

Article

Performance of Ru/La₂O₃–ZnO Catalyst for the Selective Hydrogenation of Benzene to Cyclohexene

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Abstract: Cyclohexene is an important intermediate product for a highly efficient and greener formation of major end products like adipic acid, nylon 6, and nylon 6.6. By using a complex tetra-phase system (g/l/l/s) including hydrogen (g), water (l), an organic phase, *i.e.*, benzene (l), and a supported ruthenium catalyst (s) it is possible to get the desired intermediate cyclohexene based on benzene. We prepared an oxide-supported ruthenium catalyst that was applied together with minimal amounts of the additive NaDCA (sodium dicyanamide) in a batch and continuous apparatus for the selective benzene hydrogenation. We compared these two processes and reached by an optimization of the reaction parameters in continuous process selectivities up to 50% at conversions of 36%. This corresponds to cyclohexene yields of 18% over a period of 100 h. Finally, the catalyst was characterized using X-ray diffraction (XRD), transmission electron spectroscopy (TEM), inductively coupled plasma optical emission spectrometry (ICP-OES), and laser scattering to understand the performance of the catalyst and the effect of the small deactivation.

Keywords: benzene; cyclohexene; ruthenium; hydrogenation; continuous; tetra-phase system

1. Introduction

Because of the rising costs of raw materials and energy, it is of great interest that the production of major end products like adipic acid, nylon 6, and nylon 6.6 becomes more economical. The state of the art is the hydrogenation of benzene over nickel or platinum catalysts to cyclohexane followed by an air oxidation at 150 °C to a mixture of cyclohexanone and cyclohexanol at low conversions (10%–12%) [1]. Instead of the described process, an oxidation with H_2O_2 and gold supported on carbon under mild conditions is described in the literature [2,3]. A much better and more cost-efficient way to produce cyclohexanol is shown in Figure 1. The process starts with a selective hydrogenation of benzene over a supported ruthenium catalyst forming cyclohexene and subsequently cyclohexene was hydrated to cyclohexanol using a zeolite-like HZSM-5 as catalyst [4,5].

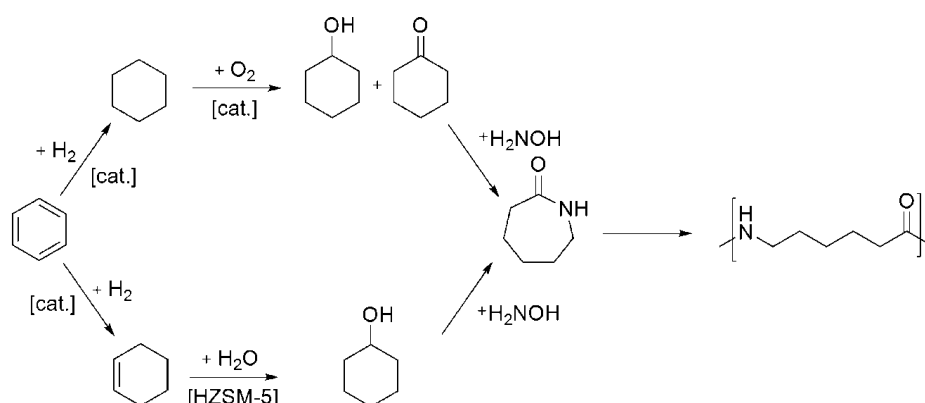


Figure 1. Two reaction pathways to form nylon 6 based on benzene.

Because of the free standard reaction enthalpies (formation of cyclohexene: -23 kJ/mol, formation of cyclohexane: -98 kJ/mol) and due to kinetic reasons (high reactivity of cyclohexene vs. benzene) it is difficult to achieve high yields of cyclohexene. To form cyclohexene in high yields requires a complex tetra-phase system (g/l/l/s), consisting of hydrogen (g), an organic (l) and an aqueous phase (l), and a solid catalyst (s). The concept for the selective hydrogenation in the liquid phase is shown in Figure 2.

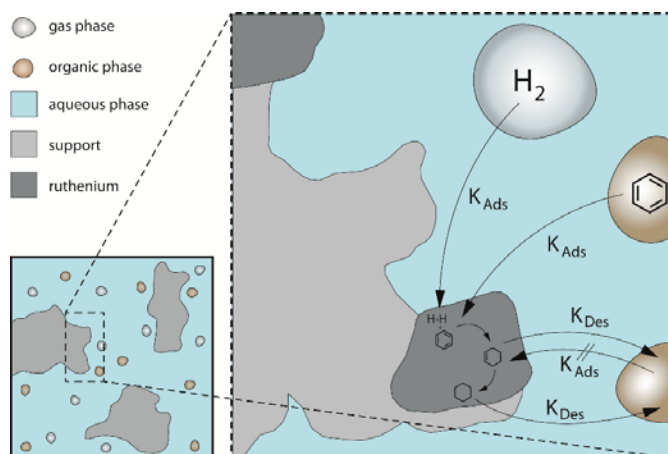


Figure 2. Concept of the selective benzene hydrogenation to cyclohexene using a complex tetra-phase system (g/l/l/s).

In the past decades it has been demonstrated that ruthenium-based catalysts supported on different metal oxides like Al_2O_3 , ZrO_2 , ZnO , or La_2O_3 are the most effective. Additionally, the ruthenium catalyst is rendered hydrophilic by dissolving large amounts of inorganic salts (ZnSO_4 or NaOH) in the aqueous phase. These salts adsorb on the catalyst surface and achieve a more hydrophilic structure. The catalyst is developing a hydrate shell that prevents re-adsorption of the formed cyclohexene because of inferior solubility of cyclohexene in water compared to benzene (factor of 6 at 150 °C, 50 bar) [6]. In previous studies performed by our group [6,7], we developed a process that does not use large amounts of these inorganic salts as additives but rather applies minimal amounts of the salt NaDCA (sodium dicyanamide).

The present work focuses on a detailed study of the aforementioned system in the presence of a self-prepared ruthenium catalyst supported on $\text{La}_2\text{O}_3\text{--ZnO}$ and minimal amounts of NaDCA. The catalyst performance was tested in recycling tests in a batch reactor and subsequently in a continuously laboratory process under different reaction conditions.

2. Results and Discussion

Table 1 shows a brief literature overview of known parameters for the selective benzene hydrogenation in a batch reaction. Ruthenium catalysts with large amounts of additives (organic and inorganic) in liquid phase have been found to be the most effective catalysts. For a better comparison of the performances we define a specific space-time yield (STY), shown in Equation (1):

$$\text{STY} = \frac{m(\text{cyclohexene})_{Y, \max}}{m(\text{Ru}) \cdot t_{Y, \max}} \left[g_{\text{cyclohexene}} \cdot g_{\text{Ru}}^{-1} \cdot h^{-1} \right] \quad (1)$$

Furthermore, Table 1 shows the molar ratios of ruthenium/benzene (Ru/BEN), benzene/additive (BEN/Add), and additive/ruthenium (Add/Ru). The best and most efficient catalyst systems have a high space-time yield (STY), a low ruthenium/benzene ratio, a high benzene/additive ratio, and a low additive/ruthenium ratio or preferable no additive because the usage of additives often resulted in corrosion and separation problems. Therefore, researchers developed catalysts without additives for the partial hydrogenation of benzene [8–12]. One of the main and most effective additive-free catalysts (1.95Ru-B/TNS, STY = 19173) was developed by Liu *et al.* [12]; it afforded cyclohexene yields of 50.7%.

Our catalyst system (2Ru/ $\text{La}_2\text{O}_3\text{--ZnO}$) has the highest benzene/additive ratio (12,488) and the lowest additive/ruthenium ratio (0.15). Thus we just need a small amount of an additive to form cyclohexene with high selectivity. Furthermore, the ruthenium/benzene ratio (0.53) is also very low. This implies that we can use minimal amounts of ruthenium to get cyclohexene yields of 18% in a batch reaction.

Table 1. Overview of the catalyst systems described in the literature.

Catalyst (wt. % Ru/Support)	<i>t</i> (h)	STY (g _{cyclohexene} ·g _{Ru} ^{−1} ·h ^{−1})	Ru/BEN (1000 mol/mol)	BEN/Add (mol/mol)	Add/Ru (mol/mol)
2Ru/Al ₂ O ₃ [8]	3.47	82	0.14	-	-
5Ru/Al ₂ O ₃ [13]	1.5	395	0.18	1371	4.14
7.4Zn–Ru [14]	1	334	1.48	155	4.43
9RuB–2.5Zn/ZrO ₂ ·xH ₂ O [9]	0.92	253	1.59	-	-
4Ru/Ga ₂ O ₃ –ZnO [15]	2	131	1.18	14	62.67
2Ru/La ₂ O ₃ –ZnO [15]	2.16	224	0.59	14	125.34
8Ru–Zn/ZrO ₂ [16]	0.38	656	1.41	40	17.58
18.4Ru0.08La18.86B/ZrO ₂ [17]	1	94	4.64	312	0.69
Ru/SiO ₂ [18]	0.66	605	0.85	9	125.02
3.8Ru1.2CoB/Al ₂ O ₃ [10]	0.5	1048	0.45	-	-
12Ru–La/SBA-15 [19]	0.57	387	2.12	13	35.51
3Ru/ZnO–ZrO _x (OH) _y [11]	3.08	196	0.76	-	-
8Ru–B/ZrO ₂ –T [20]	0.25	1083	1.41	8	88.41
5Ru/La ₂ O ₃ [7]	3.5	74	0.44	9872	0.23
10Mn–Ru [21]	0.25	157	11.45	9	9.51
Ru + CeO ₂ [22]	0.33	127	11.34	9	9.61
2.8Zn–Ru [23]	0.25	171	12.24	5	15.84
Ce–Ru(0,19) [24]	0.25	165	11.34	5	17.11
2.5Ru–Zn/HAP [25]	0.83	366	0.88	8	151.11
2Ru/La₂O₃–ZnO	3.5	97	0.53	12,488	0.15
1Ru/La ₂ O ₃ [26]	1.15	187	0.53	833	2.27
7.4Ru/B–ZrO ₂ [27]	0.5	598	1.30	81	9.5
8.8Ru–La/ZrO ₂ –MCM41 [28]	0.25	968	1.55	12	51.57
1.95Ru–B/TNS [12]	0.25	19,173	0.09	-	-

2.1. Batch Reaction

Figure 3 shows the selectivity and yield of cyclohexene against the conversion of benzene by using a 2Ru/La₂O₃–ZnO catalyst and 4 mg sodium dicyanamide (NaDCA) as additive. We observe an initial selectivity to cyclohexene of 90% at low conversions. Furthermore, cyclohexene is the main product up to a conversion of 35% and the maximum cyclohexene yield of 18% is observed at a benzene conversion of 50%.

The reusability of the catalyst system for the selective hydrogenation of benzene was investigated under the same conditions as stated above. The results are given in Figure 4. The catalyst could be reused at least five times without any notable changes in activity and cyclohexene yield. In this way we achieve almost constant conversions of benzene of 45% with a consistent cyclohexene yield of 18%. These values indicate that the catalyst system had good stability and holds potential for industrial applications in a continuous process. The high initial cyclohexene selectivity up to 90% is especially interesting for an application in a continuous process.

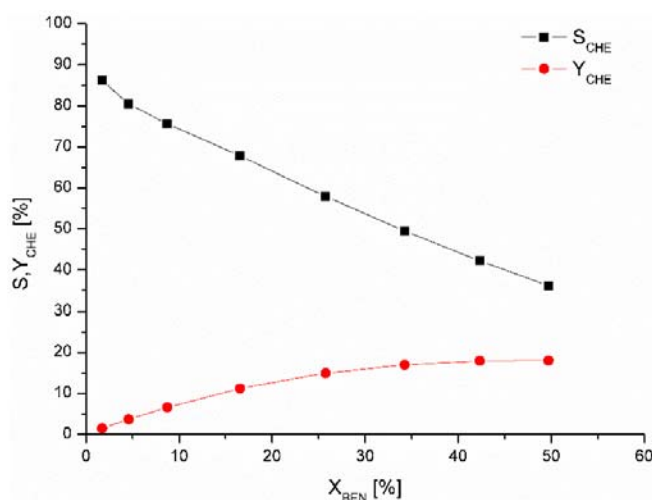


Figure 3. Cyclohexene selectivity and yield against the conversion of benzene. (Reaction conditions: 1.5 g 2Ru/La₂O₃–ZnO, 4 mg NaDCA, 20 bar H₂, 100 mL H₂O, 50 mL benzene, 1000 rpm, 150 °C).

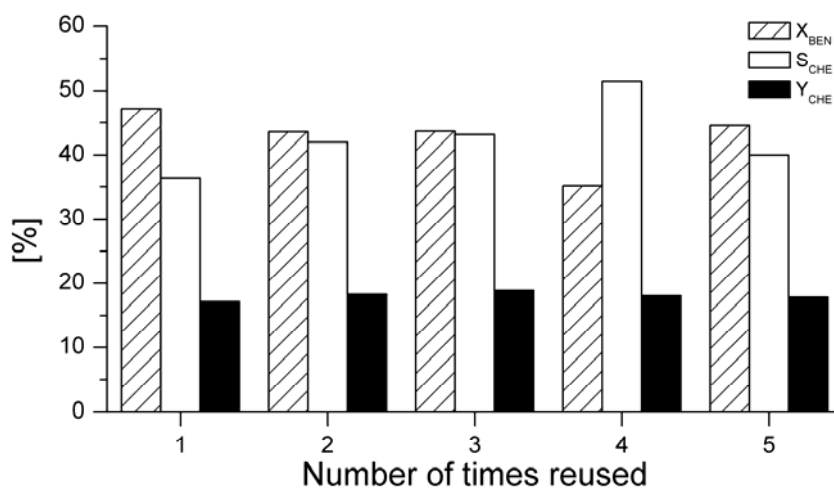


Figure 4. Recycling test of 2Ru/La₂O₃–ZnO. (Reaction conditions: 1.5 g 2Ru/La₂O₃–ZnO, 4 mg NaDCA, 20 bar H₂, 100 mL H₂O, 50 mL benzene, 1000 rpm, 150 °C, 330 min).

2.2. Batch vs. Continuous Process

Figure 5 shows the comparison between the batch reaction and the continuous process at three different flow rates (conversions) of benzene. The selectivity to cyclohexene in the continuous mode is less than in a batch process (10%) at same conversions and reaction conditions. Equivalent observations were made by Sun *et al.* [29]. However, in the beginning at low conversions high selectivities up to 70% were achieved.

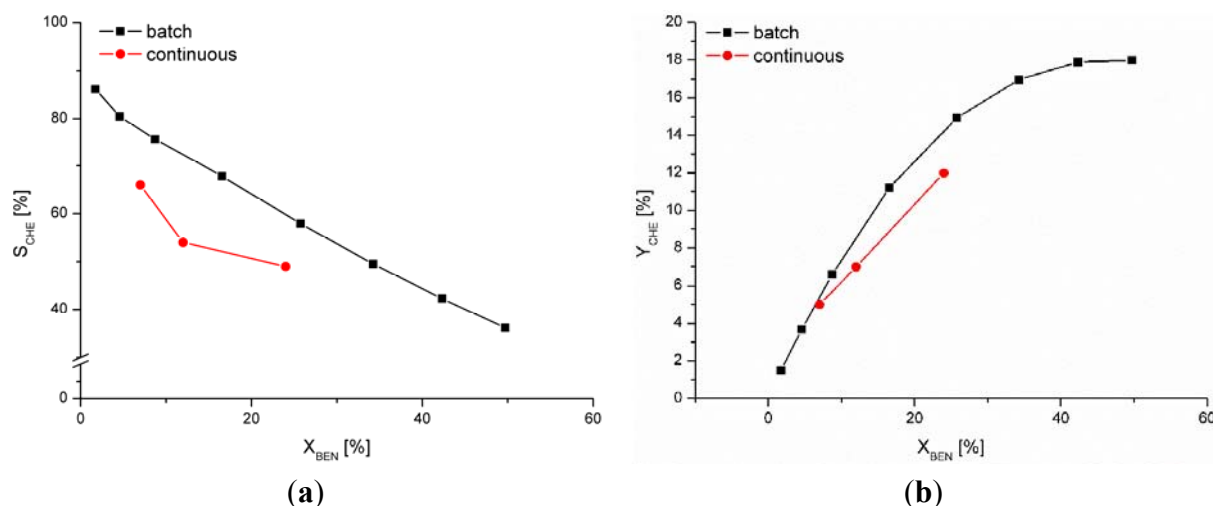


Figure 5. Cyclohexene selectivity against the conversion (a) and yield against the conversion (b) of benzene. (Reaction conditions: 1.5 g 2Ru/La₂O₃–ZnO, 4 mg NaDCA, 20 bar H₂, $V_{water}/V_{benzene} = 2/1$, 1000 rpm, 150 °C).

2.3. Continuous Process

A flow breaker prevents rotation of the reaction mass with the stirrer and by doing this we generate an optimal back mixing and turbulence of the difficult four-phase system. The idea here is generating a better emulsion and smaller particle sizes of the catalyst, leading to a better hydrate shell around the catalyst. The used flow breaker is shown in Figure 6.

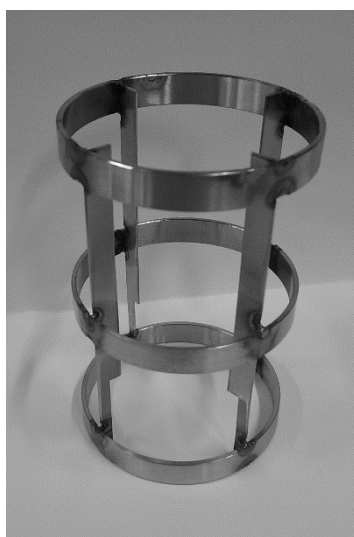


Figure 6. Used flow breaker for the optimization of the reaction conditions.

Figure 7 shows the influence of a flow breaker, the temperature, and the mass of the catalyst in a continuous process at different conversions of benzene. The use of a flow breaker in the system causes lower conversions under similar reaction conditions ($m_{catalyst}$, $V_{benzene}$, m_{NaDCA} , T), hence the influence on the system is negligible due to the similar trend in selectivity and yield against the conversion of benzene. The Ru catalyst synthesized by an impregnation method on La₂O₃ is more active compared to our new system using 2Ru/La₂O₃–ZnO as catalyst. The higher activity of 2Ru/La₂O₃ results in lower selectivity

and cyclohexene yield. Therefore, zinc oxide shows a positive influence on the selectivity of cyclohexene. Increasing the mass of catalyst from 1.5 g up to 3 g and m_{NaDCA} from 4 mg to 8 mg results in a more active system (see Table 2, Line (a)). The yield increases to 18% of cyclohexene at a benzene conversion of 45%.

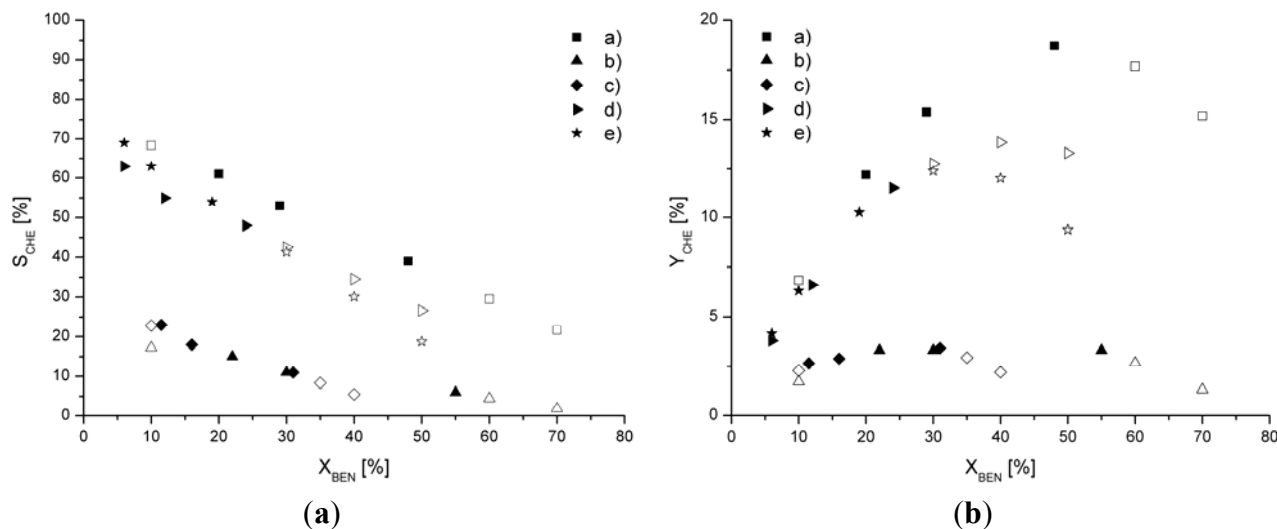


Figure 7. Cyclohexene selectivity (a) and yield (b) against the conversion of benzene. Blank symbols are fitted data points. (Reaction conditions: 1.5–3 g 2Ru/La₂O₃–ZnO and 0.5 g 2Ru/La₂O₃, 4–20 mg NaDCA, 20 bar H₂, $V_{\text{water}}/V_{\text{benzene}} = 2/1$, 800 rpm, 150 °C).

Table 2. Reaction conditions of the different experiments shown in Figure 7.

Line	Catalyst	m_{catalyst} (g)	m_{NaDCA} (mg)	Flow Breaker
(a)	2Ru/La ₂ O ₃ –ZnOIWR	3	8	no
(b)	2Ru/La ₂ O ₃ IPR	0.5	20	no
(c)	2Ru/La ₂ O ₃ IPR	0.5	20	yes
(d)	2Ru/La ₂ O ₃ –ZnOIWR	1.5	4	no
(e)	2Ru/La ₂ O ₃ –ZnOIWR	1.5	4	yes

These optimal conditions in entry (a), Table 2 (3 g 2Ru/La₂O₃–ZnO, 8 mg NaDCA, 100 mL H₂O, 150 °C, 20 bar H₂) were tested in continuous mode over a period of 100 h, shown in Figure 8. After a starting period of 30 h, we generated a steady state condition and produced cyclohexene with yields up to 18% without major catalyst poisoning over time on stream.

XPS spectra of the catalyst after the reaction show no sulfur (impurity of the hydrogen) or carbon (coking) at the catalyst surface after the reaction, which leads to the conclusion that there is no poisoning by these components [30]. The small deactivation could be attributed to a leaching of ruthenium. ICP-OES measurements (see Table 3) of the catalyst before and after the 100 h stress test show a leaching of 0.14 wt. % ruthenium.

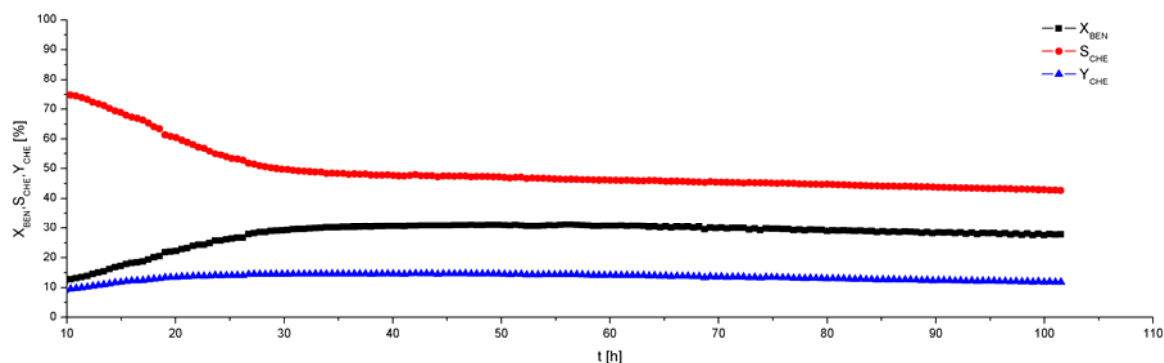


Figure 8. Cyclohexene selectivity and yield against the conversion of benzene under optimized conditions. (Reaction conditions: 3 g 2Ru/La₂O₃–ZnO, 8 mg NaDCA, 20 bar H₂, $V_{\text{water}}/V_{\text{benzene}} = 2/1$, 800 rpm, 150 °C).

Table 3. Grain size and ICP-OES measurements of the supporting material and catalyst before and after a stress of 100 h under reaction conditions (150 °C, 800 rpm, 100 mL H₂O).

Stress (h)	Mean Grain Size (μm)	wt. % Ru
0	3.8	2.2
100	5.0	2.06

2.4. Characterization

In Figure 9 a plot of the average grain size of the supporting material La₂O₃–ZnO, before (3.8 μm) and after (5.0 μm) a stress test of 100 h under reaction conditions (see Table 3) is shown. The increasing grain size results in a smaller surface of catalyst during the reaction in continuous mode.

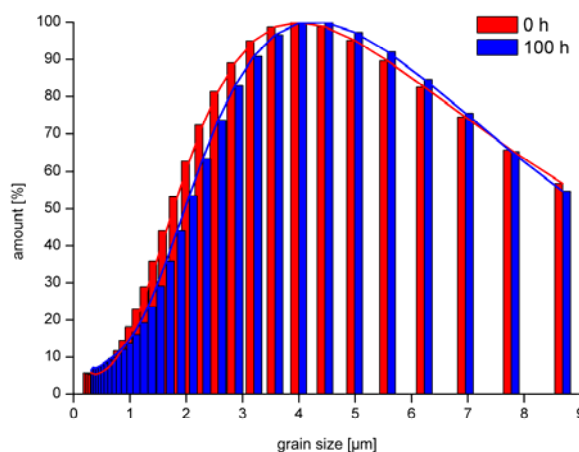


Figure 9. Grain size of the supporting material before and after a stress test of 100 h under reaction conditions (150 °C, 800 rpm, 100 mL H₂O) measured by laser scattering.

Figure 10 shows the XRD pattern of the supporting material (La₂O₃–ZnO). The small reflexes at 2-Theta of 29.35, 31.9, 39.0, and 48.6 (boxes) are assigned to sodium nitrate (NaNO₃). NaNO₃ accrues as an impurity during the precipitation. Furthermore, phases of lanthanum oxide carbonate (La₂O₂(CO₃))

(triangle) and no phases of zinc oxide are observed. The reason for the formation of $\text{La}_2\text{O}_2(\text{CO}_3)$ could be the short time of calcination (3 h) or insufficient temperature (500 °C) during the calcination process.

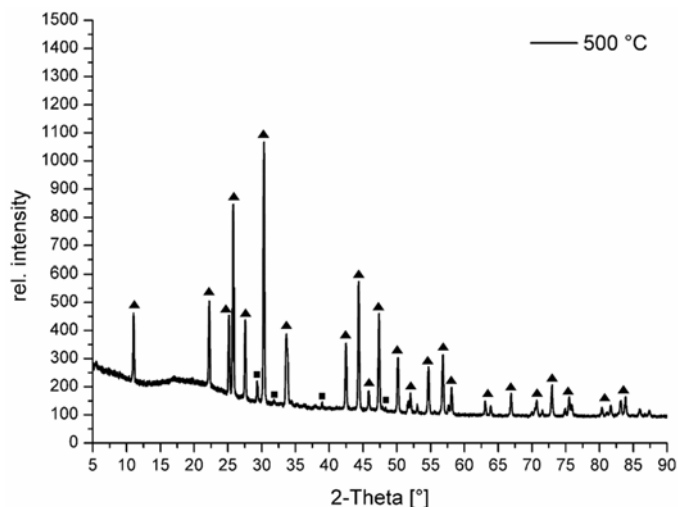


Figure 10. XRD pattern of the supporting material $\text{La}_2\text{O}_3\text{--ZnO}$ calcined at 500 °C with phases of lanthanum oxide-carbonate (triangle) and sodium nitrate (box).

Figure 11 gives the TEM image and histogram of the $2\text{Ru}/\text{La}_2\text{O}_3\text{--ZnO}$ catalyst. The TEM image shows that the Ru nanoparticle on the surface consisted of nanoscale spherical Ru crystallites. The average size of Ru nanoparticles supported on $\text{La}_2\text{O}_3\text{--ZnO}$ was around 3.5 nm.

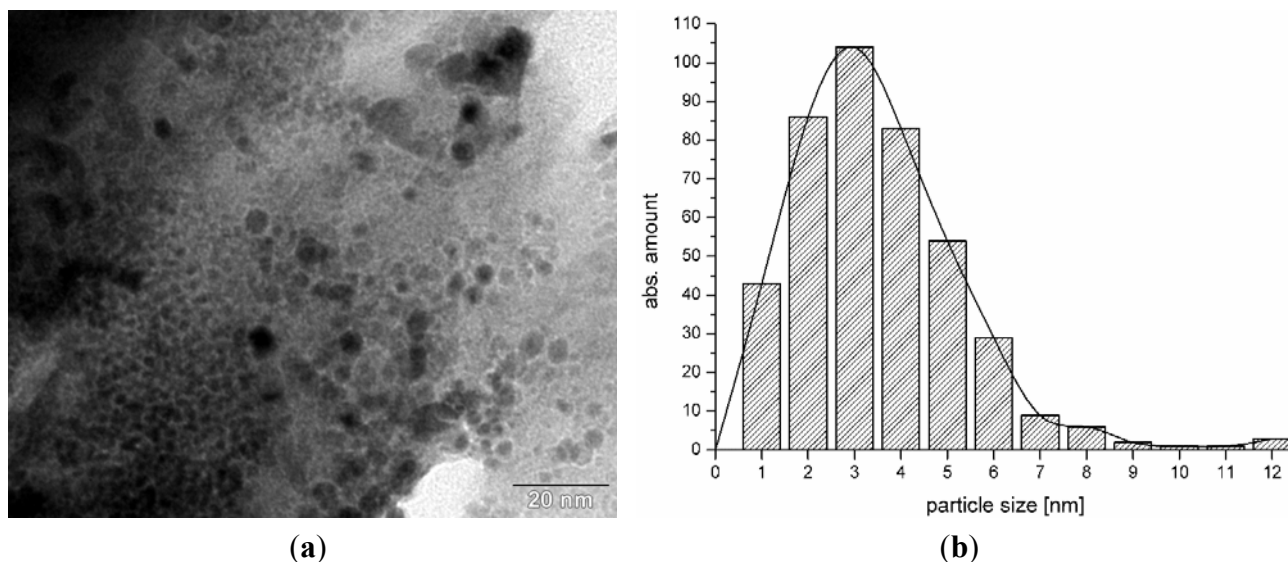


Figure 11. TEM measurement of $2\text{Ru}/\text{La}_2\text{O}_3\text{--ZnO}$ with an average particle size of 3.5 nm. TEM image of $2\text{Ru}/\text{La}_2\text{O}_3\text{--ZnO}$ (a) and the average particle size distribution (b).

3. Experimental Section

3.1. Materials

Benzene (C_6H_6), sodium carbonate monohydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), sodium dicyanamide (NaDCA), and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were bought from Sigma-Aldrich (Munich, Germany).

Lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and ruthenium chloride ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$) were bought from Alfa Aesar (Karlsruhe, Germany) and hydrogen was supplied by Air Liquid (Pfungstadt, Germany).

3.2. Catalyst Preparation

The synthesis of the catalyst was done in accordance with Hu *et al.* [15]. The supporting material $\text{La}_2\text{O}_3\text{--ZnO}$ with an atomic ratio of $\text{La}/\text{Zn} = 10/1$ was prepared according to the precipitation method. Sixty-five milliliters of an aqueous sodium carbonate solution ($c = 1 \text{ mol/L}$) were added quickly at 70°C to the solution of nitrate salts of lanthanum (12.578 g) and zinc (0.8696 g) in 250 mL distilled water. After aging for 1 h, the precipitate was filtrated and washed thoroughly with distilled water. The white powder was dried overnight at 100°C in an oven. To form the oxide, the sample was calcined in an oven from room temperature to 500°C in increments of $10^\circ\text{C}/\text{min}$ and held for 3 h.

The catalysts were prepared by an incipient wetness method. The calcined support was impregnated with a desired amount of an aqueous solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.75 mol/L). Afterwards the catalysts were dried overnight at 100°C and reduced in a hydrogen flow (100 mL/min) at 400°C for 3 h with a heating rate of $5^\circ\text{C}/\text{min}$.

3.3. Catalyst Testing

3.3.1. Batch

The desired amount of catalyst, the aqueous NaDCA solution (100 mL), and the benzene phase (50 mL) were placed in the reactor (300 mL, Parr Instruments, Frankfurt, Germany). After sealing, the reactor was flushed three times with argon (10 bar) and heated up to the requested temperature under argon atmosphere (2 bar). After reaching the desired temperature, the introduction of hydrogen defined the start of the reaction. In defined intervals samples were taken for gas chromatography analysis (Shimadzu GC 2010 Plus, Duisburg, Germany, capillary column DB-Wax, $l = 30 \text{ m}$, $d_i = 0.25 \text{ mm}$, $t_i = 0.25 \mu\text{m}$).

3.3.2. Continuous

Next, we briefly describe the procedure for the continuous process. Detailed information were recently published elsewhere [31]. The desired amount of catalyst and the aqueous NaDCA solution (100 mL) were introduced into the reactor (300 mL, Parr Instruments). After sealing, the whole apparatus was flushed three times with argon (10 bar) and heated to the desired temperature under appointed hydrogen pressure (20 bar). After reaching the adjusted temperature, the benzene flow into the reactor is guaranteed by an HPLC pump (Knauer P4.1 S, Berlin, Germany). The analysis of the separated organic product stream takes place by online gas chromatography (Shimadzu GC 2010 Plus, capillary column DB-Wax, $l = 30 \text{ m}$, $d_i = 0.25 \text{ mm}$, $t_i = 0.25 \mu\text{m}$).

3.4. Characterization

The support was analyzed by X-ray diffraction (Stoe & Cie. GmbH, Darmstadt, Germany; Ge[111]-Monochromator, $\text{CuK}\alpha_1$ -Strahlung, $\lambda = 1.540598 \text{ \AA}$; Detector: Mythen1K, Fa. Dectris, Baden, Schweiz) in order to get the specific phases of the supporting material. Furthermore, we carried out measurements by laser scattering (22 COMPACT, Fritsch, Idar-Oberstein, Germany) to get the grain size of the support before and after the reaction. The catalyst was analyzed after the reaction by X-ray photoelectron spectroscopy (VG ESCALAB 220 iXL with an Al $\text{K}\alpha$ radiation source under ambient conditions) to determine poisoning like sulfur or carbon on the catalyst surface. Moreover, the particle size was measured by TEM analysis (CM20, FEI, 200 kV).

4. Conclusions

We produce cyclohexene with high initial selectivity (90%) and yields up to 18% under application of a $2\text{Ru/La}_2\text{O}_3\text{--ZnO}$ catalyst and minimal amounts of NaDCA in a batch reactor. A recycling test of about five cycles with constant yields of 18% shows the stability of the catalyst for tests in a specially designed continuous laboratory process. Therefore, an optimization of the reaction parameters (3 g $2\text{Ru/La}_2\text{O}_3\text{--ZnO}$, 8 mg NaDCA) in continuous mode results in yields of 18% cyclohexene over a period of 100 h without major deactivation.

Author Contributions

H.S. designed and performed experiments, analyzed data and wrote the paper. M.L. and P.C. designed the experiments and gave technical support and conceptual advice.

Conflicts of Interest

The authors declare no conflict of interest.

Nomenclature

Add	additive
BEN	benzene
CHE	cyclohexene
ICP-OES	inductively coupled plasma optical emission spectrometry
$m_{(\text{cyclohexene})Y,\text{max}}$	mass of cyclohexene at maximum yield
$m_{(\text{Ru})}$	mass of ruthenium
NaDCA	sodium dicyanamide
S	selectivity
STY	Space-time yield
t	time
$t_{Y,\text{max}}$	time at maximum yield of cyclohexene
TEM	transmission electron spectroscopy
X	conversion
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
Y	yield

References

1. Ronchin, L.; Toniolo, L. Selective hydrogenation of benzene to cyclohexene catalyzed by Ru supported catalysts: Influence of the alkali promoters on kinetics, selectivity and yield. *Catal. Today* **2001**, *66*, 363–369.
2. De Almeida, M.P.; Martins, L.M.D.R.S.; Carabineiro, S.A.C.; Lauterbach, T.; Rominger, F.; Hashmi, A.S.K.; Pombeiro, A.J.L.; Figueiredo, J.L. Homogeneous and heterogenised new gold *c*-scorpionate complexes as catalysts for cyclohexane oxidation. *Catal. Sci. Technol.* **2013**, *3*, 3056–3069.
3. Carabineiro, S.A.C.; Martins, L.M.D.R.S.; Avalos-Borja, M.; Buijnsters, J.G.; Pombeiro, A.J.L.; Figueiredo, J.L. Gold nanoparticles supported on carbon materials for cyclohexane oxidation with hydrogen peroxide. *Appl. Catal. A* **2013**, *467*, 279–290.
4. Shan, X.; Cheng, Z.; Li, Y. Solvent effects on hydration of cyclohexene over H-ZSM-5 catalyst. *J. Chem. Eng. Data* **2011**, *56*, 4310–4316.
5. Shan, X.; Cheng, Z.; Yuan, P. Reaction kinetics and mechanism for hydration of cyclohexene over ion-exchange resin and H-ZSM-5. *Chem. Eng. J.* **2011**, *175*, 423–432.
6. Schwab, F.; Lucas, M.; Claus, P. Ruthenium-catalyzed selective hydrogenation of benzene to cyclohexene in the presence of an ionic liquid. *Angew. Chem. Int. Ed.* **2011**, *50*, 10453–10456.
7. Schwab, F.; Lucas, M.; Claus, P. Simple selective hydrogenation of benzene to cyclohexene in the presence of sodium dicyanamide. *Green Chem.* **2013**, *15*, 646–649.
8. Milone, C.; Neri, G.; Donato, A.; Musolino, M.G.; Mercadante, L. Selective hydrogenation of benzene to cyclohexene on Ru/ γ -Al₂O₃. *J. Catal.* **1996**, *159*, 253–258.
9. Liu, Z.; Xie, S.; Liu, B.; Deng, J.-F. Benzene-selective hydrogenation to cyclohexene over supported ruthenium boride catalysts prepared by a novel method. *New J. Chem.* **1999**, *23*, 1057–1057.
10. Fan, G.-Y.; Jiang, W.-D.; Wang, J.-B.; Li, R.-X.; Chen, H.; Li, X.-J. Selective hydrogenation of benzene to cyclohexene over RuCoB/ γ -Al₂O₃ without additive. *Catal. Commun.* **2008**, *10*, 98–102.
11. Liu, H.; Jiang, T.; Han, B.; Liang, S.; Wang, W.; Wu, T.; Yang, G. Highly selective benzene hydrogenation to cyclohexene over supported Ru catalyst without additives. *Green Chem.* **2011**, *13*, 1106–1109.
12. Liu, J.; He, S.; Li, C.; Wang, F.; Wei, M.; Evans, D.G.; Duan, X. Confined synthesis of ultrafine Ru–B amorphous alloy and its catalytic behavior toward selective hydrogenation of benzene. *J. Mater. Chem. A* **2014**, *2*, 7570–7577.
13. Suryawanshi, P.T.; Mahajani, V.V. Liquid-phase hydrogenation of benzene to cyclohexene using ruthenium-based heterogeneous catalyst. *J. Chem. Technol. Biotechnol.* **1997**, *69*, 154–160.
14. Nagahara, H.; Ono, M.; Konishi, M.; Fukuoka, Y. Partial hydrogenation of benzene to cyclohexene. *Appl. Surf. Sci.* **1997**, *121–122*, 448–451.
15. Hu, S.-C.; Chen, Y.-W. Liquid phase hydrogenation of benzene to cyclohexene on ruthenium catalysts supported on zinc oxide-based binary oxides. *J. Chem. Technol. Biotechnol.* **2001**, *76*, 954–958.

16. Wang, J.; Wang, Y.; Xie, S.; Qiao, M.; Li, H.; Fan, K. Partial hydrogenation of benzene to cyclohexene on a Ru–Zn/m-ZrO₂ nanocomposite catalyst. *Appl. Catal. A* **2004**, *272*, 29–36.
17. Liu, S.; Liu, Z.; Wang, Z.; Zhao, S.; Wu, Y. A novel amorphous alloy Ru–La–B/ZrO₂ catalyst with high activity and selectivity for benzene selective hydrogenation. *Appl. Catal. A* **2006**, *313*, 49–57.
18. Ning, J.; Xu, J.; Liu, J.; Lu, F. Selective hydrogenation of benzene to cyclohexene over colloidal ruthenium catalyst stabilized by silica. *Catal. Lett.* **2006**, *109*, 175–180.
19. Liu, J.-L.; Zhu, Y.; Liu, J.; Pei, Y.; Li, Z.H.; Li, H.; Li, H.-X.; Qiao, M.-H.; Fan, K.-N. Discrimination of the roles of CdSO₄ and ZnSO₄ in liquid phase hydrogenation of benzene to cyclohexene. *J. Catal.* **2009**, *268*, 100–105.
20. Zhou, G.; Liu, J.; Tan, X.; Pei, Y.; Qiao, M.; Fan, K.; Zong, B. Effect of support acidity on liquid-phase hydrogenation of benzene to cyclohexene over Ru–B/ZrO₂ catalysts. *Ind. Eng. Chem. Res.* **2012**, *51*, 12205–12213.
21. Sun, H.-J.; Pan, Y.-J.; Jiang, H.-B.; Li, S.-H.; Zhang, Y.-X.; Liu, S.-C.; Liu, Z.-Y. Effect of transition metals (Cr, Mn, Fe, Co, Ni, Cu and Zn) on the hydrogenation properties of benzene over Ru-based catalyst. *Appl. Catal. A* **2013**, *464–465*, 1–9.
22. Sun, H.; Chen, L.; Li, S.; Jiang, H.; Zhang, Y.; Ren, B.; Liu, Z.; Liu, S. Selective hydrogenation of benzene to cyclohexene over monometallic ruthenium catalysts in the presence of CeO₂ and ZnSO₄ as co-modifiers. *J. Rare Earths* **2013**, *31*, 1023–1028.
23. Sun, H.; Jiang, H.; Li, S.; Dong, Y.; Wang, H.; Pan, Y.; Liu, S.; Tang, M.; Liu, Z. Effect of alcohols as additives on the performance of a nano-sized Ru–Zn(2.8%) catalyst for selective hydrogenation of benzene to cyclohexene. *Chem. Eng. J.* **2013**, *218*, 415–424.
24. Sun, H.; Pan, Y.; Li, S.; Zhang, Y.; Dong, Y.; Liu, S.; Liu, Z. Selective hydrogenation of benzene to cyclohexene over ce-promoted Ru catalysts. *J. Energy Chem.* **2013**, *22*, 710–716.
25. Zhang, P.; Wu, T.; Jiang, T.; Wang, W.; Liu, H.; Fan, H.; Zhang, Z.; Han, B. Ru–Zn supported on hydroxyapatite as an effective catalyst for partial hydrogenation of benzene. *Green Chem.* **2013**, *15*, 152–159.
26. Schwab, F. Eine Grüne Route der Selektiven Hydrierung von Benzol zu Cyclohexen. Ph.D. Thesis, Technische Universität, Darmstadt, Germany, August 2014.
27. Zhou, G.; Pei, Y.; Jiang, Z.; Fan, K.; Qiao, M.; Sun, B.; Zong, B. Doping effects of B in ZrO₂ on structural and catalytic properties of Ru/B–ZrO₂ catalysts for benzene partial hydrogenation. *J. Catal.* **2014**, *311*, 393–403.
28. Liao, H.; Ouyang, D.; Zhang, J.; Xiao, Y.; Liu, P.; Hao, F.; You, K.; Luo, H.A. Benzene hydrogenation over oxide-modified MCM-41 supported ruthenium-lanthanum catalyst: The influence of zirconia crystal form and surface hydrophilicity. *Chem. Eng. J.* **2014**, *243*, 207–216.
29. Sun, H.; Guo, W.; Zhou, X.; Chen, Z.; Liu, Z.; Liu, S. Progress in Ru-based amorphous alloy catalysts for selective hydrogenation of benzene to cyclohexene. *Chin. J. Catal.* **2011**, *32*, 1–16.
30. Musser, M.T. Cyclohexanol and cyclohexanone. In *Ullmanns Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2011.

31. Spod, H.; Lucas, M.; Claus, P. Continuously conducted selective hydrogenation of benzene to cyclohexene in a four-phase system. *Chem. Eng. Technol.* **2015**, *38*, 1340–1342.

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