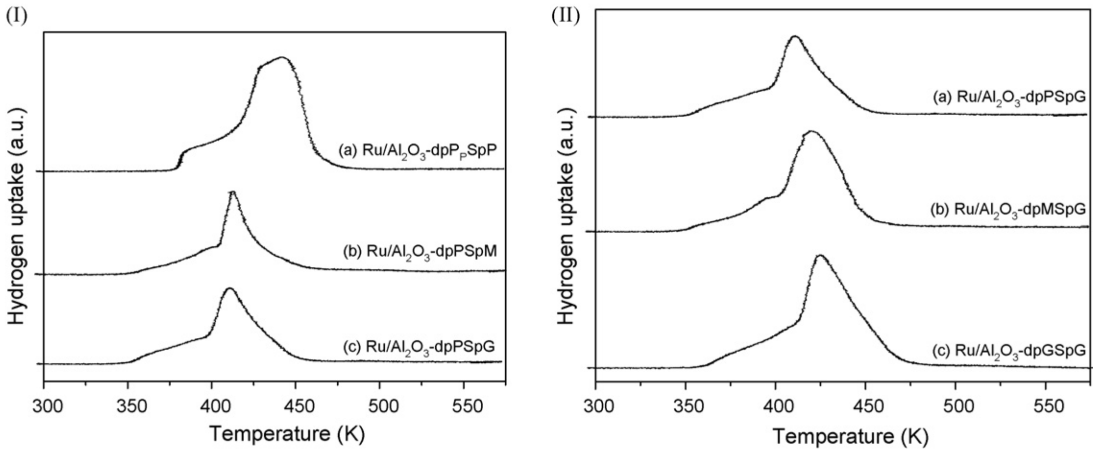

Fig. 1. TPR profiles of non-reduced Ru/Al_2O_3 catalysts. (I) Influence of the specific area for small average particle diameter catalysts. (II) Influence of the average particle diameter for large specific area catalysts.

Table 4
H_2 consumption in the TPR profiles of the catalysts.

Catalyst	H_2 consumption (μmol/mgRu)
Ru/Al_2O_3-dpP_PSpP	19
Ru/Al_2O_3-dpPSpM	15
Ru/Al_2O_3-dpMSpM	15
Ru/Al_2O_3-dpGSpM	15
Ru/Al_2O_3-dpPSpG	14
Ru/Al_2O_3-dpMSpG	14
Ru/Al_2O_3-dpGSpG	16
Ru/Nb_2O_5-dpP_PSpP	14
Ru/Nb_2O_5-dpP_PSpM	15

Table 5
Catalytic performance in the partial hydrogenation of benzene.

Catalyst	R_{max} (%)	X_{max} (%)	r_0 (mol L^{-1} min^{-1} $gcat^{-1}$)
Ru/Al_2O_3-dpP_PSpP	4.3	35	40
Ru/Al_2O_3-dpPSpM	3.6	55	39
Ru/Al_2O_3-dpMSpM	3.1	50	40
Ru/Al_2O_3-dpGSpM	2.7	60	60
Ru/Al_2O_3-dpPSpG	2.9	70	28
Ru/Al_2O_3-dpMSpG	2.7	65	31
Ru/Al_2O_3-dpGSpG	2.4	65	35
Ru/Nb_2O_5-dpP_PSpP	3.9	55	30
Ru/Nb_2O_5-dpP_PSpM	3.1	60	33

R_{max}: maximum yield of cyclohexene; X_{max}: conversion of benzene for the maximum yield of cyclohexene; r_0: initial reaction rate.

(Fig. 1.II.c) also presented an H_2 consumption peak, whose maximum levels are 420 K and 425 K, respectively. These results show that the increase in the average particle diameter for solids with a large specific area makes ruthenium reduction more difficult to occur. Such reduction can be related to the greater length of pores in catalysts with a higher particle size, which impairs H_2 access to the precursor.

From the peak areas in the TPR profiles, the total H_2 consumption was calculated for each solid under study, whose values obtained are presented in Table 4.

The average H_2 consumption obtained is around 15 μmol of H_2/mgRu^{3+}, which corresponds to the reduction of precursor $RuCl_3$, according to the chemical Eq. (3).

$$RuCl_3 + 1.5H_2 \rightarrow Ru^0 + 3HCl(15\,\mu moldeH_2/mgRu^{3+}) \tag{3}$$

The largest consumption for Ru/Al_2O_3-dpP_PSpP may be due to the most difficult reduction of Ru observed for this material, leading to a slightly higher experimental error.

3.4. Catalytic performances in the partial hydrogenation of benzene

Table 5 presents the results for the partial hydrogenation of benzene, where the only products obtained were cyclohexene and cyclohexane.

The greatest values for the maximum yield of cyclohexene (R_{max}) are obtained with the catalysts presenting the smallest average particle diameter and smallest specific area (4.3% for Ru/Al_2O_3-dpP_PSpP and 3.9% for Ru/Nb_2O_5-dpP_PSpP); therefore, regardless of the nature of the support employed (Al_2O_3 or Nb_2O_5). For the Ru/Al_2O_3 catalysts, the R_{max} is decreased as the average particle diameter increases, either for the intermediate specific area (SpM) or the large specific area (SpG). This might be associated with the largest length of the pores in the case of the largest catalyst particles, which leads to the cyclohexene hydrogenation during its process of diffusion inside the pores. In addition, the results show that the increase in the average particle diameter in Ru/Al_2O_3 catalysts practically does not influence the conversion of benzene for the maximum yield (X_{max}), though it tends to increase the values of the initial reaction rate (r_0), which might be due to a better dispersion of the Ru in the catalyst.

In relation to the specific area influence, the analysis of results in Table 5 reveals that, for equal particle diameters, the R_{max} values decrease significantly as the specific area increases, regardless of the support nature. This loss of selectivity may be associated with the greater porosity of the catalysts presenting a larger specific area, leading to the process of diffusion and hydrogenation of cyclohexene in the pores, as mentioned before. Furthermore, the results show that the augment in the specific area tends to increase the X_{max} values, which might be due to a greater dispersion of Ru in the catalyst.

Fig. 2 illustrates the evolution of the yield of cyclohexene during the reaction, i.e., with the increase in benzene conversion, for ruthenium catalysts supported in alumina or niobia.

The results prove that the increase in the yield of cyclohexene with the increment of the specific area of the catalyst, for conversions below 60% in the case of Ru/Al_2O_3 catalysts (Fig. 2.I), and during the entire reaction with Ru/Nb_2O_5 (Fig. 2.II).

4. Conclusions

For the conditions employed in this study, the results obtained show that there is practically no influence of the nature of Al_2O_3 and Nb_2O_5 supports on the selectivity of ruthenium based catalysts for partial hydrogenation of benzene in liquid phase. However, the decrease in the particle size or specific area of the solids increases the yield of desired product.

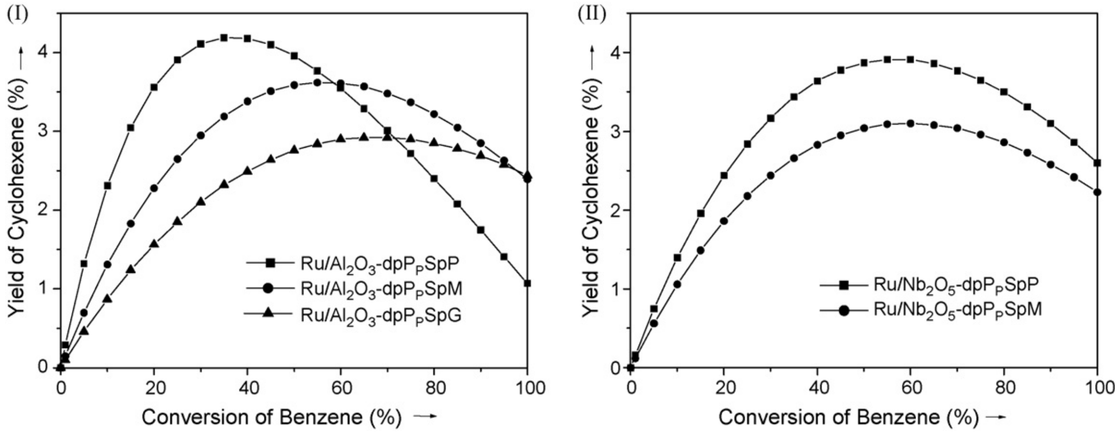

Fig. 2. Influence of the specific area on the yield of cyclohexene during the reaction for catalysts with small diameter of particle. (I) Ru/Al_2O_3; (II) Ru/Nb_2O_5.

Acknowledgments

The authors would like to thank the Brazilian Council for Advanced Professional Training (CAPES) for the financial support as well as for the scholarship granted to Michelle Fernanda Faita Rodrigues as a Master's Degree student.

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