

**Benzene Partial Hydrogenation: Advances and Perspectives**

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## ARTICLE

## Benzene Partial Hydrogenation: Advances and Perspectives

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The partial hydrogenation of benzene to cyclohexene is an economically interesting and technically challenging reaction. Over the last four decades, a lot of work has been dedicated to the development of an exploitable process and several approaches have been investigated. However, environmental constraints often represent a limit to their industrial application, making further research in this field necessary. The goal of this review is to highlight the main findings of the different disciplines involved in understanding the governing principles of this reaction from a sustainable chemistry standpoint. Special emphasis is given to ruthenium-catalyzed liquid phase batch hydrogenation of benzene.

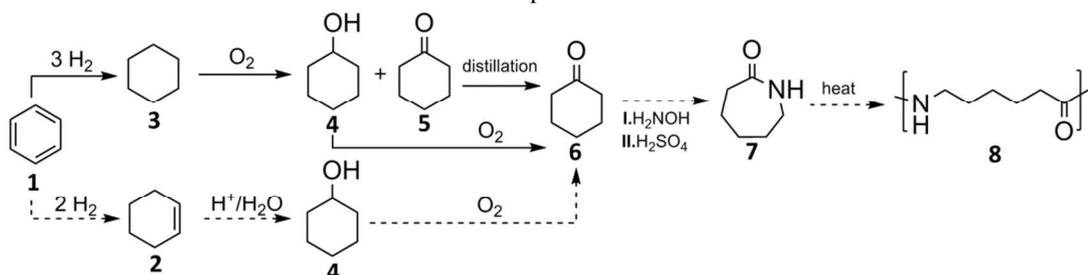
## Introduction

The partial hydrogenation of benzene (**1**) to cyclohexene (**2**) has been known for more than 100 years.<sup>1</sup> However, only in 1957 was this product in fact identified in the hydrogenation of benzene.<sup>2</sup> Since then, the occurrence of the partial hydrogenated product at low degrees of benzene conversion has been reported by several researchers, with ruthenium catalysts being particularly suited for the reaction.<sup>3</sup> Cycloolefin versatility boosted research efforts to enhance the performance of catalytic systems over the following decade. One of the most important advances was the utilization of agitated tetraphase reactors containing an organic phase and an aqueous phase, to which transition metal salts are added.<sup>4</sup> Processes based on this principle afforded high cyclohexene yields (*ca.* 60%),<sup>5</sup> thereby increasing technical feasibility.<sup>6</sup> In 1990, the first industrial plant based on such technology was conceived in Japan by Asahi.<sup>5,7,8</sup>

To date, benzene partial hydrogenation remains of high economic and environmental interest, since it provides an alternative synthetic route for Nylon (**8**), for instance through its monomer  $\epsilon$ -caprolactam (**7**), as shown in Scheme 1, avoiding costly unit operations and low-selectivity reaction steps that generate undesirable by-products.<sup>9</sup>

This concern is shown by the great number of scientific articles and patents published in the last four decades. Research work has attempted to address the issues of the Asahi-like process, such as high loads of the catalyst and additives (salts) and difficulty in separating the reaction products. The challenge is to replace tedious agitated reactors with simpler, industrially exploitable and more “green” catalytic systems without a loss in performance.

Although gas phase packed bed reactors have been investigated since the 1990s,<sup>10-16</sup> liquid-phase batch-wise approaches with little or no additives are the most commonly used today. Nevertheless, the inspection of reported results, displayed as a plot of cyclohexene selectivity *vs.* benzene conversion in Figure 1, shows that only few additive-free catalytic systems can achieve yields as high as 30%, with none of them having attained industrial maturity yet. A few review papers have been published on the partial hydrogenation of benzene (or aromatics, in general) focusing on specific aspects.<sup>17-20</sup> In this review, we intend to gather the most important literature results and evaluate general key aspects of this reaction that may lead to a deeper understanding and allow for the design of enhanced, sustainable catalytic processes in the future. We refer to ruthenium-catalyzed batch-wise liquid phase reactors unless otherwise mentioned.



Scheme 1. Standard industrial synthetic route for cyclohexanone (**6**) (full arrows) and alternative synthesis of Nylon,6 (**8**) via cyclohexene (**2**) (dashed arrows).



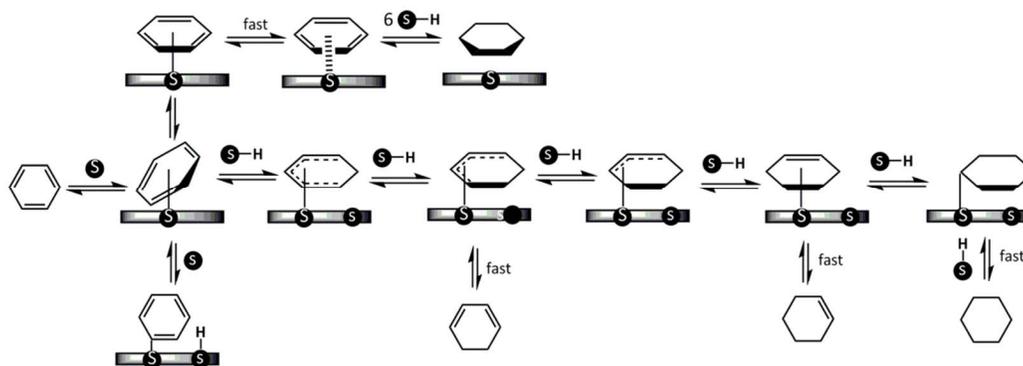


Fig. 3. Mechanisms for one-step (Rideal)<sup>31, 32</sup> and multi-step (Rooney)<sup>33</sup> benzene hydrogenation as proposed by Prasad.<sup>24</sup> S and s represent benzene and hydrogen coordinating active sites, respectively and wide dashed line Wan de Walls interactions.

Concerning the reaction temperature, it has been observed that an initial increase is followed by a decrease in selectivity towards cyclohexene with an elevation in the reaction temperature.<sup>28, 29</sup> Higher temperatures favor the desorption of cyclohexene from the ruthenium surface, an activated process, whereas it does not significantly affect hydrogen coverage, which is a weakly activated mass transfer controlled process.<sup>34</sup> As olefin hydrogenation is more affected by hydrogen coverage than benzene hydrogenation to cyclohexene, the overall effect is an increase in the yield of the partially hydrogenated product, according to equation (1), where  $k_{des}$  and  $k_H$  are the cyclohexene desorption and hydrogenation rate constants, respectively,  $\theta_H$  is the ruthenium hydrogen coverage and  $\Delta H^\ddagger$  is the desorption activation enthalpy ( $\approx 26$  kJ/mol).<sup>34</sup>

$$C_6H_{10} \text{ Select.} \approx \frac{k_{des}}{k_H \cdot \theta_H^2} \cdot e^{\left(\frac{-\Delta H^\ddagger}{R \cdot T}\right)} \quad (1)$$

An optimum temperature of 150°C was determined,<sup>34</sup> after which cyclohexene yield may drop due to an increase in olefin solubility in water,<sup>28</sup> catalyst particle agglomeration or decomposition, in the case of alloys.

## 2. Transport Phenomena Considerations

Mass transfer constraints can play an important role in the benzene partial hydrogenation reaction, since it is normally carried out with two concomitant liquid phases (benzene and an aqueous one). The influence of transport phenomena on this reaction was studied in the 1990s using unsupported ruthenium catalysts suspended in an aqueous ZnSO<sub>4</sub>-containing solution at 150°C and a hydrogen pressure of 5 MPa.<sup>34</sup> It was found, though inspection of adimensional Carberry (Ca) and Wheeler-Weisz ( $\eta\phi^2$ ) criteria, which account for the extent of external mass transport and pore diffusion limitations,<sup>35-37</sup> respectively, that the overall reaction rate during the first hour of the reaction is determined by the mass transport limitation of hydrogen through the stagnant water layer and that the reaction takes place only on the outer surface of the catalyst ( $Ca_H > 0.7$ ,

$\eta\phi^2_H > 30$ ). As the reaction proceeds, the mass transfer rate of benzene becomes the rate determining step and cyclohexene is hydrogenated to cyclohexane instead of leaving the surface due to the higher amount of adsorbed hydrogen on the catalyst surface. Furthermore, over the course of the reaction, hydrogenation may take place even in the catalyst pores, as pore diffusion resistance becomes lower ( $\eta\phi^2_H < 30$ ). At this point, the gradient of cyclohexene concentration is reversed, i.e. the cycloolefin makes its way from the organic phase to the catalytic surface, inducing a decrease in its yield. This behavior was also highlighted in other reports.<sup>30, 38</sup>

Benzene hydrogenation using an Ru/Al<sub>2</sub>O<sub>3</sub> catalyst at 60°C and 3 MPa showed the same tendency for cyclohexene selectivity whether the reaction is under mass transfer limitations or not.<sup>39</sup> It was concluded, however, that mass transport restraints are important to achieve high cycloolefin yields.<sup>40, 41</sup> It was also suggested that high hydrogen coverage could render the catalytic surface hydrophobic, disfavoring the formation of a water layer around catalyst particles and therefore dropping cyclohexene yields. Hydrogen mass transfer limitations could be thus also beneficial for benzene partial hydrogenation since it helps keeping hydrogen coverage moderate (hydrophilic surface).<sup>38, 42</sup>

## 3. Reaction Medium Modifications

### 3.1 Solvent

The beneficial effect of water as a solvent for the benzene partial hydrogenation reaction may be in part explained by the difference in the solubility of the reactive species in water, which are 125 mol/m<sup>3</sup> and 21 mol/m<sup>3</sup> for benzene and cyclohexene, respectively, i.e. a difference of six-fold.<sup>18</sup> The benzene-rich water layer surrounding the catalyst promotes cyclohexene desorption through competitive adsorption. In addition to this surface phenomenon, the lower solubility of cyclohexene in water may also increase, with respect to a water-free system, as the diffusion gradient provokes its migration into the aqueous phase, preventing further

hydrogenation.<sup>34</sup> This is depicted in Figure 4, which shows a schematic representation of the concentration profiles and mass fluxes for benzene and cyclohexene. It should be noted that, for short reaction times, the rate of diffusion may not keep up with the amount of cyclohexene and cyclohexane formed over the metal surface, thus giving rise to small organic droplets that leave the stagnant water layer around the catalyst to coalesce with the organic phase (see Figure 4).<sup>34</sup>

Recently, small amounts of cyclohexene were attained with the use of an ionic liquid (IL) medium with unsupported obtained nanoparticles.<sup>43, 44</sup> This could also be evidence of the solvent effect used to “extract” the cycloolefin during the reaction, since benzene is at least four times more soluble in the IL 1-n-butyl-3-methylimidazolium hexafluorophosphate

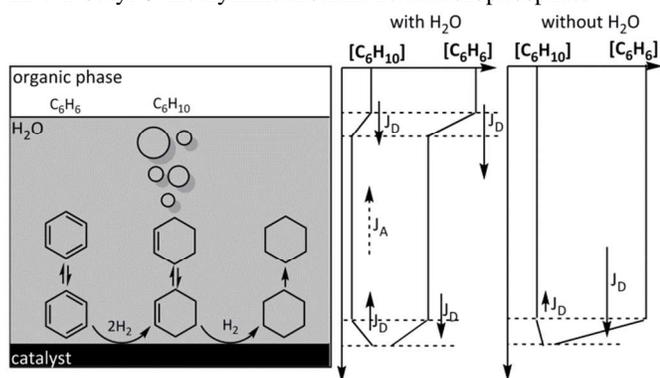


Fig. 4. Effect of stagnant water layer on the mass transport phenomena. Straight arrows indicate diffusion transport ( $J_b$ ) and dashed arrows advective transport ( $J_a$ ). Adapted from <sup>34</sup>.

(BMLPF<sub>6</sub>) than its partially hydrogenated product. Nevertheless, it should be noted that, in this case, the IL may also behave as a ligand on the metal surface, as observed for another reaction in which a simple thin layer of the IL is thought to be responsible for selectivity control.<sup>45-48</sup>

Other explanations have also been proposed for the positive effect of water on the benzene partial hydrogenation reaction, such as interactions between water and cyclohexene via hydrogen bonding, which would decrease the adsorption strength of the cycloolefin, leading to preferential adsorption of water molecules on strongly bonding ruthenium sites where cyclohexane is preferentially formed.<sup>49</sup>

Alternatively, alkanes and cycloalkanes were also tested for benzene partial hydrogenation with an enhancement in the cyclohexene yield.<sup>50, 51</sup> In these cases, the immediate dissolution of cyclohexene in the organic phase is responsible for shifting the cyclohexene adsorption equilibrium to the liquid side, favoring an increase in partial hydrogenation product selectivity as well.

### 3.2 Inorganic Additives

First introduced accidentally to the reaction media by reactor inner wall corrosion, metallic inorganic additives have been shown to act as co-catalysts to enhance cyclohexene yields in the benzene partial hydrogenation reaction.<sup>30, 52</sup> Zinc sulfate is, by far, the most commonly used inorganic additive to the

aqueous phase. Other metal salts such as Cr, Mn, Fe, Co, Ni, Zn, Ga, Cd and In-based compounds<sup>42, 53</sup> and fine oxide particles, also known as dispersing agents, (Zn, Ti, Nb, Ta, Cr, Fe, Co, Al, Ga, Si and Zr)<sup>5, 54, 55</sup> have also been tested. It was first proposed that metal ion interactions with the ruthenium surface follow Maxted's rule for catalysis poisoning.<sup>42, 56</sup> However, recent observations suggest that these relations are only partially valid,<sup>53</sup> as the tendency of cations to form hydrates also has to be taken into account.

The positive effect of ZnSO<sub>4</sub> on reaction selectivity was ascribed to three possible effects: (i) adsorbed Zn<sup>2+</sup> ions improve the ruthenium surface's hydrophilicity, which in turn increases cyclohexene selectivity by stabilizing the water layer above the catalyst surface,<sup>34, 53, 57, 58</sup> (ii) ZnSO<sub>4</sub> promotes cycloolefin desorption through a physical-chemical effect *i.e.* formation of loosely bound cyclohexene/Zn<sup>2+</sup> adducts,<sup>5</sup> and (iii) chemisorbed Zn<sup>2+</sup> ions interact with ruthenium active sites, changing their reactivity for example by blocking some of those otherwise available for cyclohexene hydrogenation.<sup>42, 53</sup>

Recently, a synergistic effect of combined ZnSO<sub>4</sub> and CdSO<sub>4</sub> salts as co-modifiers to a RuLa/SiO<sub>2</sub> catalyst leading to a cyclohexene yield of 57% was reported.<sup>59</sup> According to experimental observations and theoretical Density Functional Theory (DFT) calculations, CdSO<sub>4</sub> is more likely to modify catalyst surface, suppressing more the adsorption of cyclohexene than benzene whereas ZnSO<sub>4</sub> stabilizes the cycloolefin in a greater extent.<sup>59</sup>

Some authors have demonstrated the pronounced effectiveness of ZnSO<sub>4</sub> when used both in a pre-treatment step (catalyst reduction with H<sub>2</sub> prior to reaction) and in the reaction medium (Compare Entries 5, 8 and 9 of Table 1).<sup>18, 28, 60</sup> Under these conditions, it has been proposed that Zn<sup>2+</sup> species might be reduced to Zn<sup>0</sup> by spillover of hydrogen atoms dissociatively adsorbed on the ruthenium surface,<sup>61, 62</sup> thus forming in reality a Ru-Zn catalyst.<sup>28, 63</sup> Nevertheless, it was recently observed by Auger electron spectroscopy (AES) measurements that surface zinc from Ru-Zn catalysts synthesized from ZnSO<sub>4</sub> is present as ZnO.<sup>60</sup> It was then proposed that ZnO is able to interact with the zinc sulfate additive during the hydrogenation reaction forming (Zn(OH)<sub>2</sub>)<sub>3</sub>(ZnSO<sub>4</sub>)(H<sub>2</sub>O)<sub>5</sub>, a uniformly dispersed insoluble salt responsible for enhancing ruthenium selectivity towards cyclohexene through a combination of electronic and hydrophilic effects. These findings suggest that inorganic additives do not only act alone, but may also act in combination with promoters. An optimal concentration of 0.5 mol/L for Zn<sup>2+</sup> with Ru-La-B/ZrO<sub>2</sub> supported catalysts under 140°C and 5.0 MPa of hydrogen pressure was obtained, for instance.<sup>64</sup>

Despite the beneficial outcomes, inorganic salts present disadvantages in terms of industrial operability. Zinc sulfate, for instance, can cause fouling in the reboiler of distillation columns if the aqueous phase is carried along the process, in addition to turning the aqueous phase corrosive through Zn<sup>2+</sup> hydrolysis.<sup>65</sup> Moreover, salt loadings are typically high (*ca.* 50 times the amount of ruthenium)<sup>54</sup>, reducing the economic viability of the process. These drawbacks stimulated research into organic modifiers for benzene partial hydrogenation.

**Tab. 1.** The influence of the amount of zinc sulfate used on catalytic pre-treatment on its selectivity in the benzene partial hydrogenation.<sup>a</sup> Adapted from<sup>28</sup>.

Entry	ZnSO <sub>4</sub> ·7H <sub>2</sub> O weight (g)	C <sub>6</sub> H <sub>6</sub> conversion (mol%)	C <sub>6</sub> H <sub>10</sub> selectivity (mol %)	C <sub>6</sub> H <sub>10</sub> yield (mol %)
1	0.0	100	≈0	≈0
2	1.0	63.1	28.3	17.8
3	2.0	69.2	55.1	38.1
4	3.0	70.9	56.8	40.3
5	4.0	69.3	62.7	43.4
6	5.0	68.8	60.5	41.7
7	6.0	67.8	60.4	40.9
8	4.0 <sup>b</sup>	86.3	31.4	27.1
9	0.0 <sup>c</sup>	43.2	16.4	9.4

<sup>a</sup>Reaction conditions: 1.0 g 8.0 wt.% Ru/ZrO<sub>2</sub>, 145°C, 4.28MPa, H<sub>2</sub>O/C<sub>6</sub>H<sub>6</sub> (V/v)=2. Prereduction step with 4.0 g of ZnSO<sub>4</sub>·7H<sub>2</sub>O.

<sup>b</sup>ZnSO<sub>4</sub>·7H<sub>2</sub>O employed in the hydrogenation process rather than in the prereduction process. <sup>c</sup>Catalyst prereduced in the presence of 4.0 g of ZnSO<sub>4</sub>·7H<sub>2</sub>O first, cleaned by washing and centrifugation cycles to remove excessive zinc salt, and used in the hydrogenation process.

### 3.3 Organic Additives

Even before the use of water for liquid phase benzene partial hydrogenation, methanol and butanol had already been used to enhance cyclohexene yield up to 2.2%.<sup>66</sup> Interest in the use of alcohols was renewed in the 1990s.<sup>50, 67, 68</sup> More recently, several organic molecules have been tested as reaction additives. A summary of selected literature results achieved with these reaction modifiers is presented in Table 2. The majority of these molecules present polar groups or hydrogen bonds, such as amines (Table 2, Entries 7, 10, 11 and 16), alkanolamines (Table 2, Entries 2, 13, 14, 19 and 28), polyols (Table 2, Entries 4, 5, 8, 9, 12, 15, 20, 21, 27), lactams (Table 2, Entry 16), dicyanamide salts (Table 2, Entry 29) and ionic liquids (Table 2, Entries 23 and 24).

Firstly, organic additives are believed to interact with cyclohexene via hydrogen bonding,<sup>50, 69</sup> giving rise to competition between olefin adsorption directly to the metal surface and the formation of adducts, with the organic additive being bonded to the metal. Thanks to the generation of adducts, the overlap of the  $\pi$ -electrons of the cyclohexene C=C bond with ruthenium d orbitals is diminished. Furthermore, hydrogen bonding is weak (the enthalpy of hydrogen bonding is 3-5 kJ/mol),<sup>17</sup> so cyclohexene molecules which are hydrogen-bonded to an organic modifier can desorb at a higher rate with respect to those directly bonded to the metal surface. These hypotheses are supported by IR observations and by hydrogenation gas phase reactions experiments, in which glycol and  $\epsilon$ -caprolactame were successfully employed as modifiers to increase cyclohexene yield.<sup>16, 70</sup>

Secondly, it has been suggested that hydrophilic organic molecules can stabilize the stagnant water layer around the catalytic surface through hydrogen bonding, achieving a similar effect to the addition of inorganic additives.<sup>34, 65, 68, 69, 71, 72</sup>

**Tab. 2.** Effect of organic additives on benzene partial reaction selectivity.

Entry	Additive	C <sub>6</sub> H <sub>10</sub> Sel. (%)	C <sub>6</sub> H <sub>6</sub> Conv. (%)	C <sub>6</sub> H <sub>10</sub> Yield (%)	Ref.
1 <sup>a</sup>	None	4.9	62.4	3.0	65
2 <sup>a</sup>	<b>13</b>	33.3	38.6	12.9	65
3 <sup>b</sup>	None	23	60	14	68
4 <sup>b</sup>	<b>9</b>	27	60	16.2	68
5 <sup>b</sup>	<b>9</b>	32	60	19.2	68
6 <sup>c</sup>	None	39.2	51.9	20.4	71
7 <sup>c</sup>	<b>20</b>	44.4	52.8	23.4	71
8 <sup>c</sup>	<b>11</b>	47.2	51.5	24.3	71
9 <sup>c</sup>	<b>9</b>	43.1	60.9	26.3	71
10 <sup>c</sup>	<b>18</b>	45.2	59.2	26.7	71
11 <sup>c</sup>	<b>19</b>	62.3	44.2	27.5	71
12 <sup>c</sup>	<b>10</b>	45.4	66.3	30.1	71
13 <sup>c</sup>	<b>13</b>	66.9	45.9	30.7	71
14 <sup>c</sup>	<b>14</b>	68.8	46.8	32.2	71
15 <sup>c</sup>	<b>12</b>	43.4	79.3	34.4	71
16 <sup>c</sup>	<b>17</b>	48.0	72.6	34.8	71
17 <sup>d</sup>	None	64.9	85.1	55.2	73
18 <sup>d</sup>	<b>15</b>	-	-	58.2	73
19 <sup>d</sup>	<b>14</b>	-	-	58.9	73
20 <sup>d</sup>	<b>12-600</b>	65.2	92.6	60.4	73
21 <sup>d</sup>	<b>12-20000</b>	-	-	61.4	73
22 <sup>e</sup>	None	0	100	0	74
23 <sup>e</sup>	<b>22</b>	18	12	2.1	74
24 <sup>e</sup>	<b>21</b>	30	17	5.1	74
25 <sup>f</sup>	None	12.5	40	5	72
26 <sup>f</sup>	<b>16</b>	14	55	7.7	72
27 <sup>f</sup>	<b>9</b>	15.7	70	11	72
28 <sup>f</sup>	<b>13</b>	26.7	60	16	72
29 <sup>g</sup>	<b>23</b>	-	-	14	75

<sup>a</sup>Ru/Al<sub>2</sub>O<sub>3</sub>, 160°C, 1.38 MPa, H<sub>2</sub>O/C<sub>6</sub>H<sub>6</sub> (V/v)=1/1.

<sup>b</sup>Ru/SiO<sub>2</sub>, 150°C, 5 MPa, C<sub>6</sub>H<sub>6</sub>/H<sub>2</sub>O/additive (V/v/v')=2/1/1.

<sup>c</sup>RuCoB/Al<sub>2</sub>O<sub>3</sub>, 150°C, 5 MPa, H<sub>2</sub>O/C<sub>6</sub>H<sub>6</sub> (V/v)=4/3, ZnSO<sub>4</sub> 0.1mol/L.

<sup>d</sup>Ru-Zn, 150°C, 5 MPa, H<sub>2</sub>O/C<sub>6</sub>H<sub>6</sub> (V/v)=2/1, ZrO<sub>2</sub>.

<sup>e</sup>Ru/Al<sub>2</sub>O<sub>3</sub>, 100°C, 2 MPa, H<sub>2</sub>O/C<sub>6</sub>H<sub>6</sub> (V/v)=2/1.

<sup>f</sup>Ru/Al<sub>2</sub>O<sub>3</sub>, 100°C, 5 MPa, H<sub>2</sub>O/C<sub>6</sub>H<sub>6</sub>/n-heptane (V/v/v')=30/25/5.

<sup>g</sup>Ru/La<sub>2</sub>O<sub>3</sub>, 100°C, 2 MPa, H<sub>2</sub>O/C<sub>6</sub>H<sub>6</sub> (V/v)=2/1.

Finally, it has also been proposed that N or O atoms on the organic additive may interact with ruthenium active sites, removing electronic density from the metal.<sup>69</sup> As the cyclohexene adsorption interaction with electron-deficient Ru is weak, selectivity for the partially hydrogenated product would increase along with the Ru<sup>(δ+)</sup>/Ru<sup>0</sup> ratio.<sup>76, 77</sup> Despite supporting data from XPS studies on Cl-covered ruthenium catalysts, the above relation is not a consensus in literature. For instance, it has been proposed instead that the coordination of amines or alcohols with active metal centers renders ruthenium electron rich.<sup>71</sup>

## 4. Catalyst Structure and Formation

### 4.1 Metal Precursor

Most of the catalysts for benzene partial hydrogenation are synthesized from RuCl<sub>3</sub>, not only due to its greater availability, but also due to the results obtained with this precursor. It was observed that both supported and unsupported catalysts made from ruthenium chloride display higher cyclohexene selectivities compared to chlorine-free precursors.<sup>39</sup> These results were ascribed to residual chlorine, retained through a reaction with support surface hydroxyl groups or adsorption onto the ruthenium surface.<sup>78, 79</sup> Chlorine could enhance reaction selectivity either by (i) occupying the strongest bonding sites on the metal surface and leaving weak ones for substrate adsorption,<sup>39</sup> (ii) increasing catalyst hydrophilicity and thus stabilizing the surrounding water layer or (iii) modifying the ruthenium electronic state (formation of Ru<sup>(δ+)</sup> species).

The latter effect was further studied by means of the synthesis of Ru/Al<sub>2</sub>O<sub>3</sub> catalysts with different chlorine contents.<sup>76, 80, 81</sup> XPS analysis showed an increase in the Ru<sup>(δ+)</sup>/Ru<sup>0</sup> ratio along with the chlorine content. Cyclohexene selectivity was higher for catalysts containing more Cl, supporting the notion that electron-deficient Ru species adsorb cyclohexene more weakly, favoring its desorption before further hydrogenation. In contrast, it was also reported that pre-treatment of similar catalysts with hydrogen increased olefin selectivity, which was related to a more reduced catalyst.<sup>39</sup> It should be considered, however, that in these processes, an excess of hydrogen will lead to Ru-hydride species, thereby ending, globally, the catalyst surface electron deficiency.<sup>82</sup> Further investigations in this area are clearly required.

### 4.2 Preparation Method

Most common non-supported ruthenium catalysts for benzene partial hydrogenation are synthesized via precipitation of the precursor by the addition of a base followed by reduction to the catalytically active species Ru<sup>0</sup> in a H<sub>2</sub> stream. It was observed through chemisorption experiments that the amount of adsorbed hydrogen on the catalyst depends on the nature of the base used for precipitation, which can impact on the selectivity of the benzene hydrogenation reaction.<sup>40, 41</sup> Furthermore, unreduced catalysts treated with hydroxides display enhanced

performance.<sup>83, 84</sup> These results were explained by evoking base electronic promotion, blockade of cyclohexene chemisorption sites and OH<sup>-</sup> hydrophilic increment effects. A linear relationship between hydrophilicity and cyclohexene selectivity was found.<sup>84</sup>

Another approach for the synthesis of non-supported benzene partial hydrogenation catalysts was developed using imidazolium IL media.<sup>85, 86</sup> The so-called Ru-[BMIM]BF<sub>4</sub> catalyst was obtained using hydrazine and NaBH<sub>4</sub> as the reducing agents, the latter presenting higher cyclohexene selectivity.

In 1999, a RuB-Zn/ZrO<sub>x</sub>H<sub>2</sub>O catalyst synthesized by chemical mixing and reduction which attained 45.6% yield of cyclohexene without the use of additives or promoters was developed.<sup>87</sup> The successful application of an Ru-B catalyst to benzene partial hydrogenation was reported by several authors, either supported<sup>57, 87, 88</sup> or unsupported.<sup>89</sup> Metal boride catalysts can combine an ultrafine size and amorphous structure and are therefore expected to display different catalytic properties.<sup>90</sup> In the case of this reaction, the beneficial effect of boron was ascribed to the electronic interaction Ru-B that renders boron electron-deficient and enables this species to interact with an H<sub>2</sub>O oxygen lone pair, thereby increasing surface hydrophilicity and cycloolefin yield.<sup>57, 86</sup> Additionally, surface oxidized boron species can also interact with water through hydrogen bonding, thus enhancing the overall effect.

In the case of supported catalysts, impregnation/reduction is one of the most popular and simple methods. Hydrogen, KBH<sub>4</sub> and NaBH<sub>4</sub> are often used as reducing agents. Precipitation/reduction approaches or simultaneous catalyst and support synthesis/reduction strategies, also called “chemical mixing” (e.g. sol-gel) have been reported as well. More recently, an aqueous/organic “two-solvent” impregnation method was applied to the benzene hydrogenation reaction.<sup>59, 91-93</sup> It was reported that such a procedure affords highly dispersed small catalyst particles (*ca.* 7 nm) confined in support channels with enhanced selectivity with respect to the traditional wet impregnation approach.<sup>93</sup> A similar behavior was reported for a colloidal ruthenium catalyst supported on silica synthesized through a microemulsion approach.<sup>29</sup> It was proposed that a high dispersion of metal particles diminishes the rate of readsorption of cyclohexene, thereby enhancing reaction selectivity. Concerning the influence of metal particle size on selectivity, no relationship was found in the range 2-13 nm,<sup>39</sup> which is surprising, as benzene hydrogenation is considered a structure-sensitive reaction.<sup>94-97</sup>

### 4.3 Support

Supported catalysts have been widely employed in the benzene partial hydrogenation reaction and generally favor the formation of cyclohexene with respect to non-supported ruthenium. The most common supports are metal oxides such as ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, (see Figure 1). However, other oxides such as TiO<sub>2</sub>,<sup>38, 40, 51, 65</sup> ZnO,<sup>98, 99</sup> La<sub>2</sub>O<sub>3</sub>,<sup>75, 100</sup> Nb<sub>2</sub>O<sub>5</sub>,<sup>65, 101</sup> MgO,<sup>38</sup> Fe<sub>2</sub>O<sub>3</sub>,<sup>40</sup> Yb<sub>2</sub>O<sub>3</sub>,<sup>40</sup> CeO<sub>2</sub>,<sup>72</sup> binary oxides<sup>102, 103</sup> and materials like carbon,<sup>104, 105</sup> polymers,<sup>104</sup> polyketones,<sup>38, 40</sup>

clays,<sup>106-108</sup> hydroxyapatite,<sup>109</sup> BaSO<sub>4</sub>,<sup>38</sup> MgAl<sub>2</sub>O<sub>4</sub>,<sup>110</sup> bohemite<sup>111</sup> and metal-organic frameworks (MOF)<sup>112</sup> have also been tested. Especially relevant results with novel supports were achieved with the use of ruthenium catalysts supported on binary oxides (*e.g.* La<sub>2</sub>O<sub>3</sub>-ZnO and Ga<sub>2</sub>O<sub>3</sub>-ZnO)<sup>102, 103</sup> under alkaline conditions, under which conditions the effect of ZnSO<sub>4</sub> could be incorporated into the support, with an olefin yield up to 33% and with the development of a Ru/ZnO-ZrO<sub>x</sub>(OH)<sub>y</sub> additive-free based system (56% cyclohexene yield).<sup>99</sup>

The enhancement effect of a support for benzene partial hydrogenation is often ascribed to its hydrophilicity.<sup>38, 40, 104</sup> Nevertheless, metal-support interactions also play an important role.<sup>51, 81, 113</sup> Typically, metal reducibility and dispersion are influenced by the nature of the support-Ru interaction.<sup>51</sup> Indeed, it has been reported that the use of Al<sub>2</sub>O<sub>3</sub> furnishes more electron-deficient Ru catalysts compared to SiO<sub>2</sub>, thus favoring cyclohexene selectivity.<sup>81</sup> Alternatively, it has been suggested that an Ru/SiO<sub>2</sub> catalyst prepared by the sol-gel method could be especially interesting for benzene partial hydrogenation<sup>17</sup> since the ruthenium hydrogen adsorption capacity is reduced by coordination with the support or the preparation solvent,<sup>113, 114</sup> which could suppress the formation of cyclohexane.

Recently, a series of Ru-B/ZrO<sub>2</sub> catalysts with zirconia supports having different crystalline structures were tested in the benzene partial hydrogenation reaction; higher cyclohexene selectivity was related to a small amount of acid sites on the catalyst ZrO<sub>2</sub>-t support.<sup>115</sup> A quantitative relationship between Lewis acid sites and catalyst performance (activity and selectivity) was later established for similar catalysts with B-doped ZrO<sub>2</sub> supports, with cyclohexene selectivity displaying a volcanic-type evolution with an increasing concentration of Lewis acid sites.<sup>116</sup> These findings point out that support acid sites may influence the hydrogenation rates of the involved species. This aspect should also be considered in future studies.

#### 4.4 Promoter

Bearing in mind that additives present issues on the industrial scale, researchers have been trying to incorporate other transition metals onto the ruthenium solid catalyst to achieve similar results with an exploitable additive-free catalytic system. This is one of the most popular approaches nowadays. A summary of the results achieved in the benzene partial hydrogenation reaction with the use of promoters is shown in Table 3. Ru-Zn (Table 3, Entries 1-10), Ru-Cu (Table 3, Entries 11 and 12) Ru-La (Table 3, Entries 13-16), Ru-Fe (Table 3, Entries 17 and 18), Ru-Co (Table 3, Entries 19 and 20), Ru-Ba (Table 3, Entry 21), Ru-Ce (Table 3, Entry 22) and Ru-Cd (Table 3, Entry 23) alloys were tested and can, at certain loadings, enhance activity and/or cyclohexene selectivity in the partial hydrogenation of benzene.

In 1986, a cyclohexene yield of 31% was obtained using a Ru-Cu/SiO<sub>2</sub> catalyst synthesized by a “chemical mixing” procedure without additives.<sup>117, 118</sup> More recently, other additive-free catalytic systems such as Ru-Co-B/Al<sub>2</sub>O<sub>3</sub><sup>77</sup> and Ru-Cd/Bentonite<sup>106</sup> gave similar results, *i.e.* 29% and 25% cyclohexene yield, respectively.

Although the effect of the promoter depends on the synthetic method of catalysis, it is possible to highlight some trends. Firstly, promoters may affect the of electronic density ruthenium. Some authors have reported that Ru<sup>δ+</sup> species are formed through a partial charge transfer from ruthenium to the promoter.<sup>77</sup> Since electron-deficient ruthenium is more weakly coordinating than Ru<sup>0</sup>, this effect is believed to increase the cyclohexene yield (section 4.1). For instance, it was observed by XPS that a partial charge transfer from Ru to Co takes place over a Ru-Co-B/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>77</sup> This, together with the boron enhancement effect, provided the highest cyclohexene yield achieved with no additive at that time, 29%. It is interesting to note that the beneficial electron density effect is opposite to that proposed in other reports,<sup>60</sup> in which it was observed that the promoter in a Ru-Zn catalyst rendered Ru electron-rich.

Another electronic effect has also been proposed. Despite the inability to catalyze hydrogenation reactions, the vacant d-orbitals in a promoter could interact with cyclohexene π-electrons, rapidly removing the cycloolefin from ruthenium and thus preventing its further hydrogenation to cyclohexane.<sup>119-121</sup>

Secondly, promoters can modify the structure of the catalyst by either (i) blocking active sites where cyclohexene hydrogenation takes place, (ii) increasing the dispersion of the active component<sup>77</sup> (as discussed in section 4.2) or (iii) providing a homogeneous coordination environment for ruthenium.

## 5. Theoretical Investigations

In 2009, the first theoretical study on ruthenium catalysts for benzene partial hydrogenation was published.<sup>122</sup> DFT calculations on the (0 0 0 1) Ru-Zn surface were performed in order to understand cyclohexene adsorption and hydrogenation kinetics. It was concluded that the presence of Zn restrains the active sites available for cyclohexene chemisorption.<sup>122</sup> Furthermore, adsorbed cycloolefin hydrogenation may also be forbidden due to Zn repulsion over hydrogen atoms.<sup>122, 123</sup>

Benzene hydrogenation mechanisms over Ru<sup>124</sup> and Zn-Ru (0 0 0 1)<sup>125</sup> surfaces were also studied. A DFT-based approach to study reaction intermediates and their elementary hydrogenation energy surfaces suggested a Hoiruti-Polanyi-like step-wise hydrogenation of neighboring C atoms for both cases. It was observed that the introduction of Zn at high hydrogen coverage lowers intermediate adsorption energies, whereas the activation energy for hydrogenation to cyclohexane is increased<sup>125</sup>, *i.e.* the  $E_{a,\text{hydrogenation}}/E_{a,\text{desorption}}$  ratio increases. It was also proposed that in order to achieve high cyclohexene selectivity, the latter must be preferably π-bonded to the surface.<sup>124</sup> These studies provided an additional rational explanation to experimentally observed behaviors, although direct confrontation of theoretical data with accessible measurements remains a challenge.

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**Tab. 3.** The use of Ru-promoted catalysts for benzene partial hydrogenation reaction

Entry	Catalyst	M/Ru atomic ratio	Additives [conc. (mol/L)]	T (°C) P (MPa)	H <sub>2</sub> O/C <sub>6</sub> H <sub>6</sub> (V/v)	C <sub>6</sub> H <sub>10</sub> Sel. (%)	C <sub>6</sub> H <sub>6</sub> Conv. (%)	C <sub>6</sub> H <sub>10</sub> Yield (%)	Ref.
1	Ru-Zn	0.09	ZnSO <sub>4</sub> [0.61]	140 5	2	71.8	82.0	58.9	60
2	Ru-Zn	-	ZnSO <sub>4</sub> [0.61] Diethanolamine [1.07]** ZrO <sub>2</sub>	150 5	2	75.5	83.8	63.3	126
3	Ru-Zn	-	PEG-20000 [7.14]** ZnSO <sub>4</sub> [0.48]	150 5	2	78.9	68.7	61.4	73
4	Ru-Zn-Mn	-	ZnSO <sub>4</sub> [0.56]	150 5	2	67.3	89.0	59.9	127
5	Ru-Zn/SiO <sub>2</sub>	0.33	NaOH [0.62]	150 3.36	4/3	52	60	31	63
6	Ru-Zn/SiO <sub>2</sub>	0.25*	ZnSO <sub>4</sub> [0.2]	100 5.5	2	47.7	62.7	29.9	128
7	Ru-Zn/SiO <sub>2</sub>	0.33	NaOH [0.62]	150 3.4	4/3	55	56	31	63
8	Ru-Zn/HAP	1	NaOH [0.5]	150 5	2	47.3	69.8	33.0	109
9	Ru-Zn-B/ZrO <sub>2</sub>	0.28	ZnSO <sub>4</sub> [0.15]	160 5	2	62.3	73.1	45.6	87
10	Ru-Zn/m-ZrO <sub>2</sub>	0.14*	ZnSO <sub>4</sub> ***	145 4.28	2	62.7	69.2	43.4	28
11	Ru-Cu/SiO <sub>2</sub>	0.1*	-	180 7	5/8	37.7	83.3	31.4	117
12	Ru-Cu/ZnO	0.1	NaOH [0.3]	150 4	2/0.35	68.3	72.3	49.4	98
13	Ru-La	0.14	ZnSO <sub>4</sub> [0.61]	150 5	2	67.6	88.0	59.5	129
14	Ru-La/ZrO <sub>2</sub>	0.11*	ZnSO <sub>4</sub> [0.5]	140 5	50/29	70	35	24.5	130
15	Ru-La-B/ZrO <sub>2</sub>	-	ZnSO <sub>4</sub> [0.7] ZrO <sub>2</sub>	140 4.5	2	66.5	80.8	53.7	64
16	Ru-La/SiO <sub>2</sub>	1*	ZnSO <sub>4</sub> [0.42], CdSO <sub>4</sub> [0.00153] Zn(OH) <sub>2</sub>	140 4	2	69	82	57	59
17	Ru-Fe/TiO <sub>2</sub>	0.14	-	100 5	25/6 75/6 <sup>a</sup>	25	20	5	51
18	Ru-Fe-B/ZrO <sub>2</sub>	-	ZnSO <sub>4</sub> [0.5]	150 5	2	71.7	80.6	57.3	55
19	Ru-Co-B/Al <sub>2</sub> O <sub>3</sub>	0.27	-	150 5	4/3	45.7	62.7	28.8	77
20	Ru-Co-B/Al <sub>2</sub> O <sub>3</sub>	0.31	ZnSO <sub>4</sub> [0.175] Ethylenediamine [0.05]	150 5	4/3	48.0	72.6	34.8	71
21	Ru-Ba/SiO <sub>2</sub>	0.5	ZnSO <sub>4</sub> [0.13]	150 4	2	-	-	50.8	92
22	Ru-Ce/SiO <sub>2</sub>	0.25	ZnSO <sub>4</sub> [0.42]	140 4	2	63.3	85	53.8	91
23	Ru-Cd/Bentonite	1	-	150 5	1	43.1	57.4	24.8	106

\*in weight, \*\*in g/L, \*\*\*used for pre reduction step only, <sup>a</sup>Cyclohexene/C<sub>6</sub>H<sub>6</sub> (V/v).

## Conclusions and Perspectives

It is now well accepted that non-conjugated C=C bonds can be hydrogenated by mononuclear inorganic complexes and this reaction is structure insensitive in the case of heterogeneous catalysts. Conversely, monometallic complexes do not catalyze the hydrogenation of benzene.<sup>131, 132</sup> The hydrogenation of benzene requires more than one metal catalytically active center and is a structure sensitive reaction, *i.e.* it depends on the size and shape of the metal catalyst. The hydrogenation of 1,3-cyclohexadiene is also a structure sensitive reaction, in particular in the case of Ru and Pd-based catalysts.<sup>45, 133</sup>

In other words, the hydrogenation of benzene and 1,3-cyclohexadiene should, in principle, occur only at specific sites on the metal surface, whereas the hydrogenation of cyclohexene is much less surface metal sensitive. Therefore, one of the keys to achieving higher selectivities for the partial hydrogenation of benzene is to avoid contact of cyclohexene with the entire metal surface, not only with the original catalytic sites at which it was formed.

In this sense, mass transport phenomena can selectively control the access of reactive species to the catalytic surface, switching the cyclohexene adsorption equilibrium and preventing its further hydrogenation. Such an effect can be provoked by a significant disparity between benzene and cyclohexene solubilities, which is the case in water, commonly used as the solvent in agitated systems. A hydrophilic environment around catalyst particles is therefore also beneficial, as it assures that the reaction indeed takes place in water. Besides water, classical organic solvents and more recently ionic liquids have been the primary solutions investigated so far.

Another important aspect is to block most of the sites that are not specific for benzene hydrogenation and thus decrease the concentration of active sites for cyclohexene hydrogenation. This effect can in principle be exerted by reaction modifiers (additives) or traces of metal precursors used during catalyst synthesis.

Finally, it is also possible to improve the affinity of benzene for its active site compared to cyclohexene by decreasing the electron density of the surface metals, for instance. Although there is no consensus, this may be the one the effects induced by inorganic additives and hydroxide species. Hydrogen metal surface coverage is able to induce an augmentation in the electron deficiency, but it can also have a ligand-like effect. Indeed, the presence of such species may induce structural changes that may or may not facilitate the arrangement of benzene molecules in the correct geometry for the transfer of H from the donor to the acceptor sites. Such structural changes<sup>134</sup> have been evoked for both H<sub>2</sub> and H<sup>+</sup> species on the surface of small metal nanoparticles that strongly affect catalytic reactions.<sup>135, 136</sup>

Ionic liquids apparently play all the necessary roles, by controlling the relative solubility of the substrate/product, blocking some catalytic sites and decreasing the metal surface electron-density.<sup>11, 43, 46, 75, 137</sup>

More detailed information could be gathered by investigating the effect of the size of the metal catalyst on selectivity. Unfortunately, there are insufficient data available concerning the effect of metal size on the partial hydrogenation of benzene to test this hypothesis.

Despite of the advances in recent decades on the development of an industrially appealing benzene partial hydrogenation process, there is still a lot of room for improvement. Environmental constraints, which play a major role today, ought to be taken into account. This tendency, demonstrated by the migration from classical inorganic/organic additives to “green” additives or modifiers incorporated directly onto catalysts, has already changed catalyst design approaches over the last years and must be intensified in the future.

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## Notes and references

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This review highlights key aspects of benzene partial hydrogenation reaction as well as main contributions to the development of a sustainable catalytic system over the last decades.

