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Surface investigation by X-ray photoelectron spectroscopy of Ru-Zn catalysts for the partial hydrogenation of benzene

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ABSTRACT

Partial hydrogenation of benzene with ruthenium-supported catalysts is an interesting alternative route to produce cyclohexene, an intermediate in the production of nylon 6.6 and other fine chemicals. In this work, ruthenium chloride solution was added to xZnO/Al₂O₃ by wetness impregnation. The supports were derived from hydrotalcite compounds and tested on the partial hydrogenation of benzene. The catalyst with 10 wt.% of ZnO (Ru10ZnAl) presented the best catalytic performance reaching total conversion in 40 min of the reaction, and a maximum yield of 35% using pure benzene (without water, salts or other additives). The samples were characterized by X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF), X-ray diffraction (XRD), temperature programmed reduction (TPR) and H₂ Chemisorption. Metallic and partially reduced ruthenium surface species were identified on the surface of the Ru10ZnAl catalyst and the electronic vicinity of Ru is proposed to be responsible for promoting the cyclohexene desorption, revealing a synergistic effect. In this sense, the electronic surroundings modification of surface zinc species with ruthenium species, followed by reduction, was evidenced by using the Modified Auger Parameter (MAP). These species played an important role in the reaction.

1. Introduction

Benzene is a key organic compound for the chemical industry and is obtained mostly by fossil resources. Due to its high toxicity, new global policies have been applied in order to prevent the addition of this substance to fuels such as gasoline [1]. These constraints lead to an excess of benzene, which tends to reduce its price. On the other hand, benzene could be highly reactive in an appropriate catalytic system for different reactions, generating new substances that are industrially important.

Hydrogenation reactions of petroleum-derived chemicals have been extensively studied, since they are crucial to obtain many important intermediate compounds. One example is the hydrogenation of benzene, an attractive route to produce cyclohexene or cyclohexane, which are used in the synthesis of adipic acid and other fine chemicals [2–4].

The main challenge in the partial hydrogenation of benzene is to avoid the adsorption of cyclohexene on the ruthenium surface, inhibiting its further hydrogenation to cyclohexane. That is due to the unfavorable thermodynamics to obtain this compound – benzene hydrogenation to cyclohexene has a ΔG^0 4.3 times higher than to cyclohexane, i.e. -23 kJ mol^{-1} and -98 kJ mol^{-1} , respectively [2].

Reduced ruthenium catalysts are the most active for this reaction [5,6]. Additives such as zinc sulfate and water are used in order to avoid cyclohexene adsorption on the catalyst surface [7,8]. Zinc and water additions promote the formation of a stagnant film over the catalyst surface and, during the reaction, both hydrogen and benzene must overcome this barrier to reach the active center [9,10]. Thus, the hydrophilicity of the catalyst may reduce the adsorption extent of the cyclohexene formed, preventing its subsequent hydrogenation to cyclohexane, increasing the selectivity to cyclohexene [11]. However, the addition of water has disadvantages; it hinders the separation of products, making the cost of the process more expensive. Furthermore, a possible corrosion of the reactor is a problem with this system due to the pH of the aqueous phase to be acidic, and a gradual deactivation of the catalyst may occur due to a progressive corrosion products adsorption on the catalyst surface, from the reactor wall, mainly of iron [12,13].

The patented Asahi process uses four phases in order to promote cyclohexene yields: gaseous (hydrogen), organic (benzene), aqueous (ZnSO₄ in aqueous solution) and solid (bulk ruthenium catalyst). [14].

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In this sense, many authors also have been dedicated to achieving a supported catalyst of ruthenium that is active and selective as the commercial one. They have observed improvement in activity and selectivity to cyclohexene using zinc salts added to the liquid medium as well as to the catalyst. Hu and Chen [15] prepared Ru-Zn/SiO₂ catalysts by the simultaneous addition of ruthenium chloride and zinc nitrate to a SiO₂ support using dry impregnation. The ruthenium content was 5 wt.% and zinc content varied from 0.3 to 3.0 wt.%. According to the authors, small amounts of Zn retarded the reduction of ruthenium oxide and increased the consumption of H₂ up to 1 wt.% Zn, suggesting a partial reduction of ZnO to Zn metal. The benzene hydrogenation was carried out at 150 °C, 33.6 bar, 2.5 g of catalyst, 0.62 M NaOH, 75 mL of benzene and 100 mL of water. However, while the selectivity was increased after zinc addition, the catalyst activity was reduced, probably due to a Ru sites coating through a zinc layer during the reduction. In fact, the highest cyclohexene yield was observed at 5%Ru-1%Zn/SiO₂ (31% at 55% conversion), which suggests a faster inhibition of hydrogenation and/or cyclohexene than cyclohexane desorption.

Yuan et al. [16] observed the same effect when studying Ru-Zn/ ZrO₂ catalysts using theoretical and experimental approaches. Ru-Zn/ ZrO₂ samples were prepared by co-precipitation of ZrOCl₂ and RuCl₃ with KOH followed by ZnSO₄ impregnation and reduction (Zn content: 2.4–3.0 wt.%). The catalysts were evaluated in the benzene hydrogenation under the conditions: 2.0 g of catalyst, 80 mL of benzene, 150 mL of water and ZnSO₄ in solution (Zn²⁺ = 0.35–0.55 M). The authors observed that the activity decreased, but the selectivity for cyclohexene increased, as a result of the decrease of the benzene and cyclohexene adsorption on the catalysts, influenced by the Zn and water addition in the reaction medium. The best result was obtained with a Zn content of 2.72 wt.% with a cyclohexene yield of up to 44%.

Attempts to use other materials as support have also been made. Zhang et al. [2] prepared ruthenium-zinc catalysts in hydroxyapatite. Ru-Zn/HAP bimetallic catalysts (2.5 wt.% Ru) were prepared by the ion exchange method using RuCl₃ and ZnSO₄. The benzene hydrogenation was carried out in a 6 mL of a teflon coated stainless steel autoclave reactor fitted with a magnetic stirrer under the following conditions: 0.5 mL of benzene, 20 mg of catalyst, and 1.5 mL of an aqueous solution of sodium hydroxide. A yield of cyclohexene around 33.0% was obtained by Ru-Zn/HAP (1: 1 Ru/Zn molar ratio) at 150 $^{\circ}$ C and 50 bar. The authors reported that both metallic zinc and Zn²⁺ play an important role in increasing selectivity of cyclohexene. Compared to other supports (MgO, CeO₂ and ZrO₂), hydroxyapatite gave better activity and selectivity probably due to their adsorption capacity, high hydrophilicity and dispersion of Ru-Zn nanoparticles, and the synergistic effect of metallic Zn and Zn²⁺ cations.

Among the different supports used, there are no reports in the open literature about the use of mixed oxides prepared by hydrotalcite route for the partial benzene hydrogenation without additives. Hydrotalcite, also called layered double hydroxides, are mixed metal hydroxides which general formula is $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2][A^{m-}]_{x/m}.nH_2O$, where x is the ratio $M^{3+}/(M^{2+}+M^{3+}).$ M^{2+} and M^{3+} are, respectively, divalent and trivalent cations positioned at the octahedral sites in the hydroxyl layers and A^{m-} is the interlayer anion.

Hydrotalcite type compounds can be calcined above 450 $^{\circ}$ C generating mixed oxides with high surface area, giving rise to highly dispersed metal crystals [17]. The redox and acid-base properties of these mixed oxides will depend on the composition of M^{2+} and M^{3+} cations. These materials have been studied for many applications in catalysis, such as hydrogenation, hydrogenolysis and condensation reactions [18–21]. They are promising to associate zinc with ruthenium aiming to achieve higher selectivity to cyclohexene since Zn^{2+} is one option for these substituent cations. The catalyst separation from the reaction products provides the possibility of its reuse, increasing the productivity of the process.

Hydrotalcite based on Mg and Al can be changed by the partial or total substitution of these cations [17,22–24]. Sharma et al. [17]

studied the total hydrogenation of benzene using hydrotalcites (Ru-HT) obtained by partial substitution of Mg^{2+} or Al^{3+} cations by ruthenium metal (1.0 wt.% Ru) in octahedral layers. The reactions were carried out at 120 $^{\circ}$ C and 60 bar and the catalyst was not previously reduced. The authors observed complete conversion with 100% selectivity to cyclohexane after 2 h of reaction. No cyclohexene was observed, even with addition of water to the reaction medium.

Fukuhara et al. [18] prepared Ru-HT catalyst with 15.3 wt.% Ru and performed the partial hydrogenation of benzene, observing the influence of Zn and NaOH on both activity and selectivity. The highest yield of cyclohexene (26%) was obtained with Ru - HT with zinc and NaOH solution. Similar behavior was observed when the catalyst was subjected to a 500° C heat treatment with nitrogen before the experiment.

The adsorption and desorption phenomena are important steps of any heterogeneous catalytic process, so it is crucial to identify the surface chemical species that are involved in the benzene to cyclohexene conversion. X-ray Photoelectron Spectroscopy (XPS) is a powerful technique capable of detecting the elements present on a target surface and the different species of all elements, except hydrogen [25]. However, in XPS carbon is found as an impurity for almost every analysis. In addition, C1s photoelectron peak coexists with Ru3d region, turning the analysis more complex. Therefore, whenever the Ru3d photoelectron peak is analyzed, C1s components must be taken in account in the peak model [26,27].

In this context, the aim of the present work was to prepare Ru/Zn/ Al catalysts by the hydrotalcite route and study their performance in the partial hydrogenation of benzene without additives. A deeply XPS study of the surface of these catalysts was carried out in order to investigate the catalytic performance towards of the reaction, evidencing the role of zinc species. Aware of the complexity of Ru3d region, metallic ruthenium and ruthenium oxide were used as standard materials.

2. Experimental

2.1. Catalysts preparation

The xZnO-Al₂O₃ supports (where x was 10 or 50 wt.% of zinc oxide) were prepared by coprecipitation, with temperature and pH control, following the methodology used for the synthesis of hydrotalcites [20]. Thus, two aqueous solutions were prepared for each support using the precursor salts (Merck) Zn(NO₃).6H₂O (0.2 and 0.9 M) and Al (NO₃).9H₂O (2.6 and 1.5 M), in order to obtain the concentrations of 10 or 50 wt.% of ZnO, respectively. These solutions were mixed, transferred to a burette and added slowly to 200 mL of distilled water, maintained at temperature of 70 °C and stirring at 400 rpm. The pH was stabilized at 7.0 throughout addition of a solution (1:1) of KOH (1.6 M) and K₂CO₃ (1.6 M). After the addition, stirring was kept for 4 h. The final solution was allowed to stand for about 12 h. After this period, the solid was purified by washing at pH 7.0, followed by centrifugation and drying in an oven at 120 °C for 18 h. Using this methodology, the materials obtained were denominated 10ZnAl and 50ZnAl, which contain 10 and 50 wt.% of ZnO, corresponding to Zn/Al molar ratios of 0.07 and 0.63, respectively. Zinc oxide was obtained by precipitation of $ZnCl_2$ (36.7 g in 365 mL of deionized H₂O) with urea (8.3 g in 61 mL of deionized H₂O), adapted from the method described by Chuah et al. [28]. The precipitate was aged for 96 h with pH control at approximately 10.0, in reflux apparatus with magnetic stirring and ultrasonic bath. Subsequently, the resulting solution was washed by washing at pH 7 and drying in an oven at 120 °C for 18 h. γ-Al₂O₃, also used as support, was a commercial Harshaw Al-3916 P from Engelhard.

All supports were calcined at 400 °C for 5 h at a rate of 10 °C min⁻¹ and were maintained in the granulometric range between 200 and 270 mesh. After the preparation of all supports, an aqueous solution of RuCl₃.xH₂O was added by wetness impregnation and, thereafter, calcined at 400 °C for 5 h at 10 °C min⁻¹ in a muffle under atmospheric air originating Ru/xZnO-Al₂O₃ (x = 10 or 50 wt.% ZnO, Ru10ZnAl or

Ru50ZnAl), Ru/Al₂O₃ (RuAl) and Ru/ZnO (RuZn) catalysts (Ru = 1.0 wt.%). Before X-ray diffraction (XRD) and XPS measurements, an enough amount of each catalyst was reduced at 250 °C, for 1 h, under pure H₂ flow of 50 mL min⁻¹, cooled with He up to -80 °C and then passivated with a mixture of O₂/He (50 mL min⁻¹) during 30 min. These catalysts received the letters RP referencing the reduction followed by passivation treatments. Powdered RuO₂ and metallic Ru (Aldrich) were used in the XPS analysis as reference materials.

2.2. Catalyst characterization

The structural characteristics of the samples were obtained by X-ray diffraction in a Rigaku Miniflex diffractometer equipped with CuK_{α} radiation of 1.541 Å. The parameters were 20 from 10° to 70°, 0.02° per step, and scan time of 1 s per step. RuO2 particle diameters for all calcined catalysts were calculated by using the Scherrer equation. Chemical analysis of the calcined catalysts was performed by the X-ray fluorescence technique with a Bruker S8 Tiger spectrometer. It was assembled with a rhodium tube and operated at 4 kW. The textural analysis of the catalysts was determined by the N₂ adsorption in a Micromeritics ASAP 2020 equipment. The samples were pretreated at 300 °C and isotherms were obtained at -196 °C. Temperature programmed reduction (TPR) analysis was carried out using a Micromeritics AutoChem II equipment. The materials were dried at 150 °C, for 1 h, with nitrogen. After this step, the reduction was programmed from room temperature to 500 °C (10 °C min⁻¹), under 10% H_2/N_2 flow (50 mL min⁻¹). H_2 chemisorption was performed at the same equipment. After TPR analysis, the samples were purged with N₂ flow of 50 mL min $^{-1}$ and the H₂ pulses were carried out at 100 °C.

Surface analysis of all catalysts was carried out by X-Ray Photoelectron Spectroscopy (XPS). It was used a hemispherical spectrometer PHOIBOS 150 from SPECS, appareled with X-Ray Gun (model XR-50) with a non-monochromatic Al K α /Mg K α source. The power rating of the anode was 10 W and for survey spectra, pass energy was 50 eV, while it was 20 eV for the regions of interest. Due to the coexistence of C1s peak in the region of Ru3d, the aluminum containing samples spectra were calibrated using Al 2p peak (74.4 eV) [29] while the standards spectra were calibrated using the C1s peak at 284.6 eV. The background used to investigate the species of each spectrum was Shirley baseline and all mathematical treatment was performed using the Tags quantification available in the CasaXPS software version 2.3.16 [30]. The pressure in the analysis chamber was below 10^{-9} mbar during data acquisition.

2.3. Partial hydrogenation of benzene

The catalytic tests were performed in a PARR 4566 batch reactor with a 300 mL vessel. The catalysts were activated *in situ* with 50 mL min⁻¹ flow of pure H₂ at 250 °C for 1 h. After reduction, in order to maintain an inert atmosphere, the reactor was purged with pure N₂ and cooled down to reach the reaction temperature, which was 150 °C. Then, 100 mL of pure benzene was added to 0.5 g of catalyst. The H₂ pressure was kept at 50 bar with an agitation of 600 rpm during the 3 h of each reaction. Aliquots were collected in an interval of 10 min in the first hour and thereafter, every 30 min. The products were identified and quantified in a HP6890 gas chromatograph assembled with a NST-100 column and FID detector. The catalysts performances were evaluated by observing the conversion of benzene, selectivity and yield to cyclohexene. These were calculated by the following expressions:

Conversion (%) = (mols of reacted benzene/mols of initial benzene) \times 100

Selectivity (%) = (mols of obtained cyclohexene/mols of reacted benzene) \times 100

Yield (%) = (Conversion (%) \times Selectivity (%))/100

Table 1

Chemical analysis by XRF, TPR-H $_2$ consumption, H $_2$ chemisorption and RuO $_2$ particle diameter for all calcined samples.

Sample	Cl/Ru ^a	Al/(Zn + Al) ^b	TPR-H ₂ (μmols mgRu ⁻¹) ^c	H_2 Chemisorption (µmols gRu ⁻¹)	D _{Ru} (nm)
RuAl	3.1	1	15.2	113	29
Ru10ZnAl	3.3	0.94	47.3	828	8
Ru50ZnAl	3.4	0.63	14.3	60	44
RuZn	0	0	17.8	41	24

^a Molar%.

^b Atomic ratio.

 c Stoichiometric reduction for RuO_2: 19.8 and RuCl_3: 14.8 $\mu mol\,s$ H_2 mg Ru $^{-1}.$

3. Results and discussion

Chemical analysis of the calcined samples, obtained by using XRF, is shown in Table 1. After impregnation and calcination at 400 °C, all aluminum-containing samples presented an atomic Cl/Ru ratio between 3.1 and 3.4, close to the stoichiometric 3.0. RuCl₃.xH₂O was used as the precursor salt and, according to the literature, alumina has the characteristic of retaining chloride ions [31–34]. Concerning textural analyses, RuAl, Ru10ZnAl and Ru50ZnAl presented specific areas of 220, 297 and 211 m² g⁻¹, respectively. Accordingly, the pore volumes were 0.47, 0.56 and 0.33 cm³ g⁻¹. All catalysts presented type IV isotherms regarding mesoporous materials with hysteresis loop type H2. All samples presented a monomodal distribution of pore diameters with a mean of approximately 50 Å. The RuZn catalyst presented a very low specific area (< 10 m² g⁻¹) as well as the smallest pore volume (0.01 cm³ g⁻¹).

Fig. 1 shows the TPR profiles of the calcined catalysts. RuAl and Ru10ZnAl exhibited a reduction peak around 140 °C, which can be attributed to the RuCl₃ reduction [35]. On the other hand, Ru50ZnAl and RuZn TPR profiles did not show the peak related to RuCl₃ reduction. The reduction peak observed in the temperature range between 190 °C and 220 °C was attributed to the RuO₂ reduction [35,36]. RuAl catalyst presented a shoulder around 160 °C that can be related to well-dispersed Ru species [35]. Last but not least, Ru10ZnAl presented a broad reduction peak between 275 °C and 375 °C, which can be related to the reduction of zinc species. Furthermore, the H₂ consumption by TPR for this catalyst was higher than the stoichiometric, as shown in Table 1.

The H_2 chemisorption data, which are commonly used to determine the metallic dispersion, are also given in Table 1. The order for the H_2 chemisorption was Ru10ZnAl > > RuAl > Ru50ZnAl > RuZn.







Fig. 2. TPR profiles of calcined Ru10ZnAl and 10ZnAl.

These results indicate that the ruthenium particles are more dispersed on the 10ZnAl support surface, while the other catalyst presented a lower metallic dispersion.

In order to investigate if the aforementioned reduction region in the Ru10ZnAl catalyst profile – 275 °C–375 °C – is in fact associated to the consumption of H₂ by zinc species, a TPR analysis of the 10ZnAl-calcined support was performed. Fig. 2 shows that there is a reduction around 400 °C, which suggests a partial reduction of zinc oxide in the support. After ruthenium impregnation, the reduction temperature of ZnO is shifted to lower temperatures. The difference between the Ru10ZnAl catalyst and the support, regarding the temperature of reduction of ZnO, probably is due to the interaction of Ru and support. The presence of ruthenium is responsible for promoting the strong metal-support interaction (SMSI) and/or spillover effects, phenomena that may cause the partial reduction of zinc, already reported in literature [2,15,37–39]. That may explain the high H₂ consumption result for the Ru10ZnAl catalyst, Table 1.

X-ray diffractograms of the 10ZnAl and 50ZnAl supports before calcination are shown in Fig. 3. Considering the Al/(Al + Zn) atomic ratio presented in Table 1, Zn-Al hydrotalcites are not expected, since according to Cavani et al. [22], they are only formed in the range of 0.20 and 0.33 of Al/(Zn + Al) atomic ratio. The 10ZnAl support showed the typical boehmite structure (JCPDS 1-088-2112). No hydrotalcite phase was observed on this support. Besides, the absence of the ZnO phase (JCPDS 36-1451) suggests that this species is amorphous or well dispersed in the boehmite structure. However, the 50ZnAl support presented typical structure of hydrotalcite [23,24].

XRD patterns of all aluminum containing calcined catalysts are



Fig. 3. XRD patterns of the Zn-Al supports before calcination.



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Fig. 4. XRD patterns of the calcined aluminum-containing catalysts. *:RuO₂; #: $ZnAl_2O_4$; dashed line: γ -Al₂O₃.

presented in Fig. 4. The reflections at $2\theta = 37.2^{\circ}$, 46.0° and 66.9° (JCPDS 1-088-2112), observed for RuAl, are characteristic of the y-Al₂O₃ support. It is noted that RuAl, Ru10ZnAl and Ru50ZnAl presented the three peaks relative to crystalline RuO₂, which are $2\theta = 28^{\circ}$, 35° and 54° (JCPDS-40-1290). The spinel formation (ZnAl₂O₄) was observed for both Ru10ZnAl and Ru50ZnAl catalysts with the main peaks observed at 20 = 31.2°, 36.7°, 44.7°, 49.1°, 59.3° and 65.3° (JCPDS-05-0669) [40]. In addition, Ru50ZnAl catalyst also presented a displacement of the main line $(2\theta = 36.7^{\circ})$ to $2\theta = 36.2^{\circ}$. This suggests that for this sample segregation of ZnO occured. XRD result of RuZn is presented in Fig. 5 and only two peaks corresponding to RuO_2 – i.e. $2\theta = 28^{\circ}$ and 54° – can be well distinguished for RuZn. The peak at $2\theta = 35^{\circ}$ is probably superimposed by the very intense ZnO characteristic peaks. The RuO₂ diameter calculated by the Scherrer equation, for the calcined catalysts is presented in Table 1. The particle size for Ru50ZnAl is approximately 6 times larger than the found for Ru10ZnAl. This observation agrees with the H₂ chemisorption analysis, also presented in Table 1, showing that ruthenium tends to aggregate on the 50ZnAl support surface, while for the 10ZnAl support more dispersed ruthenium particles are observed.

The ruthenium reduction was also investigated by X-ray diffraction and it was used to reinforce the hypothesis of the partial reduction of the support for the Ru10ZnAl catalyst due to the interaction between ruthenium and zinc. Diffractograms of Ru10ZnAl and Ru10ZnAl-RP are shown in Fig. 6. For Ru10ZnAl-RP, the peaks related to the ruthenium oxide disappeared while two new showed up. At $2\theta = 44^{\circ}$ (JCPDS-06-



Fig. 5. XRD pattern of calcined RuZn catalyst. *:RuO2.



Fig. 6. XRD patterns of Ru10ZnAl and Ru10ZnAl-RP samples.*:RuO₂ ; #: Zn⁰; $^{\circ}$:Ru⁰.

0663), the peak of metallic ruthenium appeared, and reduced zinc was observed at $2\theta = 42^{\circ}$ (JCPDS-04-0831). These observations corroborate with the hypothesis of partial reduction of zinc in Ru10ZnAl catalysts, also evidenced by TPR analysis. Additionally, these results indicated that the reduction, followed by the passivation procedure were effective to stabilize the metallic particles of ruthenium.

XPS characterization of the Ru 3d region is admittedly complex, mainly due to the overlapping of C1s and Ru 3d regions. Alternatively, the Ru3p region can be used in order to support the Ru3d analysis. Therefore, Ru3p regions of commercial metallic ruthenium and ruthenium (IV) oxide were recorded. Ru3p was detected by observing the doublet separation of approximately 22.2 eV [41] for all samples. Table 2 shows the binding energies for the Ru3p_{3/2} and Ru3d_{5/2} species compilation found for each reference and catalyst sample in this work. As can be seen, the $Ru3p_{3/2}$ binding energies for metallic ruthenium and RuO₂ samples were 461.4 eV and 462.5 eV, respectively, agreeing with those observed by Morgan [41]. All calcined catalysts presented $Ru3p_{3/2}$ binding energies values lower than the RuO_2 reference sample, indicating that the supported ruthenium particles are surrounded by less electronegative atoms such as Al and Zn. After RP procedure, the Ru3p_{3/2} peak of all catalysts showed significant shifts to lower binding energies values, confirming, at least, a partial reduction of the ruthenium particles.

According to the literature, metallic ruthenium and RuO_2 , an asymmetric line shape gives the best fit for the $3d_{3/2}$ and $3d_{5/2}$ lines processing. A study considering the line shape asymmetry for different ruthenium compounds including metallic ruthenium and RuO_2 , obtaining very accurate peak models was performed by Morgan [41]. Thus, in the present work, all Ru3d peak fittings were carried out by applying the line shapes parameters reported by this author. As metallic ruthenium and RuO_2 have very similar Ru3d doublet separation values,

Table 2

Compilation of all $Ru3d_{5/2}$ and $Ru3p_{3/2}$ peaks for the ruthenium samples by XPS.

Sample	Ru3p _{3/2} Binding Energy (eV)	Ru3d _{5/2} Binding Energy (eV)			
		Ru ⁰	Ru ⁴⁺	Ru ^{4+SAT}	$Ru^{\delta+}$
RuO ₂	462.5	-	280.4	282.5	-
Metallic Ru	461.4	280.0	-	-	-
RuAl	461.9	-	280.5	282.5	-
RuAl-RP	461.4	279.9	-	-	281.5
Ru10ZnAl	461.6	-	280.3	282.4	281.2
Ru10ZnAl-RP	461.2	279.8	-	-	281.0
Ru50ZnAl	462.1	-	280.0	282.8	281.9
Ru50ZnAl-RP	461.0	279.2	280.8	283.0	281.9





Fig. 7. Ru3d XPS spectrum for metallic ruthenium (a) and RuO₂ (b) standards.

this parameter was set to 4.17 eV for all Ru3d doublets in each peak model and the area ratio was set to 0.67. The residual plot for each peak model, supplied by the CasaXPS software [30], showed that all employed parameters resulted in very accurate peak models.

Fig. 7a shows the Ru3d XPS spectrum for the commercial metallic ruthenium powder. Ru⁰ was observed at 280.0 eV in a very good agreement with the literature [26,41,42]. In addition, the adventitious carbon was observed at 284.6 eV. The Ru3d spectrum for the other reference material, ruthenium (IV) oxide powder (commercial), is exhibited in Fig. 7b. Two Ru3d_{5/2} components were observed at 280.4 eV and 282.5 eV B.E. The lower B.E. peak was attributed to Ru⁴⁺ and also is in good agreement with the literature [26,41]. Many authors that have studied this oxide have assigned the photoelectron peak at higher binding energies to Ru⁶⁺ [42–44]. However, others explained that the aforementioned peak would not be corresponding to the RuO₃, but satellite peaks, plasmon peaks and/or different surface terminations [41,45–47]. Therefore, in this work, whenever a Ru⁴⁺ species related to the ruthenium (IV) oxide was observed for the supported ruthenium catalysts, its satellite was considered in the peak model. In addition, two components related to adventitious carbon were found, as expected.

The prepared RuAl and Ru10ZnAl catalysts were analyzed by XPS and the Ru3d photoelectron region is exhibited on Figs. 8 and 9, in which the calcined samples are presented in Fig. 8 and the ones, which were reduced and passivated (RP), are presented in Fig. 9. The corresponding binding energies are shown in Table 2. The goal was to investigate surface modification prior and after RP process. After fitting the data for the RuAl catalyst, two peaks - Ru⁴⁺ at 280.5 eV and its satellite at 282.5 eV - were observed (Fig. 8a). The Ru10ZnAl catalyst

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Fig. 8. Ru3d XPS spectrum of RuAl (a) and Ru10ZnAl (b).

presented Ru⁴⁺ at 280.3 eV and its satellite at 282.4 eV (Fig. 8b). It is important to note that, differently than the RuAl catalyst, a third peak appeared at 281.2 eV ($Ru^{\delta+}$), which suggests an interaction between ruthenium and the support in the Ru10ZnAl catalyst. This effect was previously discussed during the analysis of XRD and TPR results and has already been reported in literature [2,15,37-39]. Also, the coexistence of Ru-Cl species within the Ru $3d_{5/2}$ (Ru⁴⁺) satellite peak cannot be discarded because residual chloride was found at 199.1 eV, which is characteristic of metal-chloride interaction. RuCl₃.xH₂O was employed as the precursor salt. Therefore, even after the calcination step, residual chlorine was detected, which was also confirmed by TPR and XRF techniques. On the other hand, after the reduction and passivation procedures (Fig. 9a and b), only Ru⁰ (279.9 and 279.8 eV) and Ru^{δ +} (281.5 and 281.0 eV) were detected for both RuAl-RP and Ru10ZnAl-RP catalysts, respectively. The difference of 0.5 eV between the so-called $Ru^{\delta+}$ species among the samples RuAl-RP and Ru10ZnAl-RP suggests that the interaction of ruthenium with the support is different for each catalyst. In addition, although RuAl-RP and Ru10ZnAl-RP have similar ruthenium surface species, it is apparent that the peak related to $Ru^{\delta+}$ is relatively more pronounced for the Ru10ZnAl-RP sample than that observed for the RuAl sample.

The electronic surroundings on the surface of Ru50ZnAl and Ru50ZnAl-RP catalysts were also investigated. The Ru3d XPS spectrum for the calcined Ru50ZnAl sample (Fig. 10a) presented Ru⁴⁺ at 280.0 eV and its respective satellite at 282.8 eV. Similar to the calcined Ru10ZnAl sample, a peak at 281.9 eV (Ru^{δ +}) was also detected. After the RP procedure (Fig. 10b), metallic ruthenium was observed at 279.2 eV. It is important to note that the binding energy values corresponding to Ru⁴⁺ (Ru50ZnAl) and Ru⁰ (Ru50ZnAl-RP) were

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Fig. 9. Ru3d XPS spectrum of RuAl-RP (a) and Ru10ZnAl-RP (b).

significantly lower than the found for the reference samples in this work. Larichev et al. [48] studied Ru/MgO catalysts and observed a similar phenomenon related to a differential charging effect. According to Grünert et al. [49], differential charging may be expected with large particles. This may explain the difference in the values found for these species for the Ru50ZnAl samples. In addition, it is notable that the binding energy values for the $Ru^{\delta+}$ species of Ru50ZnAl and Ru50ZnAl-RP samples are shifted toward higher binding energies values compared to the Ru10ZnAl and Ru10ZnAl-RP samples. This shift could be related to the presence of Ru-Cl species, once the calcined Ru50ZnAl sample presented a surface Cl/Ru ratio, by XPS, approximately 7.4 times higher than the calcined Ru10ZnAl. Last but not least, a peak at 280.8 eV was detected and considered as non-reduced RuO₂, because of the satellite feature at 283.0 eV. This result was very similar to that observed by Morgan [41], which noted a Ru 3d_{5/2} satellite feature 1.9 eV distant than the Ru 3d_{5/2} peak, for a RuO₂ sample. The presence of RuO₂ on surface of the Ru50ZnAl-RP sample indicates that, even after the RP procedure, it was not possible to reduce all the RuO₂, stabilizing the Ru⁰ particles, probably due to the RuO2 particle aggregation (observed by the low H₂ chemisorption and, consequently, the larger particle size). A careful quantitative analysis by XPS, was performed by using the Ru3d peak models of the RP samples. The quantification of Ru3d region, expressed as the relative percentage of ruthenium surface species on the catalysts is presented in Table 3. Ru⁴⁺ surface species did not appear for the RuAl-RP and Ru10ZnAl-RP samples after RP process. Ru10ZnAl-RP sample presented the higher $Ru^{\delta+}$ relative percentage among the other RP samples. It can be observed that the Ru50ZnAl-RP sample

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Fig. 10. Ru3d XPS spectrum of Ru50ZnAl (a) and Ru50ZnAl-RP (b).

Table 3

Surface chemical analysis by XPS for all RP samples.

Sample	Relative percentage (%)			$Ru^{\delta+}/(Ru^0+Ru^{4+})$ atomic ratio
	Ru ⁰	Ru ⁴⁺	$Ru^{\delta+}$	
RuAl-RP Ru10ZnAl-RP	82.2 53.8	-	17.8 46.2	0.22 0.86
Ru50ZnAl-RP	29.0	39.1	31.9	0.47

presented a Ru⁴⁺ relative percentage of 39.1%, which was the major oxidation state found on the surface of the samples studied. Table 3 also shows the Ru⁸⁺/(Ru⁰⁺ + Ru⁴⁺) atomic ratio calculated by the TAG methodology, based on the CasaXPS software manual [30]. The calculated Ru⁸⁺/(Ru⁰⁺ + Ru⁴⁺) atomic ratio for the Ru10ZnAl-RP sample was 0.86, approximately the double that found for the Ru50ZnAl-RP sample.

In order to investigate if the ruthenium impregnation and the RP procedure changed the chemical environment of the zinc on the supports surfaces, high resolution spectra were performed in the regions of Zn2p photoelectron peak (Fig. 11a) and ZnLMM Auger peak (Fig. 11b) for the 10ZnAl and 50ZnAl supports and Ru10ZnAl-RP and Ru50ZnAl-RP catalysts, respectively. Table 4 shows the values of the $Zn2p_{3/2}$ peak for all samples. It can be observed that there is a shift of 0.4 eV to higher binding energies of the $Zn2p_{3/2}$ peak after the RP procedure for the Ru10ZnAl catalyst. Also, the Modified Auger Parameter (in this work



Fig. 11. $Zn2p_{3/2}$ shift (a) and ZnLMM Auger (b) for the hydrotalcite-like samples.

Table 4

 $Zn2p_{3/2}$, ZnLMM peaks and Modified Auger parameter between the hydrotalcite-like supports and their respective reduced ruthenium catalysts.

Sample	$Zn2p_{3/2}^{a}$	ZnLMM ^b	MAP ^c
10ZnAl Ru10ZnAl-RP 50ZnAl Ru50ZnAl-RP	1022.0 1022.4 1022.2 1021.9	987.2 987.5 987.5 987.8	2009.2 2009.9 2009.7 2009.7

^a Binding energy (BE - eV).

^b Kinetic energy (KE - eV).

^c MAP = $Zn2p_{3/2}$ (BE) + ZnLMM (KE).

abbreviated as MAP), which is the sum of the Auger peak (ZnLMM) kinetic energy and the main photoelectron peak (Zn2p_{3/2}) binding energy [50], was used to confirm the Ru-Zn interaction in the Ru10ZnAl catalyst after the ruthenium impregnation and RP procedure. As can be seen in Table 4, the MAP value for the 10ZnAl support was 2009.2 eV, which is characteristic of ZnAl₂O₄, and it is in good agreement with the literature [50,51]. However, the MAP value found for the Ru10ZnAl-RP sample was 2009.9 eV (0.7 eV higher than the observed for the 10ZnAl support). On the contrary, the MAP value for the Ru50ZnAl-RP sample remained the same as for the support 50ZnAl (2009.7 eV). The difference of 0.5 eV between the MAP values for the supports 10ZnAl and 50ZnAl is coherent. Strohmeier et al. [52] varied the zinc contents in Zn/Al₂O₄ catalysts and observed an increasing in the MAP values for



Fig. 12. Conversion of benzene (a) and selectivity to cyclohexene (b) in function of time for all catalysts.

the catalysts with zinc loadings above 20 wt.%, probably due to the ZnO formation on surface, also observed by XRD in this work for the Ru50ZnAl sample. These results suggest that even with a low content of ruthenium on the catalyst surface (nominal content of 1 wt.%), the presence of this metal changes the electronic environment of the zinc for the Ru10ZnAl catalyst. Therefore, the ruthenium impregnation associated with the RP procedure were responsible to provoke an electron transfer between zinc and the reduced ruthenium species, as already discussed by Peng et al. [53].

The conversions of benzene and selectivity to cyclohexene in function of the time for all catalysts are illustrated in Fig. 12a and b. After 10 min, the Ru10ZnAl catalyst reached a maximum yield to cyclohexene (35%). This catalyst reached 100% conversion in approximately 40 min of reaction. RuAl was also active for this reaction but converted only 20% of the benzene during 180 min of reaction and presented a maximum yield of 0.2% at 10 min. Ru50ZnAl and RuZn were not active for this reaction. Suryawanshi et al. [54] obtained a maximum yield to cyclohexene of 3.0% using a 4%Ru/Al₂O₃ catalyst in 30 min of reaction. Zhang et al. [55] varied the zinc content in Ru-Zn catalysts supported in a MCM-41 zeolite and reached a maximum yield to cyclohexene of 3.5% in 35 min.

The reaction rates were calculated as described by Cobo et al. [56]. Thus, RuAl catalyst presented a reaction rate of 1.5 mol min⁻¹ gRu⁻¹ and Ru10ZnAl catalyst presented a much higher activity of 1075.7 mols min⁻¹ gRu⁻¹. The remarkable results obtained with Ru10ZnAl catalyst were repeated twice with very good reproducibility (1075.7 \pm 111.9 mol min⁻¹ gRu⁻¹). In addition, the catalyst was reused and approximately the same activity was obtained (1156.8 mol min⁻¹ gRu⁻¹) and no Ru leaching was observed by XRF. The Ru50ZnAl and RuZn catalysts showed no catalytic activity on benzene partial

hydrogenation reaction. These reaction rates cannot be directly compared with the literature because data were obtained at distinct conditions, such as pressures and temperatures. However, Cobo et al. [56] worked with Ru/Al₂O₃ and Ru/CeO₂ catalysts in different particle sizes under pressure of 50 bar H₂ and 100 °C and achieved maximum activity of 1.7 mols min⁻¹ gRu⁻¹. Milone et al. [57] found that Ru/Al₂O₃ catalysts synthesized with the RuCl₃ precursor led to better results in cyclohexene selectivity and activity in the benzene hydrogenation reaction than catalysts prepared with the ruthenium acetylacetonate (Ru (acac)₃) and nitrosyl nitrate precursors. (Ru(NO)(NO₃)), reaching an activity of 1.7 mol min⁻¹ gRu⁻¹.

Markedly different from other mentioned studies, the present work did not use water - which is used to increase the cyclohexene yields [12,58]. According to Foppa and Dupont [58], the addition of water improves the cyclohexene selectivity because of a difference in solubility, where benzene is six-fold more soluble than cyclohexene, $125 \text{ mol } \text{m}^{-3}$ and $21 \text{ mol } \text{m}^{-3}$, respectively. Thus, when added, a stagnant water layer is formed surrounding the catalyst surface, promoting the feeding of benzene and desorption of the formed cyclohexene. However, mass transport phenomena play an important role when the reactional medium is composed with four phases in order to promote cyclohexene yields: gaseous (hydrogen), organic (benzene), aqueous (ZnSO₄ in aqueous solution) and solid (bulk ruthenium catalyst). Struijk et al. [12,59] studied the phenomena of external mass transport and pore diffusion limitations of partial benzene hydrogenation using Carberry numbers and the Wheeler-Weisz group calculations and experimental data. The authors noted that the liquid/solid transport of hydrogen is the reaction rate controlling step in the first hour of the reaction and the mass transfer limitation of benzene gradually increases, becoming the limiting step in the reaction sequence. These constrains reduce the overall benzene hydrogen rate but increase cyclohexene yields as reported by many authors. Besides, the addition of water may be considered a disadvantage to the process because an additional step of organic / aqueous phase separation must necessarily be included.

In the present paper, in the absence of water, the most selective catalyst to cyclohexene – Ru10ZnAl – presented the highest $Ru^{\delta+}/dt^{\delta+}$ (Ru⁰+Ru⁴⁺) atomic ratio by XPS after reduction, among the other reduced catalysts in this work. At first, one can suggest that the higher the metallic ruthenium dispersion on the surface, better would be the performance of the catalyst in the partial hydrogenation of benzene, once hydrogenation reactions require metallic sites in heterogeneous catalysis. However, Mazzieri et al. [60,61] studied supported ruthenium catalysts by XPS, and observed that other species detected in higher binding energies than Ru^0 , ascribed as $Ru^{\delta+}$, contributed to greater cyclohexene selectivity values. Similar results were reported by Fan et al. [62], which tested Ru-Co-B supported in alumina catalysts in partial hydrogenation of benzene. The authors obtained a yield of cyclohexene of 28.8% (62.7% conversion and 45.7% selectivity) at 150 °C and 50 bar H₂ after 30 min of reaction but using water (3 mL benzene and 4 mL water). Fan et al. [62] identified by XPS, that the presence of cobalt have induced electron transfers between Ru and Co. generating electron-deficient ruthenium particles that are favorable to achieve better cyclohexene yields. Both, Mazzieri et al. [61] and Fan et al. [62] observed electron-deficient $Ru^{\delta+}$ in $RuCoB/\gamma-Al_2O_3$ and $Ru/\gamma-Al_2O_3$, respectively, and ascribed the presence of this species to an improvement of the selectivity to cyclohexene because cyclohexene is weakly adsorbed and easily desorbed on electron-deficient ruthenium species. Thus, the higher activity and cyclohexene selectivity of Ru10ZnAl could be related to its higher $Ru^{\delta+}/(Ru^0 + Ru^{4+})$ atomic ratio after reduction.

Zhang et al. [2] reported that an interaction between Ru and Zn atoms would be due to the ruthenium electronic characteristics. The difference in electronegativity values between Ru and Zn is considerable. Ruthenium is 0.6 eV more electronegative than zinc. Thus, ruthenium tends to attract zinc electrons, creating an interaction between the two metals, which promotes the reduction of Zn^{2+} particles.

Recently, a few theoretical studies using molecular modeling have been performed in order to outline the effects of the Ru-Zn alloy on the partial hydrogenation of benzene. Yuan et al. [16,63] determined by Density Functional Theory (DFT), that zinc acts in two ways: reducing the ruthenium strength of chemisorbing cyclohexene and causing the repulsion of hydrogen atoms available to hydrogenate cyclohexene. These phenomena prevent the hydrogenation of cyclohexene to cyclohexane, increasing the selectivity to cyclohexene. Therefore, the presence of zinc and its surface species modification is beneficial to the partial hydrogenation of benzene.

4. Conclusions

Ruthenium supported in mixed oxide synthesized from hydrotalcite route with different Zn contents were tested in the partial hydrogenation of benzene. Even though the typical hydrotalcite phase was not observed for the catalyst support precursor with 10 wt.% of ZnO content, it showed the best performance reaching a maximum yield of 35% at 10 min and 100% of conversion at approximately 40 min of reaction. XPS measurements detected that even after reduction, electron deficient ruthenium species (Ru⁸⁺) remained on the surface of the catalysts, which was attributed to the ruthenium-support interaction.

A careful quantification was performed to estimate the surface ruthenium species distribution prior to the benzene partial hydrogenation. Ru10ZnAl-RP presented the highest Ru⁸⁺ content proving that, not only Ru⁰, but also Ru⁸⁺ are required to increase cyclohexene yields. In addition, this catalyst showed a $\text{Zn2p}_{3/2}$ main peak displacement to higher binding energies when reduced, indicating a stronger Ru-Zn interaction. This phenomenon promoted a partial reduction of the support (reducing zinc) – detected by XRD and TPR analysis – which makes the surface of the catalyst more hydrophilic, promoting the cyclohexene yields.

The Modified Auger Parameter (MAP) concept by XPS was crucial to elucidate the surface chemical modification of zinc particles after ruthenium impregnation and RP procedure for the Ru10ZnAl catalyst, confirming the Ru-Zn interaction. However, there was no difference in MAP values between the 50ZnAl support and Ru50ZnAl-RP. These observations confirmed that the presence of zinc was a good promoter for ruthenium catalysts to enhance cyclohexene selectivity in the benzene partial hydrogenation, but only in the presence of Ru-Zn interaction.

In summary, XPS analysis showed its powerful capability to provide understanding of the surface chemical modifications of Ru/Zn/Al catalyst. The XPS results also collaborated to explain how the catalyst with 10%wt ZnO content has shown interesting catalytic performance in the partial hydrogenation of benzene.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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